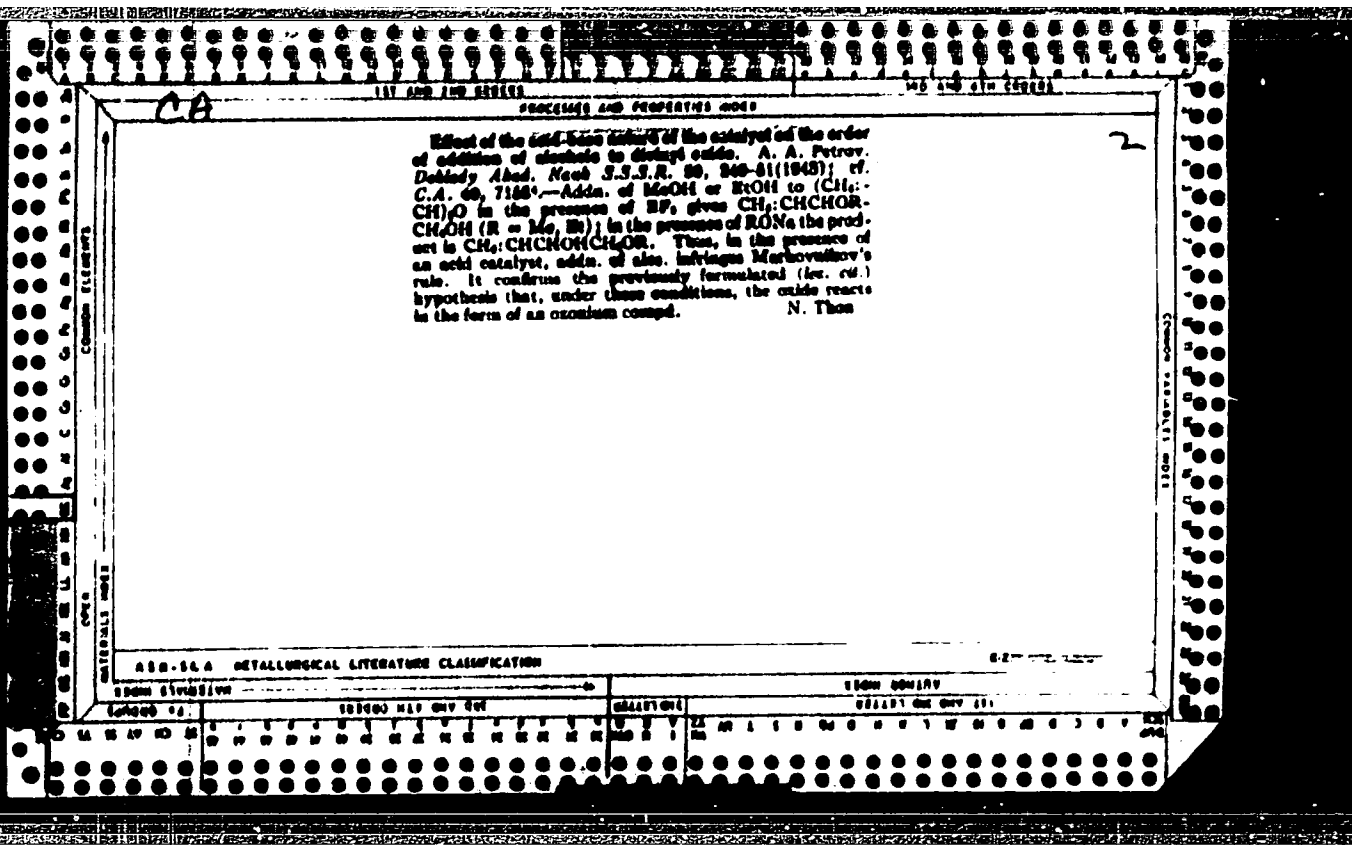


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Conjugated systems XXVI. Synthesis and proper ties of α -chlorobutadiene. A. A. Petrov and N. P. Sapozhnikova (Tashkent Aviat. Inst.) J. Gen. Chem. (U.S.S.R.), 15, 981 (1945) (English summary); J. C. I., 30, 2057 (1945).
It was shown that the action of KOH on α -CICH₂CH=CH₂ yields pure CICH₂CH=CH₂. Butadiene (340 cc.) containing 9% pseudobutylene in 1000 cc. CCl₄ was dibromide (probably 1-chloro-3,6-dibromo-1-butene), b.p. 72-73°C. To 100% excess of treated at -5° to +10° with 122 g. Cl₂ with good stirring 80-3.5°, d₄²⁰ 1.8935, n_D²⁰ 1.5676. To 100% excess of treated at -5° to +10° with 122 g. Cl₂ with good stirring 80-3.5°, d₄²⁰ 1.8935, n_D²⁰ 1.5676. To 100% excess of treated at -5° to +10° with 122 g. Cl₂ with good stirring 80-3.5°, d₄²⁰ 1.8935, n_D²⁰ 1.5676. To 100% excess of treated at -5° to +10° with 122 g. Cl₂ with good stirring 80-3.5°, d₄²⁰ 1.8935, n_D²⁰ 1.5676. To 100% excess of treated at -5° to +10° with 122 g. Cl₂ with good stirring 80-3.5°, d₄²⁰ 1.8935, n_D²⁰ 1.5676.

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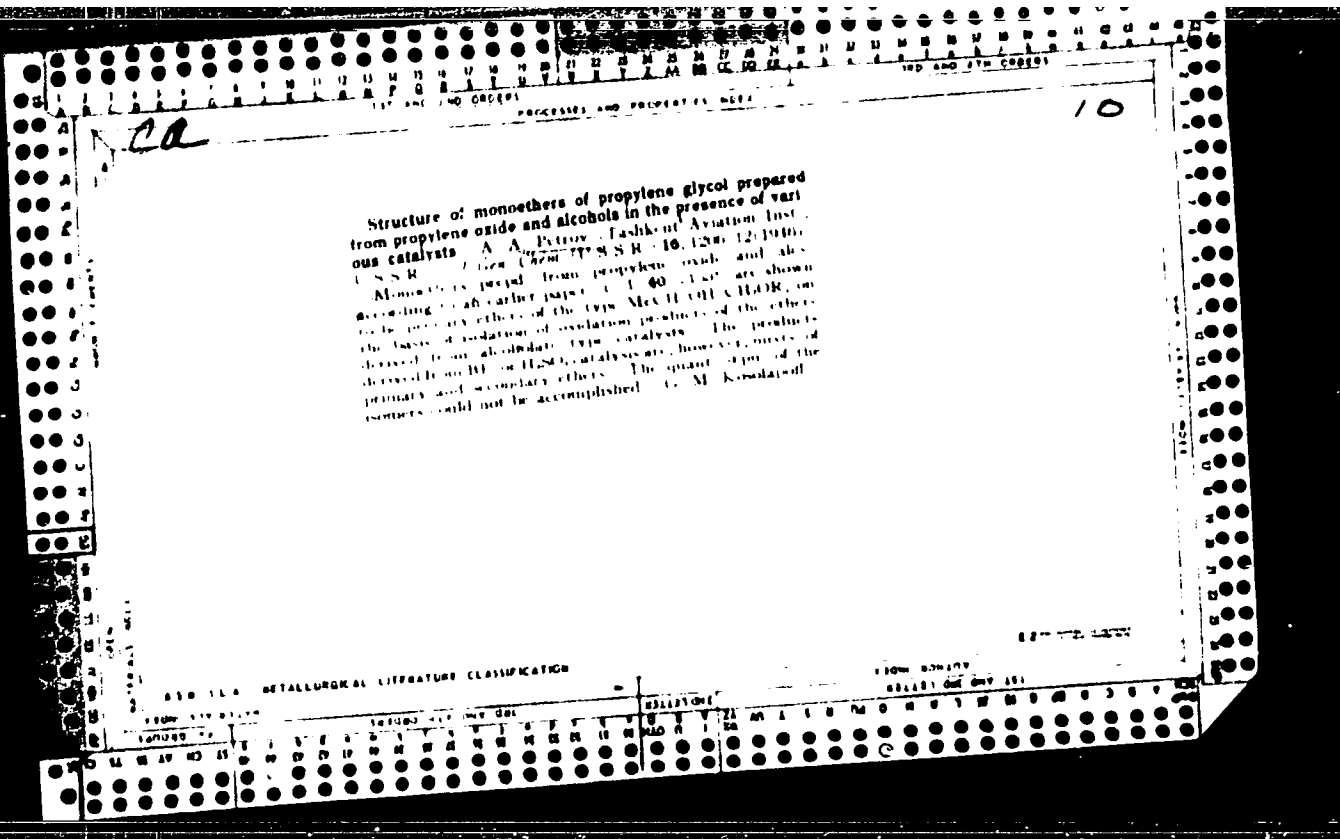
PETROV, A. A.

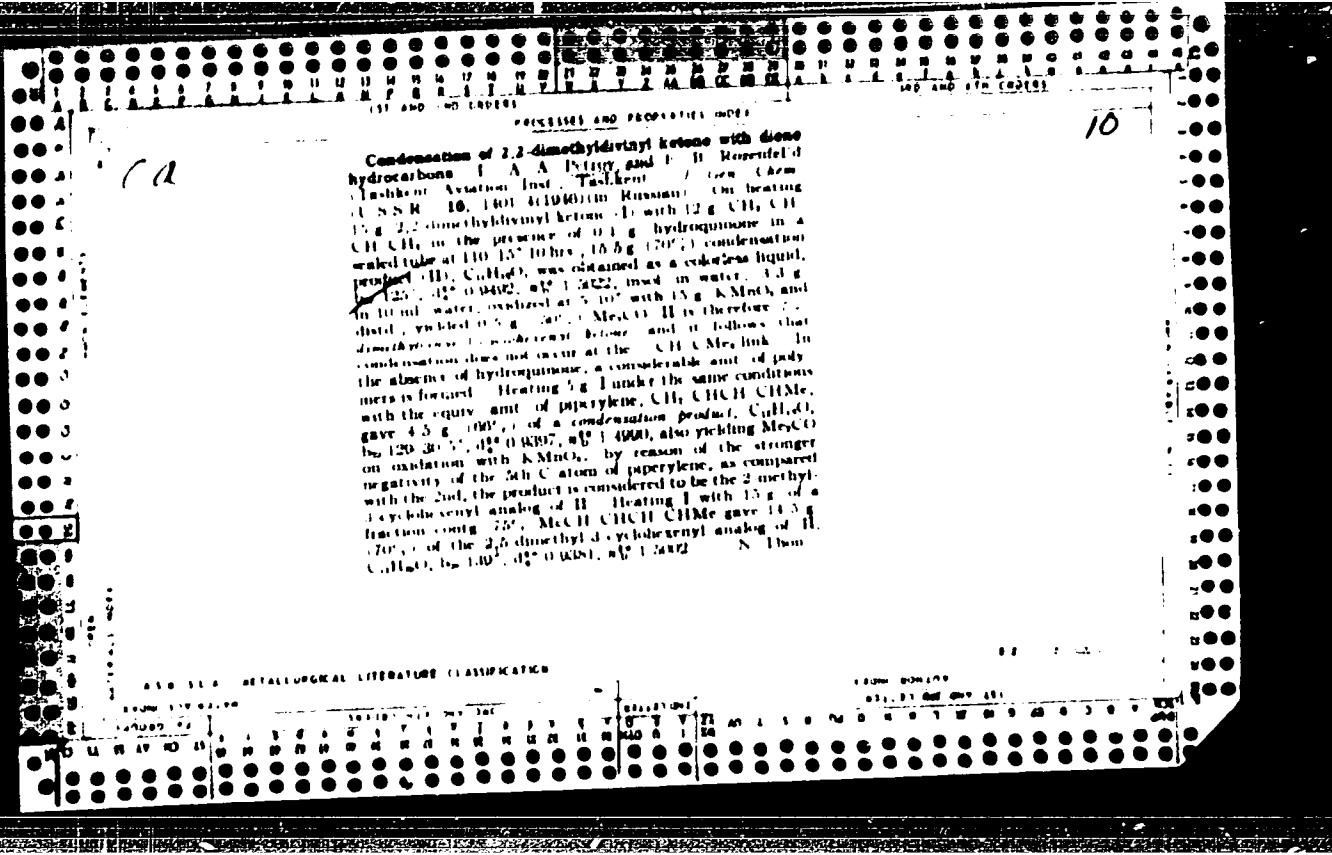
Petrov, A. A. (Tashkent Aviat. Inst.)Reactions of organic oxides with organotin compounds in the presence of hydrogen fluoride. II. Reaction of propylene oxide with ketones.

J. Gen. Chem. USSR., Vol. 16, 1946, p. 41-42.

Chem. Abstr., Vol. 41:113^a

Me₂CO (22 cc.) was treated with 0.25 cc. SnEt₂O, followed by slow addition of 1.0 cc. propylene oxide at 20-30° for 2 hrs., to yield 2.6 g. 2,2,4-trimethyl-1,3-dioxolane, b. 99-100°, d₄²⁰ 0.9090, n_D²⁰ 1.4019, and 3.3 g. of a polymeric product. The same reaction using MeEtCO gave 25% 2,4-dimethyl-2-ethyl-1,3-dioxolane, b. 123-4°, d₄²⁰ 0.9048, n_D²⁰ 1.4072, and 70% polymer. Propylene oxide (11.6g.) and 3.2 g. MePrCO under the above conditions gave 25% 2,4-dimethyl-2-propyl-1,3-dioxolane, b. 145.5-7°, d₄²⁰ 0.8954, n_D²⁰ 1.4122, and 70% polymer. The dioxolanes readily react with H₂O to propylene glycol and the ketone on shaking for a few min. with 5% H₂SO₄. -- Kosolapoff.

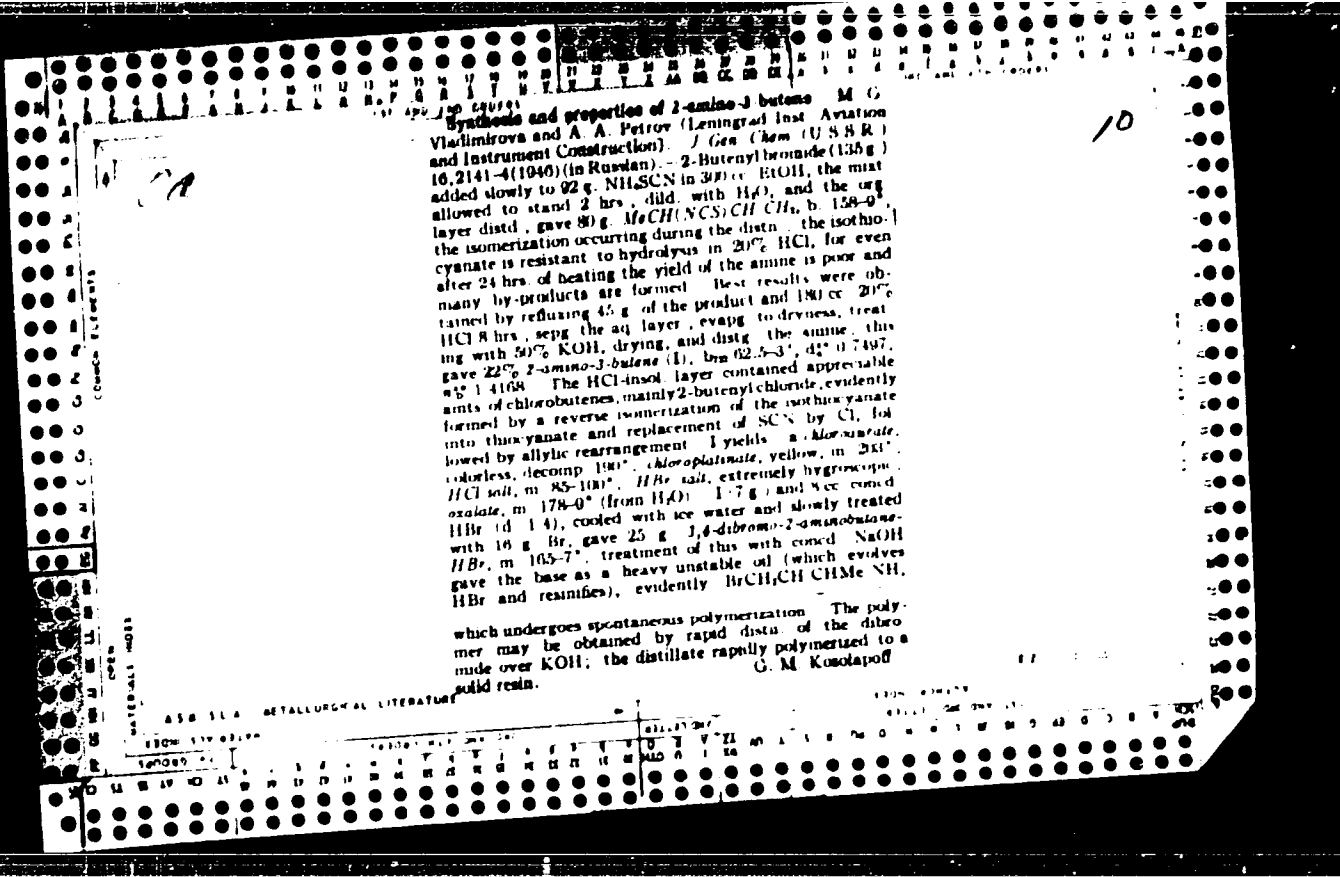




CA

The effect of the acid-base nature of the catalyst on the order of addition of alcohols to divinyl oxide. A. A. Petrov. *Zhur Obshchei Khim (J. Gen. Chem.)* 16, 1625-32 (1944). *Chem. Zentr.* 1947, I, 1079-80, cf. C.A. 43, 2079d. The action of alcs on $(CH_2=CH)_2O$ in the presence of alcoholates yielded *erythrol ethers*, which were secondary alcs and from which alkoxymethyl Et ketones were obtained by addn. of H_2 in $CHCl_3$, oxidation with chromic acid, and reduction with Na-Hg. In the presence of BF_3 , the isomeric primary alcs were obtained. This reaction is explained by assuming the formation of oxonium salts. The following compds were obtained in the presence of alcoholates: *Erythrol mono-Me ether*, $C_4H_{10}O$, mol. refraction 143.10, bp 141.5-1.75°, d_4^{20} 0.9161, n_D^{20} 1.4310, mol. refraction 27.95. The *acetate*, bp 164.5°, d_4^{20} 0.9811, n_D^{20} 1.4222, mol. refraction 37.34. Bromination yielded $C_4H_8O_2Br_2$, bp 128.9°, d_4^{20} 1.8248, n_D^{20} 1.5265, mol. refraction 44.12. The *methoxymethyl Et ketone* yielded the *dinitrophenylhydrazone*, $C_{11}H_{14}N_2O_4$, m 190.5° (from

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 AcOEt. *Et ether*, $C_4H_{10}O$, bp 141.25-1.5°, d_4^{20} 0.9190, n_D^{20} 1.4312, mol. refraction 32.71. *acetate*, $C_6H_{12}O_4$, bp 174.5°, d_4^{20} 0.9520, n_D^{20} 1.4220, mol. refraction 41.98. *Its addn. product*, $C_{11}H_{14}O_2$, bp 130.4°, d_4^{20} 1.2050, n_D^{20} 1.5110, mol. refraction 48.70. *isoxymethyl Et ketone di-nitrophenylhydrazone*, $C_{11}H_{14}N_2O_4$, orange needles from AcOEt, m 146°. The following compds were obtained in the presence of BF_3 : The *Me ether*, $C_4H_{10}O$, mol. refraction 143.10, bp 141.5-2.0°, d_4^{20} 0.9447, n_D^{20} 1.4310, mol. refraction 28.02. *acetate*, bp 164.5-5.5°, d_4^{20} 0.9820, n_D^{20} 1.4217, mol. refraction 37.26. *Its addn. product*, $C_{11}H_{14}O_2$, bp 130.8°, yielded approx. 20% crystals, m 50.61° (from petr. ether), on standing. Instn. of the Me ether over KOH in the presence of 2 drops $BF_3 \cdot Et_2O$ at a temp. not exceeding 100° yielded *methoxypropene*, bp 72.4°, d_4^{20} 0.8270, n_D^{20} 1.4112. Sapon. with 2% H_2SO_4 yielded the *Me vinyl ketone*, which with $CaO/CH_2=CH_2$ at 125° yielded *1-cyclohexenyl methyl ketone*, bp 70.5-80°, n_D^{20} 1.4098. *p-nitrophenylhydrazone*, $C_{11}H_{14}N_2O_4$, m 141.2°. *semicarbazone*, $C_{11}H_{14}N_2O_4$, m 165°. The *Et ether*, $C_6H_{14}O$, bp 150.0-0.75°, d_4^{20} 0.9194, n_D^{20} 1.4308, mol. refraction 52.67, the *acetate*, $C_{12}H_{18}O_4$, bp 174.5-4.0°, d_4^{20} 0.9511, n_D^{20} 1.4214, mol. refraction 41.82. M. G. Moore



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Condensation of diene hydrocarbons with butynone.
 A. A. Petrov. *Compt rend acad sci URSS* 33, 3507 A (1946) (in English). CH₃COOMe (1.0 g, 0.01 mol) with CH₂=CH-CH=CH₂ in CCl₄ in sealed glass tubes at 125-300°C for 12-16 hrs. gives 80% 1,4-dihydro-2-phenone (II), bp 105-5.5°C, d₄²⁰ 1.0120, n_D²⁰ 1.5110, MR_D 30.12, IR (KBr) 1615 cm⁻¹. Similarly, 1,4-dihydro-2-phenone (II) is obtained from 2,3-dimethyl-1,3-butadiene with 2,3-hexadiene gives 80% 1,4-dihydro-2,3-dimethyl-2-phenone (III), bp 105-5.5°C, d₄²⁰ 1.0120, n_D²⁰ 1.5110, MR_D 30.12, IR (KBr) 1615 cm⁻¹. 2,4-dinitrophenylhydrazones in 151.3-1.1 m, IR 1615 cm⁻¹. 2,4-dinitrophenylhydrazones in 151.3-1.1 m with CH₂=C(Me)-CMe=CH₂ gives 80% 1,4-dihydro-2,3-dimethyl-2-phenone (III), bp 127.5-8°C, d₄²⁰ 1.0120, n_D²⁰ 1.5110, MR_D 30.12, IR (KBr) 1615 cm⁻¹. 2,4-dinitrophenylhydrazones in 214.157. 2,4-dinitrophenylhydrazones in 214.157. 2,4-dinitrophenylhydrazones in 214.157. H and III, distil over S, give H₂S and, resp., PhCOMe and 2,3-Me₂C=CHCOMe. I. P. Danby.

6 27 OCT 1967

METALLURGICAL LITERATURE CLASSIFICATION

SEARCHED		SERIALIZED		INDEXED		FILED	
1	2	3	4	5	6	7	8
9	10	11	12	13	14	15	16
17	18	19	20	21	22	23	24
25	26	27	28	29	30	31	32
33	34	35	36	37	38	39	40
41	42	43	44	45	46	47	48
49	50	51	52	53	54	55	56
57	58	59	60	61	62	63	64
65	66	67	68	69	70	71	72
73	74	75	76	77	78	79	80
81	82	83	84	85	86	87	88
89	90	91	92	93	94	95	96
97	98	99	100	101	102	103	104

CA
 Order of addition of alcohols to glycidic ethers. M. G. Vladimirova and A. A. Petrov (Leningrad Aviation Instrument Inst.). *J. Gen. Chem. (U.S.S.R.)* 17, 51-4 (1947) (in Russian). The effect of the nature of the catalyst (RONa or BF₃·Et₂O) on the addn. of alcs. to glycidic ethers was studied. Me or Et glycidic ether was added to 10 parts of the corresponding alc. in which 1-1.5% Na was dissolved. The mixt. was heated 10 hrs. at 100° in a sealed tube; distn. gave products which cor-

responded in their properties to the α,γ -glycidic ethers, with the following yields: 1-Me 85%, Me Et 75%, di-Et 65%. In all cases the products distd. within a 0.5-1.0° range and were pure substances. $MeOCH_2CH(OH)CH_2OMe$, bp 161.5°, dn 1.4212, d₄²⁰ 1.0374, n_D²⁰ 1.4235; $CH_3OCH_2CH(OH)CH_2OEt$, bp 94.5°, d₄²⁰ 0.9758, n_D²⁰ 1.4212; $EtOCH_2CH(OH)CH_2OEt$, bp 184.5°, dn 1.4212, d₄²⁰ 0.9248, n_D²⁰ 1.4214. When, however, the Me or Et glycidic ethers in 10 vols of the corresponding alc. were treated with 0.5 cc. BF₃·Et₂O and allowed to stand in a closed tube at room temp. 24 hrs. there was obtained 65% of the di-Me ether and 62% di-Et ether; these were not pure α,γ -ethers, as shown by their wider boiling ranges, and may have contained up to 15% of the α,β -diethers. Attempts to show this by chem. methods failed. Both sets of products on oxidation gave dialkyl acetones. The BF₃-catalyzed products had the following constants: di-Me, bp 166.7°, dn 1.0390, n_D²⁰ 1.4215, d₄²⁰ 1.4216; di-Et, bp 188.10°, dn 1.0530, n_D²⁰ 1.4216. In a typical oxidation exp. 0.05 mol di-Me ether was stirred with an equiv. amt. of Na₂Cr₂O₇ in a small vol. of H₂O at 25-2 hrs. with dropwise addn. of 20% H₂SO₄, extr. with Et₂O and treatment of the rat. with 2,4-(NO₂)₆-C₆H₃NH₄ gave dimethylacetone. 2,4-dinitrophenyl hyd. azoxo., m. 119.20° (from EtOH). The relatively small effect of the nature of the catalyst is explained by the predominance of the ROCH₂-CH(OH)-CH₂ structure in

G. M. Kowdajoff

glycidic ethers

PA 15T76

PETROV, A. A.

USSR/Chemistry - Unsaturated Compounds
Chemistry - Butynone

Mar 1947

"Investigation in the Field of Conjugate Systems:
XXVIII, Diene Syntheses With Participation of
Butynone," A. A. Petrov, 5 pp

"Zhur Obshch Khim" Vol XVII, No 3 - p.497-501

Study of the condensation of butyn-1-one-3 with
diene hydrocarbons-divinyl,2,3-dimethylbutadiene-1,3
and hexadiene-2,4.

15T76

1947, A. A.

1947

USSR/Chemistry - Ethoxy Group
Chemistry - Methoxy group

Mar 1947

"Investigation in the Field of Conjugate Systems:
XXIX, The Condensation of Alcoxyrenes With
Methyl Vinylcetone," A. A. Petrov, 3 pp

"Zhur Obshch Khim" Vol XVII, No 3 - p.140

Study of the condensation of the methoxy and
ethoxyrenes with the subject compound.

15T82

Order of elimination of hydrogen halides from certain unsaturated di- and trihalogen derivatives A. A. Petrov (Leningrad Inst. Aviation Instruments) J. Gen. Chem. (U.S.S.R.) 17, 936-40(1947) (In Russian). (1) In 1,2-dichloro-3-butene, the structure $\text{CH}_2\text{Cl}-\dot{\text{C}}\text{HCl}-\text{CH}=\text{CH}_2$ is represented with a considerable wt. owing to its resonance with $\text{CH}_2\text{Cl}-\text{CHCl}-\dot{\text{C}}\text{H}-\text{CH}_2$, which leads to a dipole moment μ of 0.5 debye (Syrkin, C. A. 38, 5701², 8 and Shott-L'vova, C. A. 39, 3710²), whereas the structures $\dot{\text{H}}\text{C}=\text{CHCl}-\text{CHCl}-\text{CH}_2$, $\text{CH}_2\text{Cl}-\dot{\text{C}}\text{HCl}-\text{CH}=\text{CH}_2$, and $\text{CH}_2\text{Cl}-\text{CH}=\dot{\text{C}}\text{HCl}-\text{CH}_2$, characteristic of satd. hydrocarbons ($\mu = 0$), must be negligible. by the position of the mobile H in the 1st structure, the product of elimination of HCl by alkalis must be chloroprene, as actually found. the same is true, by literature data, for 1,2-dibromo-3-butene, 3,4-dichloro-2-methyl-1-butene, 3,4-dibromo-2-methyl-1-butene, 2,3,4-trichloro-1-butene, etc. (2) By similar considerations, the predominating structures in 1,4-dichloro-2-butene are $\dot{\text{H}}\text{C}=\text{CHCl}-\text{CHCl}-\text{CH}_2$ and $\text{CH}_2\text{Cl}-\dot{\text{C}}\text{H}-\text{CHCl}-\text{CH}_2$, with elimination of HCl with solid alkalis resulting in 1-chloro-1,3-butadiene, also on account of the gain in resonance energy owing to the formation of a conjugated system. The same scheme has been found for 1,4-dibromo-2-butene and 1,4-dibromo-2-methyl-2-butene. (3) The formation of diethers $\text{CH}_2(\text{OR})\text{CH}=\text{CHCl}$ or $\text{CH}_2\text{Cl}-\text{CH}(\text{OR})\text{CH}=\text{CH}_2$ in the elimination of HCl from 1,4-dihalo-2-butenes by alk. alkalis is attributable to the mobility of the halogen atoms and ease of ionization (C^-H , $\text{CH}=\text{CH}-\text{CH}_2\text{Cl}$, C^-HCl , $\text{CH}_2\text{Cl}-\text{CH}=\text{C}^-\text{H}$), also on account of the closeness of the double bond, as against the stability of Cl in 1,2-dihalo-2-butenes owing to the vicinal effect; this mechanism prevails in the reactions of 1,4-dichloro-2-butene, 1,4-dibromo-2-butene, and 1,4-dibromo-2-methyl-2-butene with alk. alkalis.

(4) That elimination of HCl from trihalobutenes, if brought about by solid alkalis, produces mainly $\text{CH}_2=\text{CXCH}=\text{CH}_2$, and only with alk. alkalis also some amt. of diethers, is due to a depression of the mobility of the substitutable halogen X at positions 1 and 4 by the X at 2, the structure $\text{CH}_2\text{Cl}-\text{C}^-\text{Cl}-\text{CH}=\text{CHCl}$ depressing the wt. of structures (such as those given under 3) favoring ionization of X at 1 and 4. the vicinal effect, $\dot{\text{C}}\text{OH}$, $\text{C}^-\text{Cl}-\text{CH}=\text{CHCl}$, acts in the same direction. The mode of elimination of HCl is detd. first, by H, which is more mobile at 4 than at 1 owing to the predominant wt. of $\dot{\text{H}}\text{C}=\text{CHCl}-\text{C}^-\text{Cl}-\text{CH}=\text{CHCl}$ and $\dot{\text{H}}\text{C}=\text{CHCl}-\text{C}^-\text{Cl}-\text{CH}=\text{CHCl}$ over $\text{CH}_2\text{Cl}-\text{C}^-\text{Cl}-\text{CH}=\text{CHCl}$ and $\text{CH}_2\text{Cl}-\text{C}^-\text{Cl}-\text{CH}=\text{CHCl}$, and by the greater mobility of X at 4 than at 1, due to the greater no. of ions structures in the 1st case and to the vicinal effect in the 2nd case. This scheme applies to 1,2,4-trichloro-2-butene, 2-chloro-1,4-dibromo-2-butene, and 1,2,4-tribromo-2-butene. (5) Dehalohydrogenation of $\text{CH}_2\text{Cl}-\text{CHCl}-\text{CH}=\text{CH}-\text{COOH}$ gives 3-chloro-1-carboxy-1,3-butadiene, $\text{CH}_2=\text{CClCH}=\text{CH}-\text{COOH}$, owing to the preponderance of the structure $\text{CH}_2\text{Cl}-\text{CHCl}-\dot{\text{C}}\text{H}-\text{CH}-\text{COOH}$ which stabilizes X at 2 and at the same time facilitates ionization of H at 2 on account of the resonance of $\text{CH}_2\text{Cl}-\text{CHCl}-\dot{\text{C}}\text{H}-\text{CH}-\text{COOH}$ and $\text{CH}_2\text{Cl}-\text{CHCl}-\text{CH}=\dot{\text{C}}\text{H}-\text{COOH}$. (6) In contrast, $\text{PhCH}=\text{CH}-\text{CHCl}-\text{CH}_2\text{Cl}$ splits off HCl to give 4-chloro-1-phenyl-1,3-butadiene, $\text{PhCH}=\text{CH}-\text{CH}=\text{CHCl}$, the structure $\text{CH}_2\text{Cl}-\text{CHCl}-\dot{\text{C}}\text{H}-\text{CH}-\text{Ph}$ opposing ionization of H at 2 and facilitating that of X at 2. N. Thon

Chlorination of butadiene and properties of the chlorides.
 A. A. Petrov and N. P. Supov (Leningrad Inst. Aviation Instr.). *J. Gen. Chem. (U.S.S.R.)* 17, 1105-10(1947) (in Russian). — Butadiene was chlorinated under conditions given previously (C.A. 40, 6400). Distn. of the low-boiling fraction (b₀ 40-5°, d₄²⁰ 1.1383, n_D²⁰ 1.4500) gave 80% (on wt. of the 40-5° fraction) pure 1,2-dichloro-3-butene, which showed that the low-boiling fraction contained appreciable amts. of dichlorobutane (evidently the 2,3-isomer) if the butadiene used was the unpurified 90% butadiene, contg. 10% pseudobutylene, as specified by Klebanik, Sorokina, and Khavkin (C.A. 42, 5144). The amt. of the said. product tends to rise with increased opportunity of butadiene to form low polymers. Distn. of the high-boiling fraction of the chlorides gave a fraction, b₀ 110-30°, from which it was possible to isolate the *trans*-chloride, m. 73-4°, but this isolation tended to be more difficult as the degree of chlorination was increased. The 110-30° fraction contains less Cl than theoretically required for the tetrachloride and consists of the tetrachloride isomers and polymers of butadiene. The following yields were obtained in the study of chlorination under various conditions: 340 g. butadiene in 1000 cc. CHCl₃ and 112 g. Cl gave 26% dichlorides (30 g. 1,2-isomer and 48 g. 1,4-isomer); 650 g. butadiene and 210 g. Cl in 1040 cc. CHCl₃ gave 20% dichlorides (40 g. 1,2- and 38 g. 1,4-isomers); 650 g. butadiene and 312 g. Cl in 1000 cc. CHCl₃ gave 24% dichlorides (54 g. 1,2- and 61 g. 1,4-isomers); 300 g. butadiene and 110 g. Cl in 550 cc. petr. ether gave 23% dichlorides (28 g. 1,2- and 25 g. 1,4-isomers). To 40 g. CH₂:CHCHCl:CH₂:Cl in 80 cc. CHCl₃ was added slowly with cooling 10 cc. Br in 18 cc. CHCl₃; after washing with 80% soda soln. there was obtained 72% of a mixt. of liquid 1,2-dichloro-3,4-dibromobutane, b₀ 120-2° (d₄²⁰ 2.0088, n_D²⁰ 1.5548, and a solid isomer, m. 81.5-3°

(from EtOH), (207%), which were sepd. by freezing. In agreement with data of Klebanik, solid KOH gives CH₂:CHCH:CHCl from the 1,4-dichloride and chloroprene from the 1,2-dichloride. However, the action of alc. KOH on the dichlorides was found to be different from that given by Klebanik: the 1,2-dichloride gives chloroprene, but the 1,4-dichloride gives almost exclusively the di-Et ether of erythrene glycol; the same result is obtained with MeOH-KOH; similar reactions take place when (BrCH₂CH₂)₂ or BrCH₂CH₂·CMe₂CH₂Br are used. To 26 g. KOH in 137 cc. MeOH heated on a steam bath was added 20 g. (CICH₂CH₂)₂ and the mixt. was refluxed 2 hrs. to give 13.6 g. (MeOCH₂CH₂)₂, b₀ 63.5-3°, d₄²⁰ 0.8648, n_D²⁰ 1.4230; 6 g. of this in 20 cc. CHCl₃ with 5 g. Br in 5 cc. CHCl₃ gave 77% (MeOCH₂CHBr)₂, m. 64-5° (from EtOH), b₀ 108°. Similarly there were prepd. (EtOCH₂CH₂)₂, b₀ 73-2.5°, d₄²⁰ 0.8718, n_D²⁰ 1.4256, and (EtOCH₂CHBr)₂, m. 28-30°, b₀ 119.5-20.5° (CICH₂CH₂)₂ (10 g.) in 15 cc. CHCl₃ with 4.5 cc. Br in 5 cc. CHCl₃ gave 98% 1,4-dichloro-2,3-dibromobutane, m. 99.75-100.25° (from EtOH). To 7.7 g. 1-chlorobutadiene in 30 cc. EtOH was added 30 g. Hg oxide and 25 g. iodine in small portions with cooling and shaking, diln. of the filtered mixt. with water gave 61% ICH₂CH(OEt)CH₂CHCl, b₀ 95.5-0°, d₄²⁰ 1.6516, n_D²⁰ 1.6319, this (10 g.) refluxed 1 hr. with excess alc. KOH and gave 51% 1-ethoxyethylacetylene, b. 101.5-2.5°, d₄²⁰ 0.4560, n_D²⁰ 1.4416, this (0.5 g.) brominated with 6 g. atoms Br with cooling, followed by boiling with 5 g. Zn shavings, gave Me-EtC(O) (dinitrophenylhydrazone, m. 115°) to prove the structure of the iodo deriv. Bromination of 1-chlorobutadiene gives a product b₀ 83-3.5°, d₄²⁰ 1.9016, n_D²⁰ 1.6076, which isomerizes on standing to a lacrimatory product b₀ 89.5-90°, d₄²⁰ 1.9724, n_D²⁰ 1.5708; evidently an isomerization of the 1,2-dibromide into the 1,4-isomer takes place. G. M. K.

CA

Diene syntheses with halo dienes I. **Condensation of monohalobutadienes with α,β -unsaturated aldehydes and ketones** A. A. Petrov and N. P. Sapozhnikov, Aviaton Instrumental Inst., *J. Gen. Chem. U.S.S.R.*, 17, 1266 (1946) (1947 Russian); *Chloroprene*, 17, 1271, 1122 g. acrolein, 0.1 g. pyrogallol, and 20 cc. PhMe heated in a sealed tube 18 hrs. at 95-100° gave 6.0 g. rubbery polymer and 55% *p*-chlorotetrahydrobenzaldehyde, bp 104-6°, d_4^{20} 1.1560, n_D^{20} 1.5831, which on standing readily gives a trimer, m 137.8° from EtOH. PhMe: the monomer gives a *trans*-isomer, m 151.4° (from aq. KOH), and a *p*-nitrophenylhydrazone, m 150.8° (from aq. KOH); *o*-dimethylphenylhydrazone, m 163.7° (from EtOH). Oxidation of the aldehyde gave *p*-chlorotetrahydrobenzoic acid, m 129.5° from EtOH; the aldehyde 12 g. in 100 cc. MeCO₂CH₃ treated with 10% KOH over 15 min. with stirring and cooling, stirred 2 hrs., neutralized with H₂SO₄, and extd. with PhMe, gave 60% of the *diene ketone*, *Chloral*, bp 104.7°, d_4^{20} 1.1176, n_D^{20} 1.5210, which gives a *trans*-isomer, m 139.2° from EtOH. Chloroprene (8.9 g.) added to a soln. of MeCO₂CH₃ (1 from 11 g. ethoxybutadiene and 50 cc. 5% H₂SO₄) followed by satn. with 20% PhMe, after satn. with Na₂CO₃ in 20% PhMe and heated 12 hrs. in a sealed tube at 95° gave 1.2 g. of a yellow-brown polymer and 50% *p*-chlorotetrahydrobenzaldehyde, bp 104-6°, d_4^{20} 1.1560, n_D^{20} 1.5831, which immediately forms a trimer, m 137.8° from EtOH.

only a trace of H₂S was found and the material was substantially unchanged. CH₂Cl-CHCl-CH=CH₂ (2 g.) was shaken with 100 cc. 10% H₂SO₄ at 60° for 1 hr. in the presence of MeCO₂CH₃ and extd. by 100% PhMe, then the oil after satn. with Na₂CO₃ was distilled with a trace of chloroprene and heated in a sealed tube 18 hrs. at 95° gave 2.1 g. of a rubbery polymer and 51% *p*-chlorotetrahydrobenzaldehyde, bp 129.5-31°, d_4^{20} 1.1540, n_D^{20} 1.5810, n_D^{20} 1.5810, m 139.2°. *p*-nitrophenylhydrazone, m 170.2° from EtOH. 20% 2 g. of this ketone distd. from 2 g. S gave 1.4 g. *p*-Cl-CH₂-CH=CH₂ (bp 94°). Heating 2.5 g. CHCl-CHCl-CH=CH₂ with 2.0 g. acrolein in 5 cc. PhMe 18 hrs. at 95° gave 1 g. of a rubbery polymer and traces of a product similar to that from the condensation of acrolein with chloroprene. Bromoprene (3.3 g.) and 5.4 g. acrolein with 20 cc. PhMe heated 12 hrs. at 95° gave 3.4 g. of a dark hard rubbery polymer and 50% *p*-bromotetrahydrobenzaldehyde, bp 121.1°, which immediately forms a trimer, m 141° from PhMe. EtOH: Bromoprene, m 83.4° and MeCO₂CH₃ CH₂ from 0.2 g. ethoxybutadiene in 20 cc. PhMe heated 12 hrs. at 100° gave 0.8 g. of a polymer and 50% *p*-bromotetrahydrobenzaldehyde, bp 133.5°, d_4^{20} 1.4176, n_D^{20} 1.5224, *trans*-isomer, m 180.5° from EtOH; *p*-nitrophenylhydrazone, m 160.1°. G. M. Kosolapov

CA

Condensation of alkoxypropenes with acrylonitrile. A. A. Petrov and M. G. Vladimirova (Leningrad Aviation Inst. Inst.) *J. Gen. Chem. (U.S.S.R.)* 17, 1643 (1947) (in Russian). Methoxypropene (4.2 g) and 2.6 g. CH₃CHCN in 10 cc. MePh heated 18 hrs. at 105° gave 15% *d*-methoxy-*β*-cytobutene-1-carbonitrile (I), bp 121.0°, stabilization with pyrogallol during the condensation is necessary. Similar condensation for 12 hrs. at 145° gives 60% I, bp 125.5°, d₄²⁰ 1.0325, n_D²⁰ 1.4818. Ethoxypropene (12 g) and 0.5 g. CH₃CHCN heated 14 hrs. at 145° gave 75% *d*-ethoxy-*β*-cytobutene-1-carbonitrile (II), bp 131.5°, d₄²⁰ 1.0010, n_D²⁰ 1.4775. II (3.8 g) shaken 15 min. with 20% NaOH, at 40°, then acid. with (NH₄)₂SO₄ and acid. with H₂O, gave 80% *d*-oxy-*β*-cytobutene-carbonitrile, bp 148.5-0.5°, which gives the usual ketone derivs. (these, however, were not obtained in pure state and no instr. are given). The nitrile on standing 10 days in 10% HCl gave *d*-oxy-*β*-cytobutene-carboxylic acid, m. 105°. *p*-nitrophenylhydrazine m. 182.3°. I + 2 g. NaOH, 5 cc. H₂O, and 15 cc. EtOH boiled 10 hrs. also gave this acid after concn., acidification, and rapid drying. 1.0 g. in 50 cc. EtOH, treated with 7 g. Na, the mixt. acid. with 50 cc. H₂O and concd., and the residue acid. with H₂O gave 65% *d*-methoxy-*β*-cytobutene-*β*-aminoamine, bp 109.5-10°, d₄²⁰ 0.9654, n_D²⁰ 1.4912. Similar reduction of II gave 60% of the *ER* analog, bp 110-10.5°, d₄²⁰ 0.9648, n_D²⁰ 1.4856. The latter (3.8 g.) in 10 cc. 20% H₂SO₄ neutralized with an equiv. amt. of NaOH yielded an Et₂O-insol. resin, a crumbly, yellow solid, which appeared to be a polymer of the resulting *β*-amino-*β*-cytobutene. The free keto-amine could not be isolated either in the form of a salt or a keto group deriv.

G. M. Kosolapoff

CA

Condensation of butynyl, chloroprene, and bromoprene with acrylonitrile A. A. Petrov and N. P. Popov (Aviation Instrument Inst., Leningrad). *J. Gen. Chem. (U.S.S.R.)* 17, 2253-54 (1947) (in Russian), cf. C. I. 42, 2258/ CH₂CHCN (1) (10 g), 20 ml tech butynyl, and 0.1 g hydroquinone in 20 ml PhMe heated in sealed tubes 12 hrs at 130° gave 80% 1-cyano-3-cyclohexene, bp 83°, d₄²⁰ 0.9555, n_D²⁰ 1.4726, this (5.4 g) boiled 5 hrs with 5 g NaOH, 5 ml H₂O, and 10 ml EtOH, then acidified by 25% H₂SO₄ and extd with Et₂O, gave 1-cyano-3-cyclohexene-1-carboxylic acid, m. 17°, bp 132.5-33°, d₄²⁰ 1.0815, n_D²⁰ 1.4812 (dibromide, m. 88°). Heating a mixt of acrylic acid and butynyl in PhMe 12 hrs at 125° gave the same acid (yield not detd). The nitrile (5.4 g), 3 ml H₂SO₄, and 12 ml MeOH heated in a sealed tube 3 hrs at 125° gave 71% Me 1-cyclohexene-3-carboxylate, bp 70.5°, d₄²⁰ 0.9946, n_D²⁰ 1.4650. Reduction of the nitrile (5.4 g) by 5 g Na in 35 ml EtOH gave 75% 3-cyclohexenylamine, b. 109.5-70.5°, d₄²⁰ 0.9077, n_D²⁰ 1.4840. I (10 g), 17.6 g chloroprene, and 0.1 g pyrogallol in 20 ml MePh heated 18 hrs. to 130-5° in a sealed tube gave a main fraction, 14 g, bp 120-6°, which on standing gave 7 g solid nitrile (25%), m. 55° (from petr. ether), identified as 6-chloro-3-cyclohexene-1-carboxylic ether), in addn, some dimers of chloroprene were found in the intermediate fractions. Hydrolysis of the nitrile, as above by alk. NaOH, gave 97% 6-chloro-3-cyclohexene-1-carboxylic acid, m. 109.5-10° (from H₂O), while alcoholysis by MeOH-H₂SO₄, as above, gave 70% Me ester of this acid, bp 117.5-18.5°, d₄²⁰ 1.0523, n_D²⁰ 1.4678, reduction of the nitrile by Na-EtOH gave 55% 3-tetrahydrobenzylamine, identical with that described above (5.3 g), and 19.5 g bromoprene, stabilized by pyrogallol, heated 1 1/2 hrs to 130.5° in 20 ml MePh gave 31% 6-bromo-3-cyclohexene-1-carboxylic acid, m. 67° (from petr. ether), which on hydrolysis by alk. NaOH gave 86% 6-bromo-3-cyclohexene-1-carboxylic acid, m. 132.5-3.5° (from H₂O). Thus, in I there occurs a same character of reagent polarization as is observed in reactions with unsatd aldehydes or ketones. (C. M. Knowlton)

PETROV, A. A.

PA 01

USSR/Chemistry - Acronitrile
Chemistry - Condensation

Mar 1948

"Condensation of Acronitrile With Piperylene and Isoprene," A. A. Petrov, A. F. Sapozhnikova, Chem Lab, Leningrad Inst Avn Equipment Constr, 6 pp

"Zhur Obshch Khim" Vol XVIII (LXXX), No 3

Nitrile methylcyclohexenecarbon obtained as a result of this condensation. Corresponding amines: 2-methyl-delta³-tetrahydrobenzylamine and mixtures of 4- and 3-methyl-delta³-tetrahydrobenzylamines were obtained by reducing products of condensation. Shows that electron theory can be applied to order of condensation on isoprene and piperylene with acronitrile. Submitted 4 Mar 1947.

69718

PA 8/49T37

PETROV, A. A.

USSR/Chemistry - Ethyl Alcohol,
Decomposition of
Chemistry - Distillation

Apr 48

"Problem of the Nature of the Amylene-Piperylene
Fraction of the Condensate Formed as a Result of
the Catalytic Decomposition of Ethyl Alcohols,"
A. A. Petrov, A. F. Sapozhnikova, Chem Lab,
Leningrad Inst of Aviation Inetr Bldg, 57 pp

"Zhur Obshch Khim" Vol XVIII (LXXX), No 4
^{p. 640-4}
Shows that the piperylene in the amyene-piperylene

fraction of the condensate obtained by the
decomposition of ethyl alcohol by S. V. Lebedev's
method does not fully react with acronitrile and
8/49T37

Apr 48

USSR/Chemistry - Ethyl Alcohol,
Decomposition of (Contd)
consists of a mixture of cis- and trans- forms,
latter predominating. Establishes presence of
isoprene in initial fractions. Submitted 4 Mar
1947.

8/49T37

USSR/Chemistry - Piperylene
Chemistry - Acrolein

Jun 48

"Problem of the Structure of the Products of Con-
densation of Piperylene With Acrolein," A. A.
Petrov, Chem Lab, Leningrad Inst of Avn Instr
Bldg, 3¹/₄ pp

"Zhur Obshch Khim" Vol XVIII (LXXX), No 6

Establishes that only trans-piperylene takes part
in reaction. Shows that condensation product is
mainly or exclusively 2-methyl- Δ^3 -tetrahydroben-
zoin aldehyde. Compares structure by oxidation
to corresponding acid and prepares some hydrazine
derivatives. Submitted 10 Jun 1947.

9/49T21

USSR/Chemistry - Diene Hydrocarbons
Systems, Conjugate

Oct 48

"Research in the Field of Conjugate Systems: XXXVI,
The Condensation of Diene Hydrocarbons With Methacrylic
Acid (I) and Methylmethacrylate (II)," A. A. Petrov,
M. P. Sopotov, Chem Lab, Leningrad Inst of Avn Instr
Const., 7 1/2 pp

"Zhur Obshch Khim" Vol XVIII, No 10 p.1761-8

Condensation of I and II with 1,3-butadiene, chloro-
prene, 2,3-dimethyl-1,3-butadiene and cyclopentadiene
gave 1-methylcyclohexene-3-carboxylic acid, a mixture
of 1-methyl-3- and 1-methyl-4-cyclohexene-3-carboxylic

2/50740

USSR/Chemistry - Diene Hydrocarbons
Systems, Conjugate (Contd)

Oct 48

acids, 1,3,4-trimethylcyclohexene-3-carboxylic acid
and 2,5-endomethylenecyclohexene-3-carboxylic acid
and their methyl esters, respectively Submitted
22 Oct 47

100740

C

The order of addition of alkyl hyponalites to butadiene
A. A. Petrov, Leningrad Inst. Aviation Equipment, Com. 2
Construction, 1974, No. 2, p. 19.
Engl. translation. See also 144-10001-1, 144-10001-2, 144-10001-3.

The order of addition of alkyl hypochlorites to butadiene. A. A. Petrov. *Zhur (Doklady Akad. Nauk SSSR)* (Gen. Chem.) 19, 1046-49 (1949). Addn. of alkyl hypochlorite to butadiene (I) yields predominantly the 1,2-Cl ethers, along with the 1,4-isomers; the Br and iodine analogs yield only the 1,2-isomers between -12° and 45° . Generally, an increase of radical size reduces the total yield and the relative proportion of the 1,4-isomer; increase of temp. increases both, which may be expected in view of the higher thermal stability of the 1,4-isomers. At -10° (and its vicinity) $\text{PhSO}_2\text{NCl}_2$ reacts with I in EtOH in 2 steps, the 1st action is the formation of a compd. with I having an active Cl (at this stage the yield of Cl ethers is very low), and the 2nd step is the action of this substance on the EtOH-I-soln., yielding the Cl ethers. Some PhSO_2NH_2 always forms, apparently by the action of the dichloroamide upon 2 mols. EtOH and 2 mols. I, a reaction which is intensified by higher temps. Addn. of 63 g $\text{PhSO}_2\text{NCl}_2$ over 4 hrs. to 68 ml. I (0.76 g.-mole) in 100 ml. MeOH at -12° to -15° with stirring, followed by stirring 2 hrs., filtration, and stirring the filtrate at -5° with an excess of powd. Na_2SO_3 , then steam distn. gave 28 g (46.5%) mixed Cl ethers, b. $120-40^{\circ}$, which on re-distn. was sep'd into 83% 1-chloro-2-methoxy-3-butene (II), b.p. $121.5-4.5^{\circ}$, d_4^{20} 1.0041, n_D^{20} 1.4342, and 17% 1-chloro-4-methoxy-3-butene (III), b.p. $151-3^{\circ}$, d_4^{20} 1.0246, n_D^{20} 1.4529. Boiling II with alc. KOH gave methoxypropene, b. $74.5-5.5^{\circ}$, n_D^{20} 1.4475, while III brominated in CHCl_3 gave 1-chloro-3,4-dibromo-3-methoxybutane, b.p. $124.5-8.5^{\circ}$, d_4^{20} 1.8462, n_D^{20} 1.5295; III heated 0.5 hr. with EtOH-KOH gave $\text{MeOCH}_2\text{CH}=\text{CHCH}_2\text{OMe}$, b.p. $48-51^{\circ}$, n_D^{20} 1.4234 [which on bromination gave the 2,3-di-Br compd., b.p. 108° , m. 67° (from EtOH)], and $\text{MeOCH}_2\text{CH}=\text{CHCH}_2\text{OEt}$, b.p. 62.5° , which on bromination gave the 2,3-di-Br compd., b.p. $114-15^{\circ}$. The 1,4-di-MeO compd. was also obtained from 21.4 g ($\text{CH}_2\text{CH}_2\text{Br}$) and 20 g KOH in 40 ml. MeOH at reflux; the product

b.p. 50° , n_D^{20} 1.4234, d_4^{20} 1.0041. Bromination of III in CHCl_3 with the theoretical amt. of Br in the cold gave 75% 1-chloro-2,3-dibromo-4-methoxybutane, b.p. 126.5° , d_4^{20} 1.833, n_D^{20} 1.5110, apparently obtained as a mixt. of stereoisomers. Passage of 67 ml. gaseous I into 100 ml. MeOH with stirring at 40° , with concurrent slow addn. of 63 g $\text{PhSO}_2\text{NCl}_2$ (2.5 hrs.) and stirring 3 hrs., gave after the above purification procedure 35% mixed Cl ethers (70% II and 30% III), somewhat contaminated with 1-dichlorides. Addn. of 15 g HgO to 0.11 mol. I in 25 ml. MeOH, followed by 25 g. powd. iodine at -10° to -15° , filtration, and distn. gave 12.5 g. 1-iodo-3-methoxy-3-butene,

b.p. 64.5° , n_D^{20} 1.5148, d_4^{20} 1.6175; the 1,4-isomer was not found. Simultaneous passage of 60 ml. I and addn. of 127 g. iodine to a suspension of 63 g. HgO in 100 ml. MeOH at $35-40^{\circ}$ gave 68 g. of the same compd. and some higher-boiling fractions contaminated with butadiene diiodides. Heating the iodo ether with alc. KOH gave 74% methoxypropene. Addn. of 125 g $\text{PhSO}_2\text{NCl}_2$ at -8° to -12° with stirring over 3 hrs. to 135 ml. I in 290 ml. EtOH, stirring 3 hrs., and filtration gave 17 g. butadiene- $\text{PhSO}_2\text{NCl}_2$ addn. product, m. 56° , while the filtrate yielded 34 g. mixed chloroethoxybutenes, the residue after the distn. of which gave 30 g. PhSO_2NH_2 (from hot HgO) and a considerable amt. of $\text{PhSO}_2\text{NCl}_2$ -butadiene addn. products which did not have active Cl; in this case the halo ether isomer ratio was 96% 1,2- and 6% 1,4-isomers. These were $(\text{ClCH}_2\text{CH}(\text{OEt})\text{CH}=\text{CH}_2)$, b.p. $136-6.5^{\circ}$, d_4^{20} 0.9700, n_D^{20} 1.4320, and the 1,4-isomer, b.p. $62-4^{\circ}$, d_4^{20} 0.9912, n_D^{20} 1.4518; the small amt. of 1,4-isomer obtained required repeated distn. Bromination of the 1,2-isomer gave 1-chloro-3,4-dibromo-3-ethoxybutane, b.p. 129° , d_4^{20} 1.7232, n_D^{20} 1.5162; boiling the 1,4-isomer with excess alc. KOH gave $\text{EtOCH}_2\text{CH}=\text{CHCH}_2\text{OEt}$, b.p. $72-2.5^{\circ}$, n_D^{20} 1.4236, while heating with 35% KOH-MeOH gave $\text{MeOCH}_2\text{CH}=\text{CHCH}_2\text{OEt}$, b.p. $62-2.5^{\circ}$, and the bromination of 1,4-isomer gave 86% 1-chloro-2,3-

isobromo-4-ethoxybutane, bp 130-2°, d₄²⁰ 1.7063, n_D²⁰ 1.5174.

- Repetition of the above run with 0.5 the amts. of reagents, with completion of the reaction in 2 hrs., yielded 65% of the active Cl adduct of PhSO₂NCl₂-butadiene and 7% of the mixed Cl ethers, as well as 5 g PhSO₂NH₂ recovered from the residue. Passage of 67 g I into 145 ml EtOH at 35-40° with slow addn. of 62.5 g PhSO₂NCl₂, followed by distn. of most of the EtOH and steam distn., gave a soln. free of active Cl and the residue yielded 25 g PhSO₂NH₂ and 23 g addn. products, free of active Cl, as well as 36.5 g Cl ethers, consisting of 80% 1,2- and 20% 1,4-isomers. Addn. of 45 g *tert*-BuOCl over 8 hrs. with stirring at -12° to 80 ml I in 300 ml EtOH (with the addn. of 0.5 g *p*-MeC₆H₄SO₃H and illumination with a Hg arc in the last hr., as the reaction was very sluggish) gave 29 g. (33%) Cl ethers, consisting of 88% 1-chloro-3-*tert*-butoxy-3-butene, b. 135-40°, and 12% 1,4-isomer, bp 60-70°, d₄²⁰ 0.9987, n_D²⁰ 1.4532. Addn. of 135 ml I to 31 g Na in 500 ml EtOH at -5°, followed by passage of 71 g Cl at -6° to -7° gave a soln. contg. 5.2 g alkali-bound Na and 42.2 g Cl in ionic form; the soln. yielded 16 g. (12%) Cl ethers (75% 1,2- and 25% 1,4-isomers). Allowing 10 g CHCl₃/Cl₂ to stand 24 hrs with 1.8 g Na in 35 ml EtOH gave 4 g 1-chloro-4-ethoxy-2-butene, bp 60-5°, d₄²⁰ 0.9998, n_D²⁰ 1.4542. Addn. of 80 g PhSO₂NBr₂ over 3 hrs to 60 ml I in 175 ml EtOH at -10°, followed by treatment with NaHSO₃ and steam distn., gave 36.5 g PhSO₂NH₂ and 43 g (48%) 1-bromo-2-ethoxy-3-butene, bp 55-4.5°, as well as 0.8 g dibromodithoxybutane, bp 132-4°, d₄²⁰ 1.5200, n_D²⁰ 1.4942. Repetition at 40-5° gave 39 g (50%) of the 1,2-Br ether, and again the 1,4-isomer could not be found. To 135 ml I in 300 ml EtOH was added 154 g freshly pptd. HgO, followed at -12°

by 254 g iodine added slowly, after filtration, there was obtained 66% 1-iodo-2-ethoxy-3-butene, bp 54-4.5°, bp 74°, d₄²⁰ 1.5296, n_D²⁰ 1.5060, which with alk. KOH gave 70% ethoxyisoprene, treatment of the distn. residue (after isolation of the 1,2-iodo ether) with alk. KOH gave products of a wide boiling range, which on shaking with 5% H₂SO₄ gave a test for Ac₂; repetition of the reaction with iodine-HgO at 40-5° gave the same result (100 ml I, 185 g BuOH, and 63 g PhSO₂NCl₂ at -10° to -15° gave in 6 hrs. 42 g (60%) adduct of 1-PhSO₂NCl₂, conta. active Cl, and only 8.7 g mixed Cl ethers (64% 1,2- distn. gave about 75% 1-chloro-3-butoxy-3-butene, bp 76.5-7.5°, d₄²⁰ 0.9400, n_D²⁰ 1.4390, and 25% crude 1,4-isomer, bp 95-100°, d₄²⁰ 0.9544, n_D²⁰ 1.4498. Repetition at 40-5° gave 17% mixed Cl ethers (82% 1,2- and 18% 1,4-isomers); the 1,2-isomer distd. with solid KOH gave butoxyisoprene, bp 68-7°, n_D²⁰ 1.4445, in poor yield, while the 1,4-isomer heated with KOH in BuOH gave 55% BuOCH₂CH₂CHCH₂OBu (also obtained from (CH₃CH₂)₂ and KOH in BuOH), bp 120-32°, n_D²⁰ 1.4365, d₄²⁰ 0.8598, which on bromination in CHCl₃ gave the 2,3-di-Br compd., bp 143°, d₄²⁰ 1.3400, n_D²⁰ 1.4821 while bromination of the 1,2-Br ether similarly gave 8% ClCH₂CH₂OBu ClBrCH₂Br, bp 153-5-4.5°, d₄²⁰ 1.5751, n_D²⁰ 1.5071. G. M. K.

PETROV, A. A.

PA 64/49T14

USSR/Chemistry - Divinyl
Chemistry - Allylthiohalides Jun 49.

"The Order of Combination of Allylthiohalides
with Divinyl," A. A. Petrov, Leningrad Inst of
Ava Instr Constr, 16 3/4 pp

"Zhur Obshch Khim" Vol XIX, No 6

Investigated subject with regard to type of
halogen, magnitude of the allyl radical, temper-
ature, time consumed in the reaction, and method
employed. A mixture of 1, 2-and 1, 4-chloroethers,
with a considerably greater amount of the first,
despite method used, were always obtained when
allylthiochlorides were used, but, apparently,
64/49T14

USSR/Chemistry - Divinyl (Contd) Jun 49

only the 1, 2-type was derived in reactions using
the corresponding compounds of iodine and bromine
at -12 to +45°C. Yield of the chloroethers was
decreased by an increase in the allyl radical,
and increased by a temperature increase.
Reactions of short duration initially produced
alcoholamide, indicating that, basically,
formation of chloroethers is a two-step process.
Submitted 26 Mar 48.

64/49T14

ca

9

Redistribution of hydrogen in octenes on aluminosilicate catalysts. A. A. Petrov and A. V. Frost. *Doklady Akad. Nauk S.S.S.R.* 65, 851-2 (1949). - The self-satn of 1-octene (I), contg. possibly some 2-octene but no branched-chain isomers, was investigated at 250°, a temp. high enough to prevent polymerization and low enough to exclude decompn. The yield of the main fraction of the catalyze, b. pt. 30°, was 60-80%. The high-boiling residue constituted 10-12%. The amt. of coke deposited on the catalyst is roughly proportional to the amt. of satd. hydrocarbons in the catalyze, on the av. 0.23-0.25 g. coke/g. satd. hydrocarbons. The amt. of the latter decreases with increasing space velocity, e.g., at 0.2, 0.5, and 1.0 l./l. catalyst/hr. satd. hydrocarbons were 38, 17.3, and 11.8% of the catalyze, Br no. of the catalyze 88, 117, and 125, resp. At the same 3 space velocities, at 250°, 2-ethyl-1-hexene (II) gave satd. hydrocarbons 63, 27.2, and 22.9%, Br no. of the catalyze 61, 101, and 106, resp. Consequently, redistribution of H is more intense in an olefin with a tertiary double bond. The yield of satd. hydrocarbons increases with the vol. of the catalyst, thus, at const. space velocity = 0.2, vol. ratio catalyst: raw material = 1, 2, 3, 4, and 8, the yields were, for I, 25, 37, 51, 60, and 98%; for II, 38, 48, and 81%. The products, in the case of I, are a mixt. of octenes and octanes with branched chains, mainly 2-methyl- and 3-methylheptanes.

PETROV, A. A.

Alkenyne systems. I. Addition of bromine to vinylacetylene

(but-1-en-3-yne). A. A. Petrov and N. I. Supon, *Vysokomol. Soedin.* 1950, 20, 708-719; *Russ. transl.* 745-755. Addition of $\text{Br}\cdot\text{CHCl}_2$ to $\text{CH}_2=\text{CH}\cdot\text{C}\equiv\text{CH}$ at -10° results in formation of some tetrabromides (not examined) and of the three possible dibromides, viz. $\text{CHBr}\cdot\text{CBr}\cdot\text{CH}_2\text{CH}_2$ (55%), $\text{CHBr}\cdot\text{CBr}\cdot\text{C}\equiv\text{CH}$ (5%), and $\text{CHBr}\cdot\text{C}\equiv\text{CH}\cdot\text{Br}$ (40%). This last dibromide, on heating in HBr with CuBr , isomerizes to $\text{CHBr}\cdot\text{CBr}\cdot\text{CH}=\text{CH}_2$, which is stable to cold $\text{KOH}\cdot\text{EtOH}$, but on prolonged heating substitutes OEt for Br .

Dropwise addition of Br (160 g) in CHCl_3 to $\text{CH}_2=\text{CH}\cdot\text{C}\equiv\text{CH}$ (104 g) in CHCl_3 at -8° to -12° and removal of volatile material afford mixed bromides (190 g, 90%) separated by fractional vac. distillation into three main fractions: (a) (76 g), b.p. $43\text{--}46^\circ/10$ mm, d_4^{20} 1.9640, n_D^{20} 1.5729; (b) (44 g), b.p. $70\text{--}72^\circ/10$ mm, d_4^{20} 1.9884, n_D^{20} 1.6000, and the tetrabromides (c) (42.5 g), b.p. $116\text{--}117^\circ/6$ mm, d_4^{20} 2.5203, n_D^{20} 1.6277. Fraction (a) on oxidation with KMnO_4 in aq. COMe_2 gives $\text{H}_2\text{C}=\text{O}$ and CO_2 , and little org. halogenated material; with AgNO_3 in aq. NH_4OH , fraction (a) (5.2 g) gives $\text{CHBr}\cdot\text{CBr}\cdot\text{C}\equiv\text{C}\cdot\text{Ag}$ (1.15 g, corresponding to 11% of acetylenic material in (a)) and unchanged $\text{CHBr}\cdot\text{CBr}\cdot\text{CH}=\text{CH}_2$ (I), b.p. $43^\circ/10$ mm, d_4^{20} 1.9536, n_D^{20} 1.5802. Fraction (a) with cold 20% $\text{KOH}\cdot\text{EtOH}$ gives KBr (9.5%) and

(unchanged) I (85%), whilst with boiling 20% $\text{KOH}\cdot\text{EtOH}$ gives KBr (40.6%) and a mixture of I and other compounds (50% conversion). Fraction (b) comprises $\text{CHBr}\cdot\text{C}\equiv\text{CH}\cdot\text{CH}=\text{CH}_2$ (II) (60%), is oxidised by KMnO_4 (25% excess) in aq. COMe_2 at 15° to $\text{CH}_2\text{Br}\cdot\text{C}\equiv\text{CH}$ (46%), m.p. 45° at 100° on pressure of para. (a) it partly (60%) polymerises and partly (40%) isomerises to I. II with boiling 25% HBr and CuBr gives I containing 4.7% of acetylenic material, and with 20% $\text{KOH}\cdot\text{EtOH}$ (cold) immediately gives KBr (86%) or (at the b.p., 5 mm) gives KBr (98%), and $\text{CH}_2=\text{CH}\cdot\text{C}\equiv\text{CBr}$ (60%), b.p. $52\text{--}53^\circ/217$ mm, d_4^{20} 1.4767, n_D^{20} 1.5136.

E. S. STERN

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PEROV, A. A.

Dokl. Phys. - Phosphorescence
Luminoptors

"Influence of the Medium Upon the Phosphorescence of Crystal-Luminoptors,"
B. Ya. Svenshaikov, A. A. Petrov

"Dok Ak Nauk SSSR" Vol LXXXI, No. 4, pp. 461-464

Describes quenching (extinguishing) of phosphorescence of fluorescein, in various solutions at temperature of liquid air, with time (0-2 min). Solutions are water, hexane, alcohol, cement, boric acid, sulfuric acid, aluminum sulfate, etc. Gives direction of metastable states for various solutions. Contr. to Dokl. Akad. Nauk SSSR by Acad S. I. Lavilov.

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Order of addition of iodine to butadiene
The direct reaction of iodine with butadiene is very vigorous and yields much polymer. Reaction of iodine gives a single product of 74% yield. The yellow powder, as in the case of the reaction of iodine with styrene, is formed by the polymerization of the monomer. The yield of the polymer is 74% and the molecular weight is 44,000. The reaction is catalyzed by KI and is accelerated by the addition of a trace of sodium acetate.
Diene in contact with solid KOH. The reaction is the product of the higher temperature reaction. The reaction is catalyzed by KI and is accelerated by the addition of a trace of sodium acetate. The reaction is very vigorous and yields much polymer. Reaction of iodine gives a single product of 74% yield. The yellow powder, as in the case of the reaction of iodine with styrene, is formed by the polymerization of the monomer. The yield of the polymer is 74% and the molecular weight is 44,000. The reaction is catalyzed by KI and is accelerated by the addition of a trace of sodium acetate.

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Isomeric transformations of 1,1,2-trimethylcyclopropane
 A. A. Petrov, *Doklady Akad. Nauk S.S.S.R.* 73 (1970) 1050. Mesityl oxide with NH_4HCO_3 yielded 1,1,2-trimethylcyclopropane (bp 32.6°), which was converted by passage over platinumed clay over KOH at 200° yielding from 200 g. 150 g. of 1,1,2-trimethylcyclopropane (bp 32.6°) and 27 g. of 1,1,1-trimethylcyclopropane (bp 34.2°).
 Passage of this over Al_2O_3 at 200-250° gave $\text{Me}_2\text{C}=\text{CH}-\text{Me}$ (bp 28° to 45° at 200°) with a corresponding drop of the yield of the 2nd component. The isomerization is complete. No isomerization occurs over Pr_2O_3 at 200°. Dehydration of $\text{Me}_2\text{C}(\text{OH})-\text{Me}$ over Al_2O_3 begins at 200° and at 250° between 250° and 350° yields the same yield of dienes as above, since the trimethylcyclopropane isomerizes completely to dehydration immediately subsequent to the required temperature. M. K. Kozlov.

C/A

Simultaneous dimerization of diene hydrocarbons and their derivatives A. A. Petrov, *ibid.*, 1954, 2, 100-105.

ibid., 1954, 2, 105-108.

on the thermal polymerization of $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$ I with piperylene, isoprene, $\text{MeCH}=\text{CH}_2$, $\text{C}_6\text{H}_5\text{C}(\text{Me})=\text{CH}_2$, 1,3-cyclohexadiene, chloroprene, and alkoxyprienes show that simultaneous dimerization between the components occurs in all cases and the products may be readily split from dimers into individuals of polymers (i.e. a form of diene with six active places). Heating 102 g I with 28 g isoprene (molar ratio 1:1) in a steel autoclave in the presence of pyrogallol (10%) by steam distill. gave 20 g polymers, 80 g I dimer, and 25.2 g "codimer" ($\text{C}_{12}\text{H}_{18}$, bp 152.6°, d_4^{25} 0.844, n_D^{25} 1.4719). Catalytic dehydrogenation over Pt/C at 300°C and oxidation with KMnO_4 followed by sapon. of the MnO_2 of the resulting acids gave largely *p*- $\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{Me}$ and some *m*- $\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{Me}$, no *BzOH* was found. Hence the dimer is largely 1-methyl-4-ene-2,6-cyclohexene with a little 1-methyl-2-ene-3,6-cyclohexene. Similarly, 72 g I and 80 g $\text{C}_6\text{H}_5\text{C}(\text{Me})=\text{CH}_2$ treated as above gave 40 g polymers, 42 g I polymer, and 13.7 g codimer ($\text{C}_{14}\text{H}_{20}$, bp 177.6°, d_4^{25} 0.8481, n_D^{25} 1.476, which on treatment as above gave 61% trimellitic acid showing an initial structure largely of 1,2-dimethyl-4-ene-2,6-cyclohexene. Similarly I with chloroprene yielded a dimer ($\text{C}_{12}\text{H}_{17}\text{Cl}$, bp 78.5-80.5°, d_4^{25} 0.861, n_D^{25} 1.4908) which has the Cl atom at the double bond as it resists alc. KOH while passage over Pd cleaves Cl and EtPh is formed. Other dimers listed are: with piperylene bp 148.5°, d_4^{25} 0.8380, n_D^{25} 1.4712; with $\text{MeCH}=\text{CH}_2$ bp 109.72°, d_4^{25} 0.843; n_D^{25} 1.4729; with cyclohexadiene bp 133.15°, d_4^{25} 0.821; n_D^{25} 1.4672; with methoxypriene bp 72.7°, d_4^{25} 0.8285, n_D^{25} 1.4702; with alkoxypriene bp 84.0°, d_4^{25} 0.8090, n_D^{25} 1.477.

G. M. Kosolapoff

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Preparation and transformations of vinylcyclohexadienic hydrocarbons. A. A. Petrov and N. P. Sopot. *Doklady Akad. Nauk S.S.S.R.* 79, 811 (1950). Divinyl and its homologs were condensed with MeCOCH₃ and the resulting ketones treated with MeMgI to form the cyclo-dienyldimethylcarbinols. One was obtained in pure state, *o,o*-dimethyl-1,4-cyclohexadiene-1-methanol, bp 97.5-8.0°, d_4^{20} 0.9788, n_D^{20} 1.5012. Dehydration of the alcs. from divinyl, isoprene, or diisopropenyl to form the cyclohexadienes with (CO₂H)₂ gave alicyclic hydrocarbons, while distn with a crystal of iodine gave aromatic hydrocarbons. Only the latter were obtained from the alcs. derived from piperyl-ene or dipropenyl. Thus were secured 1-isopropenyl-1,4-cyclohexadiene (I), b 172.0°, d_4^{20} 0.8668, n_D^{20} 1.5216, and its *t*-Me (II), b 192-6°, d_4^{20} 0.8603, n_D^{20} 1.5166, and 4,5-di-*t*-Me derivs., bp 97.5-100.5°, d_4^{20} 0.8919, n_D^{20} 1.5188; *iso*-*Pr*Ph, b 181-3°, d_4^{20} 0.8646, n_D^{20} 1.4946, *o*-*iso*-*Pr*Cell, Me, b 174.5°, d_4^{20} 0.8772, n_D^{20} 1.5009; the *p*-isomer, b 174.6°, d_4^{20} 0.8583, n_D^{20} 1.4948; 1,3,5-*iso*-*Pr*Cell, Me, b 194-6.8°, d_4^{20} 0.8780, n_D^{20} 1.5048, and the 1,3,4-isomer, b 197.9°, d_4^{20} 0.8741, n_D^{20} 1.5034. The isopropenylcyclohexadienes isomerize into the resp. isopropylbenzenes readily on warming with HCl to 100°, the presence of an *o*-Me group being a great facilitating factor, since dehydration of such alcs. invariably yields only the aromatic derivs. Bromination of I gave a white tetrabromide, m 118-14°, while II gave a tetrabromide, m 126°. I with 5% KMnO₄ gave PhAc only, heated with maleic anhydride it gave (after hydrolysis) a dicarboxylic acid, m 178°. G. M. Koudapoff

USSR/Chemistry - Chloroprene, Conjugation 1 May 51

"Several Peculiarities in the Reactions of Chloroprene With Hypohalogen Compounds," A. A. Petrov

"Dok Ak Nauk SSSR" Vol LXXVIII, No 1, pp 63-66

New data attest to the possibility of addn to conjugated systems in the 1,4-position. In the case of chloroprene, 1,2-chlorohydrin cannot exist and hence cannot be a source of the 1,4-product. It has been established that the predominant place of attack in reactions of chloroprene with hypohalogen compds depends on the nature of the halogen. With

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chlorine compds this place is the 1st carbon atom, whence the reaction is completed at the 4-position. Thus chloroprene reacts as a conjugated system. In the case of bromine and iodine compds, the reaction starts at the 4th and ends at the 3d carbon atoms. It follows that there is no conjugation here and that addn proceeds at the more reactive double bond.

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PETROV, A. A.

PETROV, A. A.

USSR/Chemistry - Hydrocarbons

11 Aug 51

"Preparation and Transformations of Vinylcyclohexadienic Hydrocarbons," A. A. Petrov, N. P. Sopov

"Dok Ak Nauk SSSR" Vol LXXIX, No 5, pp 811-813

Synthesized vinylcyclohexadienes according to A. A. Petrov, "Zhur Obsheh Khim" Vol X, 1682, 1940; "Dok Ak Nauk SSSR" Vol LIII, 531, 1946, and describes their properties. Brief heating with HCl isomerizes these compds into aromatic hydrocarbons.

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PETROV, A.A.

USSR/Chemistry - Diene Syntheses

Apr 52

"Synthesis and Properties of Some Isomers, Homologues and Analogues of **cc**-Terpineols Prepared on the Basis of 1,3-Diene Hydrocarbons," A. A. Petrov, N. P. Sopov, Chem Lab of Leningrad Inst of Avn Instruments

"Zhur Obshch Khim" Vol XXII, No 4, pp 591-602

Describes the synthesis of secondary and tertiary hydroaromatic alcs from 1,3-diene compds and unsatd aldehydes and ketones. Gives the structure and phys characteristics of the compds obtained.

224T34

A.A. EFFENDI, M. SOYUN

May 1967

"S.S.R. Chemistry - Synthetic Chemistry"

"Some New Alkyd Resins of Aromatic Type and their Properties in the Presence of Inorganic Fillers"

Zhurnal Khim. Fiz., Vol. 42, No. 5, pp. 1015-1021

In condensation of 1,3-bis(methylol)propane, with a diisocyanate, $\text{C}_6\text{H}_4(\text{NCO})_2$, with methyl acetylacrylate, methyl methacrylate, and 2-ethylhexyl methacrylate, the products are obtained. The alkyd resins are obtained by the reaction of CH_3MgI in these systems, and the products are methyl acrylate, methyl methacrylate, and dimethyl-(cyclohexadiene-1,4-diyl)-carbinol and its isomers. By the action of these acids, the isomers of cumene and isopropyl, i.e. 1-cumene, 2-cumene, 1-isopropyl-isopropenyl, cyclohexadiene-1,4, and 2-ethyl-1-cyclohexadiene, will obtain. All these compounds are formed under the influence of H^+ of the cumene and isomers of cumene. With it, the alkyd must tetramerize.

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Some new allylic isomers of aromatic hydrocarbons
A. A. Petrov and N. P. Sidorov (Leningrad Inst. Aviation En-
gineering Construction) *J. Gen. Chem.* 1954, 27, 1111
RP 521052 (Engl. translation) *Sci. 47*

PETROV, A.A.

Action of chloramides on chloroprene in aqueous and alcoholic solutions.
Zhur. Obshchey Khim. 22,1516-28 '52. (MLR 5:9)
(CA 47 no.17:8643 '53)

1. Leningrad Inst. Aviation Instruments.

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Condensed systems. XLII. The order of action of alkyl hypoiodites to chloroprene and bromoprene. A. A. Petrov (Inst. Aviation Instruments, Leningrad). *Sovetsk. Khim. Akad. Nauk S.S.S.R.* 1, 262-8 (1953); cf. C.A. 33, 2112; 40, 891. Alkyl hypobromites add to both chloroprene and bromoprene predominantly in the 3,4-position, i.e., analogously to the hypoiodites. Alkyl hypochlorites, however, add to bromoprene and chloroprene predominantly in the 1,4-position. The addition to bromoprene can be explained by steric effects. To 77.5 g. chloroprene in 150 ml. MeOH was added at 5-6°, 80 g. PbSO_4NH_3 ; steam distn. left 35 g. PbSO_4NH_3 and some 7 g. material which was apparently an adduct of the amide to the diene. The distillate gave 2 products; (I), b_p 70-5°, and (II), b_p 60-5°. Treatment of I with 10% alc. KOH in the cold gave a product, b_p 72-3.5°, d_4 1.4693, n_D^{20} 1.4882, which treated with excess EtOH-KOH 0.5 hr. at reflux gave 73% $\text{CH}_2\text{=CClCH(OMe)CH}_2$, b_p 58.5-9.5°, d_4 1.0753, n_D^{20} 1.4740; a pure specimen, d_4 1.0591, n_D^{20} 1.4715. Thus the original product (20 g.) was $\text{CH}_2\text{=CClCH(OMe)CH}_2$. Redistn. of II gave 8.2 g. material, b_p 93-5°, d_4 1.0912, n_D^{20} 1.5134, which by analysis contained 80% $\text{BrCH}_2\text{CCl=CHCH}_2\text{OMe}$ and 20% chloroprene dibromides; this material on oxidation with KMnO_4 gave $\text{BrCH}_2\text{CO}_2\text{H}$ and $\text{(CO}_2\text{H)}_2$, while treatment with Zn dust gave $\text{CH}_2\text{=C=CHCH}_2\text{OMe}$. Similarly 77.5 g. chloroprene and 80 g. PbSO_4NH_3 in 250 ml. EtOH gave 64 g. Br derivs. which were b_p 110-41 g. fraction, b_p 77-82°, and numerous small fractions, b_p up to 100°. The former on redistn. gave $\text{CH}_2\text{=CClCH(OR)CH}_2$, b_p 78-9°, d_4 1.4402, n_D^{20} 1.4890,

which was still contaminated with chloroprene dibromides. This material (32 g.) treated with 1.5 g. KOH in 80 ml. EtOH gave 75% pure bromo ether, b_p 79-9.5°, d_4 1.3955, n_D^{20} 1.4804, which refluxed with alc. KOH gave $\text{CH}_2\text{=CClCH(OR)CH}_2$, b_p 74-5°, d_4 1.4210, n_D^{20} 1.4660. The higher boiling fractions of the reaction mixt. gave 7 g. material, b_p 102-6°, d_4 1.4320, n_D^{20} 1.5022; treatment with Zn dust in hot EtOH gave some chloroprene and a moderate yield of $\text{CH}_2\text{=C=CHCH}_2\text{OR}$, b_p 107-5°, d_4 0.8282, n_D^{20} 1.4384, indicating that the original product was mainly $\text{CH}_2\text{=CClCH(OR)CH}_2$. The 2 products were found in the ratio 80/14 on the basis of analysis. The previously used technique (cf. above refs.) gave from 50 g. chloroprene 0.1 g. hydroquinone, 127 g. iodine, 60 g. HgO , and 150 ml. EtOH, 102 g. iodo ethers, b_p 80-105°. Redistn. gave 21 g. product, b_p 82-3°, identified as 2-chloro-4-iodo-1-butene-2-yl ether; the higher boiling fraction, b_p 100-5°, contained mainly the 1,4-addn. product contaminated with iodides (heating with Zn dust gave a trace of allenic ether, b_p 107-9°). Reaction of 174 g. bromoprene in 500 ml. MeOH with 90 g. PbSO_4NH_3 gave 57 g. PbSO_4NH_3 and 170 g. distillable products; the latter gave several fractions, b_p up to 100°. Redistn. gave 7.3 g. 3,4-addn. product *Me* 1-chloro-3-bromo-3-buten-2-yl ether, b_p 78-5°, d_4 1.4922, n_D^{20} 1.4920; this (6.8 g.) treated with 4 g. KOH in 80 ml. EtOH at reflux gave 94% $\text{CH}_2\text{=CBrC(OMe)CH}_2$, b_p 49-9.5°, d_4 1.4120, n_D^{20} 1.5022. The higher boiling fractions of the original mixt. gave 48 g. 4-chloro-3-bromo-3-buten-2-yl *Me* ether (III), b_p 89-92°, d_4 1.5659, n_D^{20} 1.5030, which treated with Zn dust in aq. EtOH gave about 8 g. mixed allenic ether and

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A. A. PETROV

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bromoprene, b. 80-85°; heating this with maleic anhydride in a sealed ampul gave about 50% pure Me 3,3-dibromo-1-yl ether, b. 87-87°, d₄ 0.8312, n_D 1.4388. Acidification of the residual alk. soln. gave bromotetrahydrophthalic acid, m. 170°. The residue after the removal of the allelic ether and bromoprene was redistd.; b_m 73-6°, n_D 1.4950, and identified as crude 3,4-dibrom. product which was stable to Zn dust treatment. Oxidation of III with KMnO₄ gave (CO₂H)₂ and ClCH₂CO₂H. To 80 g. bromoprene h. 300 ml. MeOH was added, as above, 40 g. (PhSO₂NHBr) the usual treatment gave 45 g. distillable products, b_m up to 180°. Redistn. gave 10.5 g. Me 1,3-dibromo-3-butene-2-yl ether, b_m 88-8.5°, d₄ 1.7613, n_D 1.5145, which heated with EtOH-KOH 30 min. on a steam bath gave about 60% CH₂=C(O₂Me)CH=; b_m 40-0.5°, d₄ 1.4108, n_D 1.5020. The higher boiling material yielded about 2 g. crude 1,4-addn. product, b_m 110-20°, which was not studied beyond elementary analysis. XLIV. Condensation of esters of methacrylic acid with diene hydrocarbons. A. A. Petrov

and N. P. Sopyov. *Ibid.* 369-73; cf. C.A. 43, 3373; 48, 2662. Esters of CH₂=C(CH₃)CO₂H heated with diene hydrocarbons in ampuls 15-18 hrs. at 180° gave 60-80% yields of esters of 1-methyl-3-cyclohexenecarboxylic acid and its homologs. Dimers of the dienes were formed as by products. While MeCH=CHCH=CH₂ and CH₂=CMeCH=CH₂ could yield 2 products in such condensations the structures of these products were not studied; in other cases the structures were without doubt the ones cited below. The following methacrylates: Me, Et, Pr, iso-Pr, and Bu, and 1,3-butadienes: 1-Me, 2-Me, 1,4-di-Me, and 2,5-di-Me were run. The following 3-cyclohexene-1-carboxylates were prepd.: 1-methyl, Me ester, b_m 79°, d₄ 0.9044,

n_D 1.4600; Et ester, b_m 85-8.5°, d₄ 0.9081, n_D 1.4642; Pr ester, b_m 114-4.5°, d₄ 0.9341, n_D 1.4550; iso-Pr ester, b_m 93.5-4°, d₄ 0.9385, n_D 1.4480; Bu ester, b_m 110-18.5°, d₄ 0.9401, n_D 1.4558. 1,3-dimethyl, Me ester, b_m 91.5-2.5°, d₄ 0.9310, n_D 1.4634; Bu ester, b_m 131-2.5°, d₄ 0.9436, n_D 1.4602. 1,4-dimethyl, Me ester, b_m 80-1.5°, d₄ 0.9717, n_D 1.4610; Bu ester, b_m 129-0.5°, d₄ 0.9334, n_D 1.4270. 1,3,5-trimethyl, Me ester, b_m 101-2°, d₄ 0.9383, n_D 1.4654; Bu ester, b_m 133.5-0.5°, d₄ 0.9367, n_D 1.4606. 1,3,4-trimethyl, Me ester, b_m 103-3.5°, d₄ 0.9396, n_D 1.4666; Bu ester, b_m 141-40.2°, d₄ 0.9326, n_D 1.4617. Hydrolysis, by refluxing with 10% KOH gave 70-80% yields of the following 3-cyclohexene-1-carboxylic acids: 1-methyl, m. 77.5-0°; 1,3-dimethyl, b. 144.5-0°; d₄ 1.0323, n_D 1.4793; 1,4-dimethyl, b. 146.5°, d₄ 1.0250, n_D 1.4783; 1,3,5-trimethyl, b. 151-4°, d₄ 1.0170, n_D 1.4793; 1,3,4-trimethyl, m. 55.5-0.5°. The Me ester of the latter was treated with MeMgI yielding dimethyl 1-methyl-3-cyclohexenylcarboxylate, b_m 120°, d₄ 0.9440, n_D 1.4623, which failed to dehydrate over (CO₂H)₂; with iodine the alc. underwent an apparent isomerization and failed to yield a hydrocarbon. Treatment of the other Me esters with MeMgI failed to yield pure products. The alkyl methacrylates prepd. from the free acid and ROH in the presence of H₂SO₄ in 75-80% yields (except iso-Pr, 89%), had the following constants (R given): Me, b. 100-1°, d₄ 0.9420, n_D 1.4150; Et, b. 118-18.5°, d₄ 0.9137, n_D 1.4148; Pr, b. 140-1°, d₄ 0.9021, n_D 1.4192; iso-Pr, b. 128-31°, d₄ 0.8850, n_D 1.4182; Bu, b. 164-5°, d₄ 0.8952, n_D 1.4238. G. M. Kozolapoff

PETROV, A. A., SOPOV, N. P.

Studies of Conjugated Systems. XLIV Condensation of Esters of Methacrylic Acid with Diene Hydrocarbons, page 369
Sbornik statey po obshchey khimii (Collection of Papers on General Chemistry),
Vol I, Moscow-Leningrad 1953, pages 762-766

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PETROV, A.A.

USSR.

Conjugated systems. XLV. Condensation of diene hydrocarbons with esters of maleic and fumaric acids. A. A. Petrov and N. P. Surov (Leningrad Inst. Aviation Instrumentation); *Sbornik Statei Obshchei Khim.* 2, 853-8 (1953); *C.A.* 47, 5374g; 49, 830i. — Equimolar mixts. of the dienes and the esters (0.1 mole each) were heated in 30 ml. MePh in sealed tubes 16-20 hrs. to 150-60°. Di-Me maleate d_4 101-1.5°, d_m 1.1504, n_D^{20} 1.4433; di-Et ester, d_4 101.5-1.7°, d_m 116.5-16.7°, d_m 1.0800, n_D^{20} 1.4416. Di-Me fumarate m. 101-2°; di-Et ester, d_4 107.5-7.7°, d_m 1.0512, n_D^{20} 1.4420, d_4 111.5-11.7°. Their reactions with butadiene, piperylene, and crude 2,4-hexadiene gave the following products (the acids were obtained by hydrolysis of the esters). Di-Me cyclohexene-1,5-dicarboxylate, *cis* form, 68.5%, b. 141.5-2°, d_4 1.1450, n_D^{20} 1.4733; free acid, m. 188°; *trans* isomer, di-Me ester, 83.0%, b. 139-0.5°, d_4 1.1272, n_D^{20} 1.4682; free acid, m. 169-70°; *cis*-isomer, di-Et ester, 61%, b. 153-4°, d_4 1.0843, n_D^{20} 1.4733; *trans* isomer, di-Et ester, 69.4%, b. 150.5-1.5°, d_4 1.0630, n_D^{20} 1.4652; anhydride of the *cis* acid, m. 163-4°;

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a. a. F. Z. L. i. e. r.

that of the *trans* form, m. 155.5-5.5°. *Di-Me 1-methylcyclohexene-4,5-dicarboxylate, cis form*, 61.3%, b. 149.5-50°, d₄ 1.1141, n_D 1.4783; *trans form*, 48.0%, b. 149-9.5°, d₄ 1.1010, n_D 1.4704; *free acid, cis form*, m. 151.5-2.5°; *trans form*, m. 103-4°; *anhydride of the cis acid*, m. 88°; that of *trans form*, m. 141-2°. *Di-Me 3-methylcyclohexene-4,5-dicarboxylate, cis form*, 64.5%, b. 144-5°, d₄ 1.1101, n_D 1.4708; *trans form*, 40.7%, b. 143.5-4°, d₄ 1.0977, n_D 1.4072. *Di-Me 1,2-dimethylcyclohexene-4,5-dicarboxylate, cis form*, 83%, b. 167-7.5°, d₄ 1.0933, n_D 1.4778; *trans form*, 60.1%, b. 159.5-60.5°, m. 55°; *free acid, cis form*, m. 176-80°; *trans form*, m. 213-15°; *anhydride, cis form*, m. 78°; that of *trans form*, m. 150-7°. *Di-Me 3,6-dimethylcyclohexene-4,5-dicarboxylate, cis form*, 58.2%, b. 154.5-5.5°, d₄ 1.0990, n_D 1.4740; *trans form*, 62%, b. 150.5-1.5°, d₄ 1.0892, n_D 1.4704. *Di-Me 3,6-endoethylenecyclohexene-4,5-dicarboxylate, cis form*, 49.5%, m. 70-70.5°; *trans form*, 29.8%, m. 20-7°. XLVI. Condensation of alkoxyprenes with esters of maleic and fumaric acids. *Ibid.* 800-4—Condensation of esters of maleic or fumaric acid with alkoxyprenes was run in sealed tubes at 150-60° 15-20 hr.

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a. l. L. L.

The esters were hydrolyzed to the acids in 10% NaOH. Treatment of the esters with 25% H₂SO₄ gave the β -cyclohexanedicarboxylates. These were obtained: *Di-Me 1-methoxycyclohexane-4,5-dicarboxylate*, *cis form*, *b_m* 173°, *d_m* 1.1781, *n_D²⁰* 1.4708; *trans isomer*, *m. 67-8°*, *b_m* 169.5-70°, *d_m* 1.1425, *n_D²⁰* 1.4768; *Di-Me 1-ethoxycyclohexane-4,5-dicarboxylate*, *cis form*, *b_m* 178-8.5°, *d_m* 1.1180, *n_D²⁰* 1.4735; *Di-Et 1-methoxycyclohexane-4,5-dicarboxylate*, *cis form*, *b_m* 182.5-3°, *d_m* 1.1110, *n_D²⁰* 1.4704; *trans form*, *b_m* 151.5-2°, *d_m* 1.1001, *n_D²⁰* 1.4672; *Di-Et 1-ethoxycyclohexane-4,5-dicarboxylate*, *cis form*, *b_m* 187-7.5°, *d_m* 1.0875, *n_D²⁰* 1.4684; *trans form*, *b_m* 166°, *d_m* 1.0765, *n_D²⁰* 1.4654; *Di-Me cyclohexanone-3,4-dicarboxylate*, *cis form*, *b_m* 185.5-8.5°, *d_m* 1.2110, *n_D²⁰* 1.4740; *trans form*, *m. 64.6-5.6°*; their *semicarbazones*, *m. 139.9°* and *174-5°*, *resp.* *Di-Et cyclohexanone-3,4-dicarboxylate*, *cis form*, *b_m* 181.5-5.5°, *d_m* 1.1374, *n_D²⁰* 1.4633; *trans form*, *b_m* 191-2°, *d_m* 1.1264, *n_D²⁰* 1.4533; *Cyclohexanone-3,4-dicarboxylic acid*, *cis form*, *m. 16°*; *trans form*, *m. 138-90°*. G. M. K.

PETROV, A. A. and SOPOV, N. P.

Studies of Conjugated Systems. XLVI. Condensation of Alkoxyrenes with Esters of Maleic and Fumaric Acid, page 360, *Aornik statey po obshchey khimii* (Collection of Papers on General Chemistry), Vol 11, Moscow-Leningrad, 1953, pages 1680-1686.

Chemistry Laboratory, Leningrad Inst of Aviation Building

B. T. R.
Vol. 3 No. 4
Apr. 1954
Chemistry-Organic

6615* Progress in the Field of Diene Chemistry
by A. A. Petrov, Uspekhi Khimii, 1954, 33, No. 4,
p. 905 917
Discusses obtaining and polymerization of dienes with
application to rubber synthesis and preparation of diene
theory of organic chemistry. 701 ref.

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PETROV, A. H.

Halogenation and iodination of aromatic amines with the aid of liquid chloramines, chloroamines, azo-hypochlorites, and organic hydroperoxides. A. A. Petrov, O. A. Balzer, and D. V. Ioffe (Leningrad Techn. Univ., Leningrad). *Zhur. Obshch. Khim.* 23, 663-7 (1953).—While R_2NCl and ClNHCO_2R can be used for halogenation of aromatic amines in the presence of halides in AcOH , tert-BuOCl , and tert-BuOOH cannot be used under these conditions. To 0.01 mole amine and 0.011 mole halide or thiocyanate salt in 10-20 ml. AcOH was added with ice cooling 0.011 g. atom active Cl (in the form of R_2NCl), and after 0.5-1.0 hr. the mixt. was distd. to isolate the product. Thus, $\text{p-H}_2\text{NC}_6\text{H}_4\text{CO}_2\text{H}$ gave: 80% 5-bromo-, m. 220°, 63% 5-iodo-, m. 203°, and 92% 5-thiocyano-2-aminobenzoic acid, m. 170°. *p*-Toluidine gave 97% 5-iodo-, m. 80°, and 60% 5-thiocyano-2-aminotoluene, m. 70°. $\text{I-C}_6\text{H}_4\text{NH}_2$ gave 78% 4,1-NCSC₆H₄NH₂, m. 143°. Similar reaction with ClNHCO_2R gave: from $\text{p-H}_2\text{NC}_6\text{H}_4\text{CO}_2\text{H}$, 80% 5-bromo-, m. 220°, 60% 5-iodo-, m. 210°, and 60% 5-thiocyano-2-aminobenzoic acid, m. 170°; from $\text{p-O}_2\text{N-C}_6\text{H}_4\text{NH}_2$, 45% 2,6,4-Br(O₂N)C₆H₃NH₂, m. 200°; from $\text{p-O}_2\text{N-C}_6\text{H}_4\text{OH}$, 74% 4,2-Br(O₂N)C₆H₃OH, m. 92°; from *p*-toluidine, 45% 5,2-NCSC₆H₄Me, m. 70°; from *m*-toluidine, 66% 2,5-NCSC₆H₃Me, m. 83°; from PhNHMe , 45% *p*-NCSC₆H₄NMe, m. 78°; from $\text{I-C}_6\text{H}_4\text{NH}_2$, 97% 4,1-NCSC₆H₄NH₂, m. 143°. Treatment of Me_2NCOH and NaOH with Cl until the mixt. became neutral gave tert-BuOCl (1.2 ml. contg. 0.01 g. atom active Cl); use of this substance in the above reaction gave colored tars; with Me_2NPh was obtained 10% of a green product, m. 74°, when thiocyanation was tried. tert-BuOOH (3 ml. contg. 0.01 g. atom active Cl) was tried in a few cases; iodination of $\text{p-H}_2\text{NC}_6\text{H}_4\text{CO}_2\text{H}$ gave 54% iodanthranilic acid, m. 305°, while thiocyanation of Me_2NPh gave 17% thiocyanos deriv., m. 74°. All other attempts failed to yield the desired products. O. M. Korotapov

PETROV, A.A.

USSR .

✓ Halogenation and rhodanation of aromatic amines with
the aid of liquid chloramines, chloramides, alkyl hypo-
chlorites, and organic hydroperoxides. A.A. Petrov, G.A.
Belay, and D. B. Ioffe. *J. Gen. Chem.* 33, 1584.
683-92 (1963) (Engl. translation).—See C.A. 48, 1584.
H. L. H.

PETROV, A. A.

Chemical Abstr.
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Organic Chemistry

The order of addition of alcohols to trimethylolpropane oxide, A. A. Petrov, V. Gantseva, and O. A. Kuzkva (Leningrad, U.S.S.R. Inst., Leningrad). *Zhur. Obshchei Khim.* 28, 137-38 (1953). In the presence of RONa, ROH react with $Me_3C(CHMe)_2$ in accordance with the Markov-

nikov rule and yield secondary monoethers of $HO(CHMe)_2CHMeOH$. In the presence of H_2SO_4 or BF_3 , the reaction yields tertiary ethers of this glycol. Addn. of $Me_3C(CHMe)_2$ to $(CO_2H)_2$ on a steam bath gave 72% $Me_3C(CHMe)_2$, b. 87.5-88°, yielding with $C_2NHCONH_2$ 55% chlorohydrin, which with concd. KOH gave 79% $Me_3C(CHMe)_2O$ (I), b.

73-6°, d_4 0.8065, n_D^{20} 1.2860. Adding 8.5 g. I to 2 moles ROH concg. 0.75 g. Na, heating in a sealed tube 20 hr. at 100° and distg. gave 45-50% products listed below: $Me_3C(OH)CHMeOMe$ (II), b. 121-2.5°, d_4 0.8063, n_D^{20} 1.4130; $Me_3C(OH)CHMeOEt$ (III), b. 142-3°, d_4 0.8756, n_D^{20} 1.4126. These were also prepd. as follows: $BrCH_2CO_2Et$ (90 g.) the RONa-ROH (R = Me and Et) from 30 g. Na and 250 ml. ROH refluxed 2-3 hrs., the mixt. distd. with H_2O , distd. to remove all ROH, and the residue acidified with H_2SO_4 yielded, resp., 65% $MeCH(OMe)CO_2H$, b. 87-8°, d_4 1.0915, n_D^{20} 1.4148, and 71% OEt analog, b. 95°, d_4 1.0376, n_D^{20} 1.4155. These were esterified by ROH in presence of HCl yielding 68% $MeCH(OMe)CO_2Me$, b. 130-1°, d_4 0.9966, n_D^{20} 1.3968, and 77.5% $MeCH(OEt)CO_2Et$, b. 152-3.5°, d_4 0.9402, n_D^{20} 1.4012. These treated with $MeMgI$ in the cold, followed by hydrolysis with aq. NH_4Cl gave, resp.: 72% II, b. 331-2.5°, d_4 0.8754, n_D^{20} 1.4134, and 78% III, b. 142-3°, d_4 0.8732, n_D^{20} 1.4118. II and III treated in the cold with Ac_2O and a trace of H_2SO_4 yielding II acetate, b. 158-01°, d_4 0.9400, n_D^{20} 1.4118, and III acetate, b. 168-70°, d_4 0.9242, n_D^{20} 1.4108, in 50% yields. Considerable iso-PrAc also formed during acetylation as a result of dehydration by Ac_2O . I (5 g.) in 75 ml. $MeOH$, and 0.5 ml. H_2SO_4 allowed to react several hrs.; and then neutralized gave 25% $Me_3C(OMe)CHMeOH$, b. 143-4°, d_4 0.9177, n_D^{20} 1.4220; a 42% yield was obtained in the presence of 0.5 ml. $BF_3 \cdot Et_2O$. Similarly was obtained 42% $Me_3C(OEt)CHMeOH$, b. 152.5-4°, n_D^{20} 1.4208, d_4 0.8982. These with $Na_2Cr_2O_7$ in $AcOH$ gave $Me_3C(OR)Ac$. The Me ether with Ac_2O gave $Me_3C(OMe)CH(OAc)Me$, b. 168-70°.

A. A. PETROV

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The order of addition of alcohols to trimethylsilylene
oxide. A. A. Petrov, H. V. Ostrova, and G. A. Kiselev.
J. Gen. Chem. USSR, 21, 769-73 (1953) (Engl. translation).
See C.A. 48, 3889g. H. L. H.

PETROY, A. A.

USSR.

✓ Conjugated systems. XLVII. Condensation of buty-
lene with cyclic diene hydrocarbons. A. A. Petrov and N.
P. Sopen. *J. Gen. Chem. U.S.S.R.* ~~1953~~ (1953)
(Engl. translation). XLVIII. The order of addition of
alkyl hypodites to homologs of chloroprene. A. A. Petrov
and K. A. Leporskiya. *Ibid.* 1001-8. See C.A. 48,
8181g. H. L. H.

PETROV, A.A.; BRAVO, Ye.S.; DAVIDOVICH, V.V.; DYATKOVA, O.S.; KUZNETSOVA, G.V.

Investigations in the field of conjugated systems. Part 4. Order of
adding alkyl hypohalides to tertiary vinylacetylene alcohols. *Zhur. ob.*
khim. 23 no.7:1120-1124 J1 '53. (MLA 6:7)

1. *Laboratoriya organicheskoy khimii Leningradskogo tekhnologicheskogo
instituta imeni Lensoveta. (Halides) (Vinylacetylene alcohol)*

PETROV, A. A.

USSR/Chemistry - Conjugated Systems

Sep 53

"Investigations in the Field of Conjugated Systems.
I. Synthesis and Properties of Homologs of Bromoprene," Ye.A. Leporskaya and A.A. Petrov, Chem Lab, Leningrad Inst of Aircraft Instrument Building

Zhur Obshch Khim, Vol 23, No 9, pp 1471-1474

A series of homologs of bromoprene was obtained from homologs of vinyl acetylene by the action of HBr in the presence of Cu_2Br_2 . The addition to these substances of dimethyl maleinate and dimethyl fumarate was investigated.

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USSR, Petrov, A. D.

Conjugated systems. III. Order of addition of bromine to vinylacetylenes. A. A. Petrov and Yu. I. Fox (Leningrad Aviation Instrument Inst.). *Zhur. Obshch. Khim.* 23, 1887-73 (1953); *Ch. C.A.* 44, 7751c; 48, 8181b. — In contrast to vinylacetylene, the homologous vinylalkylacetylenes add Br mainly at the ethylenic link. The structure of the products was proved by ozonization and oxidation to $BrCH_2CHBrCO_2H$ and the corresponding unsubstituted aliphatic acids. The course of addn. of Br is explained by displacement of the reactive center under the influence of the radical R in direction of the ethylenic bond; steric factors may be contributors. Addn. of 53 g. Br in 100 ml. $CHCl_3$ to 43 g. 1-penten-3-yne in $CHCl_3$ at -8° over 5 hrs., followed by removal of the solvent and re-bromination of the unchanged material gave 120 g. bromides, b_p 80-140°. The main fraction, 76 g., b_p 79.5-81.5°; the Raman spectrum lines (cm^{-1}) at: 2347 and 2240 (triple bond), 1612 (caused by partial isomerization of the acetylenic dibromide into a diene under illumination), and 711 and 689 (C-Br links). Ozonolysis gave $BrCH_2CHBrCO_2H$, m. 64-6° and $AcOH$; oxidation with $KMnO_4$ gave the same products. The product was thus identified as $BrCH_2CHBrC(CMe)_2$, b_p 79.5-80.5°, d_{20} 1.8300, n_D^{20} 1.5588; a higher b. fraction, b_p 132-6°, d_{20} 2.3496, n_D^{20} 1.6160, was an impure tetrabromide. Similarly, 20 g. 1-

hexen-3-yne gave 82 g. bromides, from which was isolated the main fraction of 21.8 g. $BrCH_2CHBrC(CMe)_2$, b_p 57-7.5°, d_{20} 1.8920, n_D^{20} 1.5470, along with a small amt. of crude tetrabromide, b_p 100-40°, d_{20} 2.2035, n_D^{20} 1.6029. 1-Hepten-3-yne (42 g.) gave 105 g. bromides, which yielded 60.1 g. $BrCH_2CHBrC(CMe)_2$, b_p 100-2°, d_{20} 1.9068, n_D^{20} 1.5348. 1-Octen-3-yne similarly gave largely $BrCH_2CHBrC(CMe)_2$, b_p 114-15°, d_{20} 1.5191, n_D^{20} 1.5300, while 7-methyl-1-octen-3-yne gave largely $BrCH_2CHBrC(CMe)_2$, b_p 121-3°, d_{20} 1.4590, n_D^{20} 1.5239. The above dibromides (0.1 mole) in 50 ml. Et_2O were refluxed 4-6 hrs. with 50 ml. 48% HBr and 10 g. $CuBr_2$ and, after diln. with H_2O and extn. with Et_2O , gave the following diene dibromides by isomerization (yields of 70-80% of pure dibromides were obtained): $CH_2=CHCBr_2CBr_2Me$, b_p 57-atauces were obtained); $CH_2=CHCBr_2CBr_2Et$, b_p 7.5°, d_{20} 1.8304, n_D^{20} 1.5708; $CH_2=CHCBr_2CBr_2Pr$, b_p 69.5-70°, d_{20} 1.7089, n_D^{20} 1.5640; $CH_2=CHCBr_2CBr_2Bu$, b_p 85.5-9.0°, d_{20} 1.6075, n_D^{20} 1.5518; $CH_2=CHCBr_2CBr_2CMe_2$, b_p 101.5-2.5°, d_{20} 1.5319, n_D^{20} 1.5440; $CH_2=CHCBr_2CBr_2CMe_3$, b_p 111-13°, d_{20} 1.4614, n_D^{20} 1.5320. In contrast to the acetylenic dibromides, which have irritating odors, these have pleasant odors; they darken and polymerize on storage, a process that is blocked by usual inhibitors. These dibromides practically do not react in

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the cold with alc. KOH. The acetylenic dibromides treated in the cold with alc. KOH lost 60% of the Br content and after steam distn. gave the following bromovinylacetylenes in 55-60% yields: $CH_2=CB_2C_1CMe$, b_p 52-3°, d_4 1.4010, n_D^{20} 1.5256; $CH_2=CB_2C_1CEt$, b_p 67-8.5°, d_4 1.3081, n_D^{20} 1.5166; $CH_2=CB_2C_1CPr$, b_p 83-4°, d_4 1.2443, n_D^{20} 1.5092; $CH_2=CB_2C_1CBu$, b_p 102-3°, d_4 1.2005, n_D^{20} 1.5051; $CH_2=CB_2C_1CCH_2CH_2CHMe_2$, b_p 113-15°, d_4 1.1619, n_D^{20} 1.4998. These have irritating odors and polymerize rapidly to dark resins even in the presence of inhibitors; they do not react with ammoniacal Ag and show considerable exaltation of refraction (1.3-1.8). The tetrabromide of the hexynyne treated with 10% alc. KOH in the cold gave a wide range of products; a fraction, b_p 116-21°, contained less Br than expected for a tribromide. The bromination of the original alkenynes always gave small amts. of low b. products, which were probably the dienic dibromides, with their higher n values; these usually were formed in less than 10% yields.

G. M. Kosolapoff

PETROV, A. A.

USSR/Chemistry - Conversion processes

Card 1/1 Pub. 151 - 21/38

Authors : Petrov, A. A., and Sopov, N. P.

Title : Conversion of hydroaromatic aldehydes and ketones into aromatic hydrocarbons during dehydration

Periodical : Zhur. ob. khim. 24/2, 298-302, Feb 1954

Abstract : The dehydration of hydroaromatic substances having two double bonds and the oxygen atom in the side chain in alpha-position relative to the ring was investigated to determine the possibility of their conversion into aromatic hydrocarbons. It was found that during the distillation with P_2O_5 or with Al_2O_3 at $350-400^\circ$ the unsaturated hydroaromatic ketones and in the case of P_2O_5 also the aldehydes, which form during the condensation of the diene hydrocarbons and their derivatives with alpha,beta-unsaturated aldehydes and ketones of the fatty series, easily submit to dehydration forming various aromatic compounds. Fifteen references: 7-USSR; 4-USA; 1-French and 3-German (1894-1953).

Institution : Institute of Aviation Instruments, Chemical Laboratory, Leningrad

Submitted : October 2, 1953

PETROV, A. A.
USSR/Chemistry

Card 1/1

Author : Petrov, A. A.

Title : Investigation of conjugated systems. Part 54.- Sequence of addition of hypobromous acid to vinylalkylacetylene. Synthesis and properties of alpha-oxides of vinylalkylacetylenes.

Periodical : Zhur. Ob. Khim. 24, Ed. 5, 803 - 807, May 1954

Abstract : The sequence of addition of hypobromous acid to vinylmethyl- and vinylethylacetylenes was investigated. It was established that the addition takes place according to the ethylene bond. Separated and characterized were homologous bromhydrines, their acetates and bromide. The reaction of bromhydrines with alkali hydroxide led to the derivation of oxides of vinylmethyl- and vinylethylacetylenes. The hydration of the first oxide and the addition of methyl alcohol and hydrogen bromide were also investigated. Eleven references. Table.

Institution : Laboratory of Organic Chemistry at the Leno Soviet Technological Institute, Leningrad, USSR

Submitted : December 12, 1953

PETROV, A.A.

USSR/ Chemistry - Conjugated systems

Card : 1/1

Authors : Leporskaya, E. A., and Petrov, A. A.

Title : Investigation of conjugated systems. Part 55.- About the order of addition of alkylhypohalides to 3-chloro- and 3-bromohexadienes-1, 3

Periodical : Zhur. Ob. Khim., 24, Ed. 6, 1005 - 1014, June 1954

Abstract : The order of addition of alkylhypohalides to 3-chloro- and 3-bromohexadienes-1, 3 was investigated. Esters of 1, 3-halogenhexene-3-ol-2 are the main products obtained in all investigated cases. The differences in the order of addition of alkylhypohalides to halogenhexadienes, as compared with butadiene halides, are explained on the basis of the theory of electron displacements. Five references. Table.

Institution : Institute of Aviation Instrument Construction, Leningrad

Submitted : December 24, 1953

PETROV, A.A.

6) Conjugated systems. LVI. Condensation of Benzylideneacetone with propargyl aldehyde. A. A. Petrov (Leningrad Technol. Inst., Leningrad). / *Zhur. Obshch. Khim.* 24, 2122-44 (1954); cf. *C.A.* 49, 2181b; 49, 2801f. — Heating 21.5 g. HC₃CCHO (I) and 22 g. CH₂:CHCH:CH₂ in 80 ml. MePh in a sealed tube 2-4 hrs. at 115° gave 62% 2,5-dihydrobenzaldehyde (II), bp 80°, *d*₄ 1.0230, *n*_D 1.5152 (picricanone, m. 204-5°; *p*-nitrophenylhydrazones, m. 187-8°; 2,4-dinitrophenylhydrazones, m. 226°); heating with *B* gave *B*H₂; oxidation with Ag₂O gave an acid, m. 112-18° containing 65.8% C and 5.4% H. The aldehyde treated with MeMgI gave methyl(2,5-dihydrophenyl)carbinol, bp 108.5°, *d*₄ 0.9645, *n*_D 1.5068, which dehydrated with solid KOH, in line, *p*-MeC₆H₄SO₃H, (CO₂H), or Ac₂O-H₂SO₄, to 70% EtPh (the small amt. of contaminant was readily removed by heating with maleic anhydride; the crude product formed a dithionide, a solid, which was not studied further). Sensitivity, II and EtMgBr gave 74% ethyl(2,5-dihydrophenyl)carbinol, bp 111-12°, *d*₄ 0.9778, *n*_D 1.5122, which readily dehydrated to PrPh; the crude hydrocarbon in this case contained some 24% unsaturated, material as shown

by uptake of Br. Condensation of 5.5 g. I with 10 g. diisopropenyl gave 72% 2,4-dimethyl-2,5-dihydrobenzaldehyde, bp 112-18°, m. 22.5-3.5°, *n*_D 1.5176 (picricanone, m. 230°; *p*-nitrophenylhydrazones, m. 213-10°; 2,4-dinitrophenylhydrazones, m. 233-4°); with MeMgI this gave a mixt. of the corresponding carbinol and ketone, bp 123-8° (largely), which mixt. was directly dehydrated with (CO₂H), yielding crude 2,4-Me₂C₆H₃Et, purified by treatment with *B* to give the pure product, b. 187-9°, *d*₄ 0.8760, *n*_D 1.5040. Condensation of 16 g. I with 20 g. cyclopentadiene, run at room temp., gave 80% 1,5-endomethylene-2,5-dihydrobenzaldehyde, bp 80°, *d*₄ 1.0674, *n*_D 1.5218 (the *p*-nitrophenylhydrazones and 2,4-dinitrophenylhydrazones are reported, no m.pt. given, since they char on heating); the aldehyde with MeMgI gave methyl(2,5-endomethylene-2,5-dihydrocyclopentadienyl)carbinol, bp 94-6°, *d*₄ 1.0140, *n*_D 1.5140; dehydration of the alc. gave only tar. Condensation of 5.3 g. I with 12 g. 1,3-cyclohexadiene 4 hrs. at 115° in MePh gave some C₆H₆ and B₂H₄ as the sole isolated product.

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USSR.

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 Addition of γ -ary ethyl halides to divinyl and vinyl-
 acetylene. A. A. Petrov and K. V. Leets (Leningrad Technol. Inst., Leningrad). *Doklady Akad. Nauk S.S.S.R.* 66: 286-8 (1964). $-(CH_2=CH)_2$ (0.8 mole), 0.45 mole Me_2CCl , 0.5 g. $ZnCl_2$, and 0.2 ml. concd. HCl kept in a closed flask 7 days yielded about 18 g. $Me_2CCH_2CH=CHCH_2Cl$ (I), bp 40.5-7.5°, d_4^{20} 0.8790, n_D^{20} 1.4450; oxidation with $KMnO_4$ gave $ClCH_2CO_2H$ and $Me_2CCH_2CO_2H$. I loses almost all its Cl in cold $MeOH-KOH$, yielding an unsatd. ether, b. 42-3°, n_D^{20} 1.4242. A similar reaction with Me_2CBr and $ZnBr_2$ gave $Me_2CCH_2CH=CHCH_2Br$, bp 60.5-1°, n_D^{20} 1.4710, d_4^{20} 1.1180; Me_2CI similarly gave the *iso* analog, bp 77-9°, d_4^{20} 1.2429, n_D^{20} 1.5150. $HC_1C_2H=CH_2$ (0.40 mole) with 0.57 mole Me_2CCl and 1.3 g. $ZnCl_2$ in 7 days gave 33 g. $Me_2CCH_2CClCH_2CH_2$ (II), bp 43-3.5°, d_4^{20} 0.9181, n_D^{20} 1.4733 [$KMnO_4$ gave Me_2CCO_2H and a little $(CO_2H)_2$]; this heated with di-*Me* fumarate 20 hrs. to 170°, this gave *di-Me chloro(tert-butyl)cyclohexanedicarboxylate*, m. 114-15° (from $MeOH$). Heating II with $KOH-MeOH$ 1 hr. on a steam bath resulted in loss of 22% of Cl content. Similar reaction with Me_2CBr gave $Me_2CCH_2CH_2CH_2CH_2$ (III), bp 54.5-5°, d_4^{20} 1.1707, n_D^{20} 1.5010, which with di-*Me* fumarate gave 60% *di-Me bromo(tert-butyl)cyclohexanedicarboxylate*, m. 126° (from $MeOH$); treated with $KOH-MeOH$ at above III lost 19% Br content in 1 hr. Higher boiling products are also formed in this addition; these are believed to be adducts of RX to dimerized or trimerized mole. of the dienes.
 G. M. Kosheva

Petrov, A.A.

Orientation and mechanism of reaction of compounds with conjugated double bonds with halogens, hydrogen halides and hypohalites. A. A. Petrov. *Voprosy Khim. Kinetiki, Kataliza i Reaktivnosti*, Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1955, 706-77. -- Summary of available exptl. data (27 references), principally obtained by the author, on orientation of addns. to conjugated systems. Cf. C.A. 49, 8080a and earlier papers.

G. M. Kosolapoff

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Subject : USSR/Chemistry

AID P - 1569

Card 1/1 Pub. 119 - 4/5

Author : A. A. Petrov and M. L. Genusov (Leningrad)

Title : Piperylene

Periodical : Usp. khim., 24, no.2, 220-239, 1955

Abstract : Various methods of preparation of piperylene, and its physical and chemical properties are reviewed. The article is illustrated by numerous formulas. 257 references (64 Russian: 1893-1955)

Institution: None

Submitted : No date

PETROV, A.A.

Conjugated systems. LVII. Condensation of 2-vinylpyridine with olefin hydrocarbons. A. A. Petrov and W. Ludwig (Leningrad Technol. Inst., Leningrad). *Zhur. Obshchestv. Khim.*, 25, 785-74; *J. Gen. Chem., U.S.S.R.*, 25, 703-7 (1953) (Engl. translation); cf. *C.A.* 50, 2336. — Distn. of 2-(2-hydroxyethyl)pyridine (b_m 128°, d_m 1.0966, n_D²⁰ 1.5290) with a little KOH gave 2-vinylpyridine (I), b_m 60°, d_m 0.9770, n_D²⁰ 1.5518. I (16 g.) and 20 ml. (CH₂:CH)₂ in 50 ml. xylene in sealed tube in 10 hrs. at 170° gave 60% 2-(3-cyclohexen-1-yl)pyridine, b_m 125°, d_m 1.0150, n_D²⁰ 1.5444 (picrate, m. 114°; methiodide, m. 188°); oxidation with KMnO₄ gave picolinic acid, while dehydrogenation over Pt-C at 400-500° gave 2-phenylpyridine, isolated as picrate, m. 170-1°, while hydrogenation gave 2-cyclohexylpyridine, b_m 124-4.5°, d_m 0.9928, n_D²⁰ 1.5295, whose picrate m. 104°. Bromination of the cyclohexenyl deriv. in CHCl₃ gave the dibromide, m. 182-3°. I (15 g.) and 15 g. piperylene similarly gave 49% 2-(3-methyl-3-cyclohexen-1-yl)pyridine, b_m 132-3°, d_m 0.9968, n_D²⁰ 1.5374 (picrate, m. 110-11°). Isoprene similarly gave 60% 2-(4-methyl-3-cyclohexen-1-yl)pyridine, b_m 141-1.5°, b_p 103-4°, d_m 0.9966, n_D²⁰ 1.5383 (picrate, m. 104-8°). H₂-propenyl similarly gave 82% 2-(3,5-dimethyl-3-cyclohexen-1-yl)pyridine, b_m 139-42°, d_m 0.9784, n_D²⁰ 1.5284, while with bisopropenyl there was formed 60% 2-(3,4-dimethyl-3-cyclohexen-1-yl)pyridine, b_m 154°, b_p 128-30°, d_m 0.9937, n_D²⁰ 1.5410 (picrate, m. 101°). With cyclopentadiene the reaction gave 60.7% 2-(3,5-endomethylene-3-cyclohexen-1-yl)pyridine, b_m 133-4°, d_m 1.0821, n_D²⁰ 1.5578 (picrate, m. 142-3°), while with cyclohexadiene there formed but a very poor yield of 2-(3,5-endomethylene-3-cyclohexen-1-yl)pyridine, b_m 150-4°, d_m 1.0892, n_D²⁰ 1.5590 (picrate, m. 123°).

G. M. Kasalov

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PETROV, A. A.

✓ Reaction of propargyl aldehyde with organomagnesium compounds. A. A. Petrov (Leusovet, *Uchenye Zapiski Kazansk. Univ. Ser. Khim.*, 23, 1101-2 (1953); *J. Gen. Chem. U.S.S.R.* 23, 1050-02 (1956) (Engl. translation).—Oxidation of HC≡CCH₂OH with dichromate gave up to 60-65% HC≡CCHO, *b_m* 61-5°, *d₄* 0.9152, *n_D²⁰* 1.4070 (cf. Wille, *et al.*, *C.A.* 44, 6807b). This (0.5 mole) in 1 vol. Et₂O was slowly added to 0.6 mole RMgX with ice cooling. With MeMgBr the reaction product remained in soln., while EtMgBr gave a product which remained in the solid phase; higher Grignard reagents gave products which were distributed between both phases. After treatment with ice and 25% H₂SO₄, the org. layer was distd. (extrn. of aq. layer with Et₂O gave only small addnl. amts. of products from the lower Grignard reagents), yielding alkylpropargyl alcs. and diacetylenic glycols; distn. of the latter was usually accompanied by considerable decompn. and charring. The following were prepd.: HC≡CCH(OH)R (*R*, b.p., *d_m*, *n_D²⁰*, % yield) Me, *b_m* 108-9°, 0.8942, 1.4275, 60-5; Et, *b_m* 124-5°, 0.8850, 1.4350, 35-40; Pr, *b_m* 68-8.5°, *b_m* 141-1.5°, 0.8722, 1.4370, 20-5; *iso-Pr*, *b_m* 131-2°, 0.8770, 1.4357, —; Bu, *b_m* 72-2.5°, *b_m* 161.5-2.5°, 0.8660, 1.4412, 15-20; *iso-Bu*, *b_m* 65-6°, *b_m* 161.5-2°, 0.8618, 1.4380, 35-40; HC≡CCH(OAc)R were prepd. with AcCl in pyridine (*R*, b.p., *n_D²⁰*, *d_m*, shown): Me, *b_m* 37.5-8°, 1.4152, 0.9488; Et, *b_m* 50.5-1.5°, 1.4200, 0.9343; Pr, *b_m* 65-0°, 1.4233, 0.9210; *iso-Bu*, *b_m* 71-2°, 1.4260, 0.9072. The alcs. readily formed dibromides by treatment with Br-CHCl₂: BrCH₂CB₂CH(OH)R (*R*, b.p., *d_m*, *n_D²⁰* shown, resp.) Me, *b_m* 91°, 1.9095, 1.5598; Et, *b_m* 98-9°, 1.8600, 1.6488; Pr, *b_m* 108-9°, 1.7485, 1.5374; Bu, *b_m* 118-19°, 1.6306, 1.5310. The yields of the glycols HC≡CCH(OH)C≡CCH(OH)R per mole aldehyde were (*R* given): Me 12 g., Et 21 g., Pr 32 g., Bu 37 g., and *iso-Bu* 20 g.; only the Pr and the Bu derivs. were purified by distn.; the Pr deriv., *b₁* 130°, *b₂* 144°, *d_m* 1.0300, *n_D²⁰* 1.4042, absorbed 98.7% of the calcd. amt. of H over Pd.

G. M. Kosolapoff

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PETROV, A. A.

Letter to the editor. Zour.ob.khiz.25 no.7:1433-1435
(Pyridine) (MIRA 8:12)

PETROV, A. A.

4
Direction of reaction of some unsaturated halogen deriva-
tions with alcoholic alkali. A. A. Petrov (Leningrad 1951-
1955); J. C.A. 44, 7761c. Zhur. Obshch. Khim. 23, 1483-6
CH₂CH=CHCl. Refluxing unsat. halides with
2N alc. KOH resulted in the following products: BuCl
gave, after 21% conversion, a mixt. of BuCl and BuORt,
contg. 17.3% yield of the latter (82% of theoretically possible)
and about 5% CH₂:CHORt. Crotyl chloride at 90.2% con-
version gave 78% MeCH:CHCH₂ORt and less than 1%
butadiene. 4-Chloro-1-butene after 81.5% conversion gave
less than 2.5% CH₂:CHCH₂CH₂ORt and 92% butadiene.
4-Chloro-1,3-butadiene gave after 90% conversion a 0%
yield of ether and 73% hydrocarbons, estd. on vinylacetyl-
ene. The unsatd. hydrocarbons were estd. as the poly-
bromides. G. M. Kosolapoff

A 804

AID P - 3432

Subject : USSR/Chemistry

Card 1/1 Pub. 152 - 17/18

Authors : Petrov, A. A. and Ye. N. Pritula

Title : Synthesis and properties of isomeric ethers of isobutylene glycol

Periodical : Zhur. prikl. khim., 28, 5, 556-560, 1955

Abstract : The reactions of primary alcohols (methyl, ethyl, propyl, and butyl) with isobutylene oxide were studied. In the presence of alcoholates, primary ethers of isobutylene glycol were obtained, and in the presence of boron fluoride, secondary ethers. Three tables, 15 references, 3 Russian (1911-1953).

Institution: Laboratory of Organic Chemistry of the Leningrad Technological Institute im. Lensovet

Submitted : Ja 5, 1954

Piperone, 11.11

USSR/Organic Chemistry. Synthetic Organic Chemistry. E-2

Abs Jour : Ref Zhur - Khimiya, No. 8, 1957, 26691.

Author : Zyryanova, T.A., Petrov, A.A.

Inst :
Title : Research in Region of Conjugate Systems.
LXIII. Action of Benzenesulfodichloroamide
on Piperylene Solutions in Alcohols

Orig Pub : Zh. obshch. himii, 1956, No. 6, 1593 - 1601.

Abstract : The action of benzenesulfodichloroamide (I) on solutions of piperylene (II) in CH_3OH and $\text{C}_2\text{H}_5\text{OH}$ was studied. It is shown that the addition takes place in the 3,4 and 1,4 positions of the diene system of II and produces a mixture of 55 to 60% of $\text{CH}_3\text{CH}=\text{CHCH}(\text{OR})\text{CH}_2\text{Cl}$ (III) and 45 to 40% of $\text{CH}_3\text{CH}(\text{OR})\text{CH}=\text{CHCH}_2\text{Cl}$ (IV), where $\text{R} = \text{CH}_3$ (IIIa and IVa respectively), or $\text{R} = \text{C}_2\text{H}_5$ (IIIb and IVb). It is established,

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USSR/Organic Chemistry. Synthetic Organic Chemistry. E-2

Abs Jour : Ref Zhur - Khimiya, No. 8, 1957, 26691.

OCH₃ group (at C₃) of the diene system) in III is proved; c) at the action of alcohol alkali on the received mixture of IIIa and IVa, CH₃CHC(OCH₃)=CH₂ (IXa) and CH₃CH(OCH₃)-CH=CHCH₂OCH₃ (Xa) was obtained in the molar ratio of 4 : 3; the structure of IXa (obtained from IIIa) is proved by its transformation into methylpropenylketone (by the action of 5% H₂SO₄ in the cold), and the structure of Xa (obtained from IVa) is proved by the formation of CH₃CH(OCH₃)CH₂CH₂CH₂OCH₃ at the hydrogenation of Xa on colloidal Pt. It was established that together with the reaction of addition at the action of I on alcohol solutions of II, an insignificant chlorination of II with the replacement of hydrogen took place (compare with RZhKhim, 1955, 37172). 135 g of

Card 4/6

Petrov, A. A.

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~~Conjugated systems. LX. Reactions of vinyl ethyl-~~
~~acetylene with tertiary butyl chloride and bromide. A. A.~~
~~Petrov and K. V. Lests (Lezgoyr Tekhnol. Inst., Baku,~~
~~1950. Zhur. Obshchey Khim. 26, 407-11(1950); cf. C.A.~~
~~49, 8080a; 50, 2678b. — Me₃CCl (30 g.) with 51 g. EtCl-~~
~~CCH:CH₂ in the presence of 3 g. 7-Cl₂, 0.3 ml. concd. HCl,~~
~~and 0.3 g. hydroquinone in 48 days gave 55 g. products,~~
~~which yielded 8.2 g. C₈H₁₇Cl, b_p 72-3°, d₄ 0.9028, n_D²⁰~~
~~1.4737, identified as EtCCl:C:CHCH₂CM₂, which on~~
~~ozonolysis gave EtCO₂H and Me₂CCH₂CO₂H, isolated as Na~~
~~salt hemihydrate, and amide, m. 131.5°. The chloride reacted~~
~~sluggishly with alc. KOH. There was also obtained~~
~~2.5 g. C₈H₁₇Cl, b_p 110-15°, d₄ 0.9485, n_D²⁰ 1.5013, which~~
~~reacted somewhat more readily with alc. KOH; the high-~~
~~boiling fractions yielded 1.6 g. C₈H₁₇Cl, b_p 145-65°, d₄~~
~~0.9850, n_D²⁰ 1.5153. Thus the reaction gave products of~~
~~addn. at the terminal C atom of the olefin bond, the CM₂~~
~~radical thus adding contrary to the orientation of HX~~
~~addn. Me₂CBr (45 g.) with 53 g. EtCl:CCH:CH₂ in the~~
~~presence of 4.5 g. ZnBr₂, 0.2 g. concd. HBr, and 0.2 g.~~
~~hydroquinone in 48 days gave 56 g. products, from which~~
~~were isolated: 11 g. EtCBr:C:CHCH₂CM₂, b_p 88-8°, d₄~~
~~1.1178, n_D²⁰ 1.4978. Ozonolysis gave results similar to the~~
~~above. LXI. Addition of alkyl halides to diene hydrocar-~~
~~bons. Ibid. 1113-21; cf. C.A. 49, 8777].—Addn. of~~
~~butadiene, isoprene, and diisopropenyl on one hand and~~
~~primary, secondary, and tertiary alkyl halides in the pre-~~
~~sence of Zn halides goes through a complex stepwise process~~

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PETROV, I. I. L. C. C. I. S. I. V. 8
 yielding substances of a general type $R(C_2H_5)_2$. The rate rises from primary alkyls to tertiary alkyls; butadiene is at least reactive, diisopropenyl the most reactive. The 1:1 adducts were obtained only with the least reactive components. Their structure as 1,4-adducts was shown by oxidation and ozonolysis. Keybig 18 g. com. butadiene with 0.25-0.9 mole alkyl halide and 0.37 mole-% Zn halide with 0.1 mole concd. H₂O and 0.1 g. hydroquinone in a sealed ampul from 3 hrs. to 17 days at room temp. gave a substantially complete reaction when the pressure became constant. The following adducts of butadiene and tertiary halides are described: $Me_3CCH_2CH=CHCH_2Cl$, b.p. 47-75°, d₄ 0.8790, n_D 1.4456; $Me_3CCH_2CH=CHCH_2Br$, b.p. 65-70°, d₄ 1.1180, n_D 1.4710; $Me_3CCH_2CH=CHCH_2I$, b.p. 77-85-90°, d₄ 1.1180, n_D 1.4710; $Me_3CCH_2CH=CHCH_2Cl$, b.p. 63-8°, d₄ 0.8960, n_D 1.4557. The 1st substance with $KMnO_4$ gave $Me_3CCH_2CO_2H$ and $ClCH_2CO_2H$; treatment of the chloride with $MeOH-KOH$ gave $Me_3CCH_2CH=CHCH_2OMe$, b.p. 42-3°, n_D 1.4242. The addn. of Me_3CCl to butadiene also gave 80% $C_8H_{14}Cl$, b.p. 68-73°, d₄ 0.8874, n_D 1.4643, which with $KMnO_4$ gave $Me_3CCH_2CO_2H$ and $(CH_3CO_2H)_2$, as well as $C_8H_{14}Cl$, b.p. 110-32°, d₄ 0.9098, n_D 1.4700. The bromide described above formed in the addn. of Me_3CBr was treated with $KOH-EtOH$, yielding $Me_3CCH_2CH=CHCH_2OEt$, b.p. 54, 5-6°, n_D 1.4260. The iodide treated with $MeOH-KOH$ gave the Me ether described above. Addn. of Me_3EtCCl gave in addn. to the 1:1 adduct above a range of fractions from which was isolated $C_8H_{14}Cl$, b.p. 80-5°, d₄ 0.9057, n_D 1.4700. Addn. of Me_3CIBr , Me_3CEtI , and $EtBr$ to butadiene gave after 60-70 days low yields of $R(C_2H_5)_2X$ with n ranging from 5.9 to 8.3. Isoprene and Me_3CCl gave in 4 days $C_8H_{14}C_2H_5Cl$, undistillable; a similar product was formed from the bromide. Diisopropenyl gave undistillable $C_8H_{14}C_2H_5Cl$ and Br .
 G. M. Kosolapoff

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Petrov, A. A.

Chem Conjugated systems. LX. Reactions of vinylidene acetylene with tert-butyl chloride and bromide. A. A. Petrov and K. V. Leets. J. Gen. Chem. U.S.S.R. 30: 430-4 (1960) (Engl. translation).—See C.A. 50, 11936a; B. M. R. 2

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PETROV, A.A.; LEETS, K.V.

Research in the field of conjugate systems. Part 61. Addition of
alkyl halides to diene hydrocarbons. Zhur.ob.khim. 26 no.4:
1113-1121 Ap '56. (MLRA 9:8)

1. Leningradskiy tekhnologicheskii institut imeni Lensoveta.
(Halides) (Olefins)

PETROV, H. M.
 Conjugated systems. LXII. Condensation of
 hydrocarbons with propiolic acid and its methyl ester.
 A. A. Petrov and K. B. Rall (Inst. Aviation Inst., Leningrad). *Zhur. Obshch. Khim.* 26, 1588-93(1956); cf. *C.A.B.* 50, 3292c, 11936a.—Heating 3 g. HC₃CCO₂H with 8 ml. CH₂:CHCH:CH₂ in 10 ml. MePh with 0.1 g. hydroquinone in a sealed tube 10 hrs. at 145-50° gave 88% 2,5-dihydrobenzoic acid, m. 121°, which failed to condense with maleic anhydride. The acid heated with 5 min. gave BzOH, while treatment with Br in CHCl₃ gave a brominated acid, m. 151-2°. Heating 0.5 g. HC₃CCO₂Me with 10 ml. CH₂:CHCH:CH₂ in MePh with 0.1 g. hydroquinone 6 hrs. at 120° gave 70% Me 2,5-dihydrobenzoate, b_m 94-5.5°, d_m 1.0720, n_D²⁰ 1.4938, which sapon. with 10% NaOH to the acid described above. Heating 4.8 g. HC₃CCO₂H and 18 g. piperylene in MePh with 0.1 g. hydroquinone 12 hrs. at 120° gave 74% 2-methyl-2,5-dihydrobenzoic acid, m. 85-8°, which failed to condense with maleic anhydride and heated with 5 gave BzOH; heating with 20% HNO₃ to 200° gave phthalic acid. Similar reaction of CH₂:CHCH:CH₂ with HC₃CCO₂Me gave in 10 hrs. at 140-5° 71% Me 2-methyl-2,5-dihydrobenzoate, b_m 88-90°, d_m 1.0269, n_D²⁰ 1.4871, which with 10% NaOH gave the free acid, m. 85-5°, identical with the above. Heating 3.5 g. HC₃CCO₂H with 3.5 g. isoprene and 0.1 g. hydroquinone in MePh 10 hrs. at 145-50° gave 78% 4-methyl-2,5-dihydrobenzoic acid (1), m. 180-1°, which failed to condense with maleic anhydride on simple heating, but heated with it in the presence of H₂O and Pd black 6 hrs. it gave p-MeC₆H₄CO₂H; oxidation with HNO₃ gave terephthalic acid. Heating 1 in MeOH in the presence of H₂SO₄ gave the Me ester, b_m 110.5°, d_m 1.0430, n_D²⁰ 1.4920; the same ester, b_m 110.5-11.5°, d_m 1.0435, n_D²⁰ 1.4930, formed in 73% yield from 6 g. HC₃CCO₂Me and 7 ml. iso-

Petrov, A. A. and KALL, K. B.

prene heated in MePh with 0.1 g. hydroquinone 10 hrs. at 140-5°. Attempted hydrogenation of the ester over Pd gave a mixt. of partly and completely aromatized esters; hydrogenation did proceed over Raney Ni. Heating 6 g. HC₂CCO₂H with 0 g. cyclohexadiene in MePh in the presence of 0.1 g. hydroquinone 7 hrs. at 115-20° gave some C₁₁H₁₆ and 40% BrOH. Heating 3.7 g. HC₂CCO₂H with 4.2 g. 2-chlorobutadiene in MePh with 0.1 g. hydroquinone 12 hrs. at 115-20° gave 73% 4-chloro-2,5-dihydrobenzoic acid, m. 219-17°, which with dil. HNO₃ at 155° in 10 hrs. gave p-ClC₆H₄CO₂H. LXIII. Action of N,N-dichlorobenzene-sulfonamide on alcoholic solutions of piperylene. T. A. Zyryanova and A. A. Petrov (Leningrad Technol. Inst., Leningrad). *Zhur. Obshchei Khim.* 26, 1593-601 (1956); cf. C.A. 50, 3990d. To 135 g. piperylene in 600 ml. MeOH was added in 4-4 hrs. at 0-5° 135 g. PhSO₂NC₆H₄; after standing until active Cl was nearly absent, the mixt. was steam distd. in the presence of a little Na₂SO₄. Fractionation of the distillate gave unreacted piperylene, 2 g. crude chloropentadiene, b. 100-7°, and 2.8 g. of a mixt. (I) of MeCH:CHCH(OMe)CH₂Cl and MeCH(OMe)CH:CHCH₂Cl, b. 55-60°, d₂₀ 0.9784-08.56, n_D²⁰ 1.4431-1.4451 (the products were partially sep'd. by fractionation). Ozonolysis gave AcOH and ClCH₂CO₂H. Refluxing the ethers with KOH in MeOH 18 hrs. gave MeCH:CH(OMe)CH₂, b. 105-7°, d₄ 0.8160, n_D²⁰ 1.4565 (with 5% H₂SO₄ this gave MeCOCH:CHMe), and MeCH(OMe)CH:CHCH(OMe), b. 52.5-4.5°, d₄ 0.8982, n_D²⁰ 1.4220, which hydrogenated over Pd to the sat. analog, b. 111.5-5°, d₄ 0.8381, n_D²⁰ 1.4064. Hydrogenation of I over Raney Ni in the presence of CaCl₂ in MeOH gave a series of fractions containing: MeCH:CH(OMe)CH₂, b. 105-7°, d₄ 0.8160, n_D²⁰ 1.4565; MeCH(OMe)CH:CHCH(OMe), b. 52.5-4.5°, d₄ 0.8982, n_D²⁰ 1.4220; MeCH:CHCH(OMe)CH₂ and MeCH(OMe)CH:CHCH(OMe), which hydrogenated

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over Pt gave the pure *trans* ether, b. 88-8.5°, d₂₀ 0.7540, n_D²⁰ 1.3840; an authentic specimen was prepd. from MeI and KOH heated with *sec*-amyl alc. in a sealed tube at 100°; the product, b. 88-8.5°, d₂₀ 0.7534, n_D²⁰ 1.3840. Hydrogenation of I also gave a mixt. (Ia) of MeCH:CHCH₂OMe, Cl and PrCH(OMe)CH₂Cl (II), b₇₀ 48-8.5°, which hydrogenated over Raney Ni at 70 atm. H₂ yielded pure II ether, b. 142-4°, b₇₀ 48-8.5°, d₂₀ 0.8390, n_D²⁰ 1.4250; bromination of Ia gave some 14% pure II, which heated with KOH in Cellosolve 4 hrs. gave a little 2-methoxy-1-pentene (III), b. 80-80°, d₂₀ 0.7888, n_D²⁰ 1.4062; this shaken with 5% H₂SO₄ gave MeCOPr, which confirmed the structure. Ozonolysis of III gave PrCO₂H. Reaction of 68 g. piperylene in 200 ml. EtOH with 87.5 g. PhSO₂NCl₂ as described above gave a mixt. (IV) of MeCH:CHCH(OEt)CH₂Cl (IVa) and MeCH(OEt)CH:CHCH₂Cl, partially sepd. in fractions, b₇₀ 61-61°, d₂₀ 0.8676, n_D²⁰ 1.4390, and b₇₀ 61-4°, d₂₀ 0.9613, n_D²⁰ 1.4427; these were combined and examd.; ozonolysis gave AcOH and ClCH₂CO₂H; refluxing with EtOH-KOH 18 hrs. gave 2-ethoxy-1,3-pentadiene, b. 124-4°, d₂₀ 0.8294, n_D²⁰ 1.4500 (with 5% H₂SO₄ this gave MeCOCH:CHMe), and MeCH(OEt)CH:CHCH₂OEt (IVb), b₇₀ 76.5-7°, d₂₀ 0.8664, n_D²⁰ 1.4235. IVb hydrogenated over Pd in MeOH to MeCH(OEt)CH₂CH₂CH₂OEt, b₇₀ 73-5°, d₂₀ 0.8511, n_D²⁰ 1.4102. Hydrogenation of IV over Raney Ni in MeOH at 120 atm. H₂ gave mixed MeCH(OEt)CH:CHMe and MeCH(OEt)Pr (V), b. 106-7° (the mixt. hydrogenated over Pd gave the pure V, b. 105-6°, d₂₀ 0.7536, n_D²⁰ 1.3880, identical with a specimen from *sec*-amyl alc. and EtI with KOH), and a mixt. of 1-chloro-2-ethoxypentane (VI) and IVa, b₇₀ 60-1°; further hydrogenation of the latter mixt. over Ni gave the pure VI, b₇₀ 60-60.5°, d₂₀ 0.8356, n_D²⁰ 1.4230. The results indicate that in the reaction of piperylene with PhSO₂NCl₂ the molar ratio of products of 3,4-addn. and 1,4-addn. is 5-5 to 4. Thus, the presence of a Me group in piperylene greatly increases the yield of 1,4-adducts, with fixation of the Cl atom on the 4-position.

G. M. Kosolapoff

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1/10/56
ZYRYANOVA, T.A.; PETROV, A.A.

Conjugated systems. Part 63: The action of benzenesulfodichloramide
on alcoholic solutions of piperylene. Zhur.ob.khim. 26 no.6:1593-1601
Je '56. (MIRA 11:1)

1. Leningradskiy tekhnologicheskii institut imeni Lensoveta.
(Piperylene) (Chloramide)

PETROV, A.A.

Conjugated systems. LXII. Condensation of diene hydrocarbons with propionic acid and its methyl ester. Petrov and K. B. Kall. *J. Gen. Chem. U.S.S.R.* 26, 1740 (1957) (English translation).—See *C.A.* 51, 1887e. LXIII. Action of *N,N*-dichlorobenzene-sulfonamide on alcoholic solutions of piperylene. T. A. Zyryanova and A. A. Petrav. *Ibid.* 1785-03.—See *C.A.* 51, 1887i. B.M.R.

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USSR/ Organic Chemistry - Synthetic organic chemistry

E-2

Abs Jour : Referat Zhur - Khimiya, No 4, 1957, 11652

Author : Petrov A.A., Al'bitskaya V.M.

Title : On Interaction of Divinyl Oxide with Amines

Orig Pub : Zh ogshch. khimii, 1956, 26, No 7, 1907-1909

Abstract : Reaction of divinyl oxide with primary and secondary amines takes place according to Markovnikov's rule with formation of alkylaminobutenols $\text{CH}_2=\text{CHCHOHCH}_2\text{NRR}^1$ (I). Addition is promoted in alkaline media. To an excess of aqueous, 35-40% solution of amine the divinyl oxide is added dropwise, while stirring. After 8-10 hours treated with K_2CO_3 and I isolated by distillation. Prepared were the following I (listing R, R^1 , yield in %, BP in $^\circ\text{C}/20$ mm, n_D^{20} , d_4^{20} , MP of picrolonate in $^\circ\text{C}$): H, CH_3 , 65, 80.5-81. 1.4608, 0.9282, 192-193; H, C_2H_5 , 72, 86-87, 1.4570, 0.9114, 211-212 (decomposes); H, C_3H_7 , 83, 95-96.

Card 1/2

USSR/Organic Chemistry. Synthetic Organic Chemistry. E-2

Abs Jour : Ref Zhur - Khimiya, No. 8, 1957, 26692.

Author : Zyryanova, T.A., Petrov, A.A.

Inst :
Title : Research in Region of Conjugate Systems.
LXIV. Action of Benzenesulfodibromoamide
on Piperylene Solutions in Methyl and Ethyl
Alcohols.

Orig Pub : Zh. obshch. Khimii, 1956, 26, No. 3, 1915 -
1926.

Abstract : At the action of benzenesulfodibromoamide (I)
on piperylene (II) solutions in methanol and
ethanol, the addition of methylhypobromite,
or correspondingly, of ethylhypobromite to II
in the 3,4 and 1,8 positions takes place; the
molar ratio of the 3,4 and 1,8 adducted matters
is 7.5 : 1 to 1 : 1. II produces considerably

Card 1/6

USSR/Organic Chemistry. Synthetic Organic Chemistry. E-2

Abs Jour : Ref Zhur - Khimiya, Moscow, 1957, 24602.

more 1,4 adducted matter than the earlier investigated divinyl. On the other hand, alkylhypobromites add to II in the 2,4 position to a greater degree than the earlier investigated alkylhypochlorites. 40% of a mixture (A) with the boiling point at 65° to 71°/20 mm, of 4-bromo-3-methoxypentanol-2 (III) and 1-bromo-4-methoxypentanol-2 (IV) was received from 62 g of II (70 to 75% of the trans-form) and 94.5 g of I in 250 ml of CH_2Cl_2 under conditions described earlier; besides, methylpropenylketone forming obviously from III was separated. CH_3COOH and BrCH_2COOH were obtained by the ozonization of A. 56 g of A with 28 g of KOH in 120 ml of CH_3OH was heated 9 hours. 7.5 g of 2-methoxypentadiene-1,3 (VI) (mixture of cis-trans form) (boiling

Card 2/6

USSR/Organic Chemistry. Synthetic Organic Chemistry. E-1

Abs Jour : Ref Zhur - Khimiya, 1958, 26622.

point 106.5 to 107.0, $n_D^{20} = 1.4875$, $d_4^{20} =$

0.8250) and 1.0 g of dimethyl ester of pentene-2-diol-1,4 (VII) boiling point 82 to 83/100 mm,

$n_D^{20} = 1.4850$, $d_4^{20} = 0.8082$ were separated. The

molar ratio of VI (forming from III) and VII (forming from IV) is about 1.5 to 1.0. 1.5 g of

V, boiling point 110 to 111, $n_D^{20} = 1.4855$, $d_4^{20} =$

0.8654, was obtained by shaking 5 g of VI with 50 ml of 5% H_2SO_4 ; 4-dinitrophenylhydra-

zone, boiling point 140 to 150 (from alcohol). 5 g of A in 200 ml of CH_2OH was hydrogenated

on 20 g of powdered Ni and 20 g of $CaCO_3$ (150,

Card 3/6

USSR/Organic Chemistry. Synthesis of Organic Chemistry. E-2

Abs Jour : Ref Zhur - 1951(1952)

6 hours, at low pressure. The frac-
tions (a) and (b) at low pressure
(5 g) and (c) at high pressure (20 g) were
separated. A small amount of (a) in
cellulose Pt, $C_7H_{12}O_2$, boiling point
22 to 22.50, $n_D^{20} = 1.4500$, $n_D^{25} = 1.4410$, was

formed; (b) was then generated repeatedly and
after the first generation, $C_7H_{12}O_2$ in
methoxyacetone, boiling point 22 to 22.50, $n_D^{20} = 1.4500$,
 $n_D^{25} = 1.4410$, was obtained;

under the action of 10% alcohol, 1-bromo-
2-methoxyacetone produced $C_7H_{12}O_2(OCH_3) = CH_2$,
boiling point 22 to 22.50, $n_D^{20} = 1.4600$.

Card 4/6

USSR/Organic Chemistry / Synthetic Organic Chemistry. 1-2

Abs Jour : Ref Zhuravskaya, ...

147- ... result between ...
of II ... of the trans ...
of I ... mixture ... was ... the
major part ... was ...
2001 ... The ... investi-
gated in the same ... is ...
action of ...
containing ... and trans
forms ...

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The ...
CH₂, ...

Card 5/-

USSR/Organic Chemistry. Synthetic Organic Chemistry. E-3

Abs Jour : Ref Zhur - Khinaya, *ibid.*, 1957, 36603.

$d_4^{20} = 0.7565$, and 1-bromo-2-methoxypentane,

boiling point 58 to 59°/10 mm, which produced pentene-1 after treatment with Zn dust. Pure cis forms of VI, boiling point 105 to 105.5°,

$n_D^{20} = 1.4570$, $d_4^{20} = 0.8403$, and of VIII, boiling point 124 to 124.5°, $n_D^{20} = 1.4530$, $d_4^{20} = 0.8404$,

were received by the introduction of pure cis-II into the reaction with I in CH_3OH and C_2H_5OH .

Card 6/6

Петров, Н. Н.

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318* (Russian) research in the Field of Conjugate Systems.
 Исследования в области сопряженных систем. LXV. Hydro-
 genation of Vinyl Ethyl Acetylene in the Presence of Colloidal
 Palladium. Гидрирование винилэтилэцетилена в присутствии
 коллоидного палладия. Кн. V. Баллон, А. А. Петров, and
 И. Е. Порфирова. Zhurnal Obshchei Khimii, v. 40, no. 7, July
 1970, p. 1928-1935.

A study of hydrogenation of vinyl methyl acetylene and vinyl
 ethyl acetylene in the presence of colloidal Pd.

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ZYRYANOVA, T.A.; PETROV, A.A.

Investigations in the field of conjugated systems. Part 66: The
action of benzosulfodichloro- and benzosulfodibromoamide on alcohol
solutions of isoprene. Zhur. ob. khim. 26 no.8:2189-2195 Ag '56.
(MLRA 10:11)

1. Leningradskiy Tekhnologicheskii institut imeni Lensoveta.
(Amides) (Isoprene)

Petrov, A. A.

Conjugated systems. LXVI. Reaction of benzoyl-
chloro- and benzoylthioamides with alkene
solutions of isoprene. A. A. Zyranova and A. A. Petrov.
J. Gen. Chem. U.S.S.R. 26, 2447-52 (1956) (Russian transla-
tion).—See C.A. 51, 4927i.
B. M. R.

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4e2eij
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PETROV, A.A.; SOPOV, N.P.

Research in the field of conjugate systems. Part 57. Condensation
of propargylic aldehyde with 2-halo- and 2-alkoxybutadienes. Zhur.
ob.khim. 26 no.9:2452-2457 S 156. (MLRA 9:11)

1. Leningradskiy institut aviatsionnogo priborostroyeniya.
(Propiolic aldehyde) (Butadiene)

PETROU, A. A.

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Conjugated systems. LXVIII. Diene syntheses with fluoroprene. I. Condensation of fluoroprene with α,β -unsaturated aldehydes and ketones. A. A. Petrov and A. V. Tumancva, *Zhur. Khim. Akad. Nauk SSSR*, 26, 2744-9 (1960), cf. C.A. 47, 2785b; 51, 4927f. Heating 31.5 g. fluoroprene, 20 g. acrolein, 20 ml. MePh, and 0.6 g. hydroquinone in sealed tube 12 hrs. at 120° gave 20 g. polymers and 15% *t*-fluoro-1,2,5,6-tetrahydrobenzaldehyde trimer, m. 164-5°. Similarly, AcCH:CH₂ and fluoroprene in MePh at 140° in 10 hrs. gave 73% *t*-fluoro-1,2,5,6-tetrahydroacetophenone, bp 95-9.5°, *d*₄ 1.0705, *n*_D 1.4505 (1,4-dinitrophenylhydrazones, m. 121-2°, semicarbazone, m. 170-2°), which with MeMgI gave 67.7% dimethyl(*t*-fluoro-5-cyclohexenyl)carbinol, bp 108-9°, *d*₄ 1.0478, *n*_D 1.4680 (acetals formed by heating with Ac₂O to 200° contained some *t*-fluoro-*t*-isopropenyl-5-cyclohexene, bp 58-62°, *d*₄ 0.9256, *n*_D 1.4025, which with Pt-C at 300° gave crude *p*-fluoroisopropylbenzene, b. 151-3°, *d*₄ 0.8854, *n*_D 1.4880). Heating 20 g. fluoroprene with 60 ml. MePh sola. of about 12 g. AcC:CH and 0.2 g. *p*-*tert*-butylpyrocatechol 12 hrs. at 120° gave 67% *t*-fluoro-1,2-dihydroacetophenone (I), bp 105-6°, *d*₄ 1.1290, *n*_D 1.4922, m. 41-2° (after chilling), which with maleic anhydride gave no reaction even after heating; I gave *p*-nitrophenylhydrazones, m. 221-3° (from solid fraction of ketone), or m. 212-15° (from liquid fraction). I with MeMgI gave dimethyl(*t*-fluoro-1,4-cyclohexadienyl)carbinol, bp 100-2°, *d*₄ 1.1265, *n*_D 1.4910, which with (CO₂H)₂ gave apparently *t*-fluoro-1-isopropenyl-1,4-cyclohexadiene, bp 75-7°, *d*₄ 1.0134, *n*_D 1.4900, which heated to 100° with

AcOH-HCl 2 hrs. gave *t*-fluorocumene, bp 64.5-5.5°, *d*₄ 0.9788, *n*_D 1.4718, which with 25% HNO₃ at 100° gave *p*-fluorobenzoic acid. Heating I with chloranil gave *p*-fluoroacetophenone, bp 78.5-0°, *n*_D 1.5100. G. M. Kosolapoff

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Petrov, A.A.

1. Conjugated systems. LXIX. Diene synthesis with participation of fluoroprene. 2. Condensation of fluoroprene with derivatives of α - β -unsaturated succinic acids. A. A. Petrov and A. V. Tumasova. *Zhur. Obshch. Khim.* 20, 2001-2111(1948); cf. C.A. 51, 772g. Heating 36 g. $\text{C}_6\text{H}_5\text{C}(\text{H})=\text{C}(\text{H})_2$ (I), in the presence of a little *p*-tert-butyl-catechol, with 63 g. $\text{C}_6\text{H}_5\text{C}(\text{H})=\text{C}(\text{H})_2$ in 20 ml. MePh 10 hrs. at 140° gave 50% *Me 4-fluoro-cyclohexene-3-carboxylate*, bp 116-10°, n_D^{20} 1.4235, n_D^{25} 1.4104; this with aq. KOH gave 92% free acid (II), bp 140-1°, n_D^{20} 1.4104, which with SOCl_2 yielded 74% *acyl chloride*, bp 87.5-88.5°, 1.2403, 1.4710, converted with cold aq. NH_4OH to 63% *amide*, m. 149° (from II, 1); this chloride reduced with MeOH gave the Me ester (III), identical with the above specimen. This ester with $\text{HCl}(\text{aq})$ gave 60% *dimethyl(4-fluoro-3-cyclohexen-1-yl)-carbinol*, bp 92-3.5°, 1.0482, 1.4680, which, heated 2 hrs. at 220° with excess Ac_2O , yielded 49% presumably *4-fluoro-1-isopropenyl-3-cyclohexene*, bp 64-0°, 0.9607, 1.4640, which, in turn, heated with Pt-C at 300° gave mixed cumene and fluorocumene, b. 150-1°, 0.8885, 1.4848; contg. some 3% F; oxidation of the mixt. with dil. HNO_3 gave BrO_2H and

p- $\text{FC}_6\text{H}_4\text{CO}_2\text{H}$. II and EtMgBr gave 68% *diethyl(4-fluoro-3-cyclohexen-1-yl)carbinol*, bp 117-18°, n_D^{20} 1.3864, 1.4760, dehydrated as above with Ac_2O to a mixt. of fluorohydrocarbons, $\text{C}_{10}\text{H}_{16}$, bp 90-100°; the main part bp 93-7°, 0.9458, 1.4887. Heating 14.5 g. I with 20 g. $\text{C}_6\text{H}_5\text{C}(\text{H})=\text{C}(\text{H})_2$ in MePh with a little hydroquinone 14 hrs. at 150° gave 89% *Me 4-fluoro-1-methylcyclohexene-3-carboxylate*, bp 88.5-2°, 1.0880, 1.4168, yielding with aq. KOH the

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Peterson A.H. Jumanan, Ph.D.

free acid, m. 81-82°; bp 141-2°. Similarly I and C11a-C12aCO₂Hs gave about 80% of 4-fluoro-1-methylcyclohexene-1-carboxylate, bp 123-4°, d₄²⁰ 1.0163, n_D²⁰ 1.4481. Heating 14.8 g. I with 10.8 g. CH₃CN in MePh in the presence of hydroquinone 16 hrs. at 140° gave 68% 4-fluorocyclohexene-1-carboxylic acid, bp 100.8°, n_D²⁰ 1.4375, 1.4570, which, heated with aq. alc. NaOH, yielded Ia; the nitrate in EtOH treated with Na gave 69% 4-fluoro-2-tetrahydrocyclopentane, bp 98°, d₄²⁰ 1.174-5°, n_D²⁰ 1.4035, 1.4033. LXX. Diene syntheses with participation of fluorene. 3. Condensation of fluorene with esters of α,β-unsaturated dibasic acids. *Ibid.* 2085-7. Heating 7.2 g. CH₃CFCF₂CH₂ (II) in MePh in the presence of hydroquinone with 14.4 g. di-*trans* maleate dicarboxylate as the *cis* isomer, bp 137-1°, bp 145-7°. *Cis* acid, m. 168-9° (cf. U.S. 2,451,813, C.1. 43, 271&); di-*Et* maleate similarly gave the corresponding di-*Et* ester (*cis* isomer), bp 144-5°, bp 158-9°, n_D²⁰ 1.3390, 1.4553. I and isomer of di-*trans* maleate (14.4 g.) similarly gave 10 g. *trans* 129-00°, bp 144-5°, n_D²⁰ 1.3080, 1.4672, while di-*Et* fumarate gave the corresponding *trans* isomer of the di-*Et* ester, bp 140°, bp 155°, n_D²⁰ 1.3008, 1.4500. Refluxing 30 g. (1CCO₂H)₂ (II) with MeOH with 8 g. H₂SO₄ 8 hrs. gave 8 g. (1CCO₂H)₂, bp 97-8°, n_D²⁰ 1.4478. This (7.1 g.) and 3.6 g. I heated in MePh 7 hrs. to 120-5° in a sealed tube gave 81% di-*trans* 4-fluoro-1,4-cyclohexadiene-1,2-dicarboxylate, bp 138.5-9°, n_D²⁰ 1.3524, 1.4808, which with aq. KOH yielded the free acid, m. 170° (from EtOAc-pet. ether). II and EtOH similarly gave (1CCO₂H)₂, which, heated with I as above, yielded 82% di-*trans* 4-fluoro-1,4-cyclohexadiene-1,2-dicarboxylate, bp 161-60.5°, n_D²⁰ 1.3735, 1.4712.

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O. M. Kowalski

PETROV, A.M.; TUMANOVA, A.V.

Synthesis in the field of conjugate systems. Part. 20. Diene syntheses with aid of fluoroprene. Part 3. Condensation of fluoroprene with esters of α, β -unsaturated dibasic acids. *Zhur.ob.khim.* 26 no.11:2285-2287 N195.

(MLRA 10-1)

(Fluoroprene) (Condensation products (Chemistry))

PETROV, A.A.

Conjugated systems. LXXI. Dimerization of fluorene. A. A. Petrov and A. V. Tumanova. Zbur. Obshch. Khim. 36, 2814-18 (1966); cf. C.A. 51, 8002c. Heating $CH_2=CFCH=CH_2$ in sealed tube 1 day at 120° gave 65-65% dimer and 25-30% polymer. The dimer on fractional distn. gave mainly a product, b.p. 85-8°; b.p. 148-8°; $d_{20} 1.0644$, $n_D^{20} 1.4383$, although small amts. of material of same mol. wt. were collected up to b.p. 120-40°, $d_{20} 1.0911$, $n_D^{20} 1.4622$. Treatment of the dimer with $KMnO_4$ gave succinic acid and β -carboxyadipic acid, m. 113-16°. Dehydrogenation of the dimer over Pt-C at 300° gave a range of products, b. 141-3°, $d_{20} 0.9824$, $n_D^{20} 1.4740$, which agreed with constn. of β -fluoroethylbenzene, but oxidation with HNO_3 gave $BzOH$ and $FC_6H_4CO_2H$. Treatment of the dimer with $PhSO_2NH_2$, followed by steaming and heating the crude product with $Zn-AcOH$ gave 60% β -fluoro- Δ^2 -tetrahydroacelophenone, b.p. 94.5-5.5°, $d_{20} 1.0695$, $n_D^{20} 1.4580$ (semicarbazone, m. 156-7°, 2,6-dinitrophenylhydrazones, m. 122-4°). Infrared spectra of the fractions of the dimer indicate (spectra are shown) that it consists mainly of *trans*- β -fluoroethylcyclohexene. Heating 1:1 fluorene-butadiene at 120° 1 day gave 44% mixed dimers, b. 60-148°, which gave 28% true mixed dimer of the 2 components, which b. 125-8°, $d_{20} 0.9901$, $n_D^{20} 1.4490$. Dehydrogenation of this over Pt-C gave C_8H_6F , b. 135-7°, $d_{20} 0.9104$, $n_D^{20} 1.4828$, which on oxidation with HNO_3 gave $BzOH$ and $FC_6H_4CO_2H$ (cf. C.A. 51, 7325g). G. M. K.

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PE TROV, A. A.

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The order of addition of bromine, hydrogen bromide, and alkyl hypobromites to allylmethylacetylene (1-hexen-4-yne), A. A. Petrov (Leningrad Technol. Inst., Leningrad), *Zhur.* 057:234 RZh: 26, 3319-24 (1956); cf. Bal'yan, *et al.*, *C.A.* 51, 4927k.—Passage of $\text{MeC}\equiv\text{CH}$ into EtMgBr from 1.5 g. atoms Mg, followed by 40 g. Cu_2Cl_2 and dropwise addn. of 1 mole $\text{CH}_2=\text{CHCH}_2\text{Br}$ gave after refluxing 10 hrs. and treatment with $\text{H}_2\text{O}-\text{HCl}$ 60-65% $\text{MeC}\equiv\text{CHCH}_2\text{CH}=\text{CH}_2$ (I), b_p 83-85°, d_4 0.7630, n_D^{20} 1.4368, Raman spectrum (cm^{-1}) 367(4), 407(4), 462(2), 520(4), 992(3), 1299(6), 1323(4), 1382(6), 1425(4), 1642(8), 2240(10), 2303(10), 2451(2), 2896(8), 2923(8), 2961(2), 3018(6), 3048(8), 3093(4). I (0.3 mole) in CHCl_3 was treated with ice-cooling with 0.2 mole Br in CHCl_3 yielding 81% 1,3-dibromo-4-hexyne (II), b_p 93-95°, d_4 1.0665, n_D^{20} 1.5428, Raman spectrum 327(2), 384(4), 553(2), 602(2), 653(8), 852(2), 1214(6), 1380(4), 1434(4), 2244(8), 2316(6), 2460(6), 2916(8), 2973(6). Infrared spectrum shown. II (16 g.) treated with 3 g. KOH in MeOH and refluxed briefly after 1 hr. gave a mixt. of 44% monobromide and 56% Me ether, MeOC_6H_9 ; the mixt., b_p 152-7°, b_p 60-60°, d_4 1.0358, n_D^{20} 1.4855. Treatment of I with 2 moles Br gave 60% 1,3,5-tribromo-4-hexyne, b_p 154.5-5°, d_4 2.2098, n_D^{20} 1.6010, also formed to some extent in the 1st expt. Shaking 16 g. I 3 hrs. with 25 ml. 63% HBr gave 60% (or 5-bromo-1,4-hexadiene (III), b_p 133-3.5°, d_4 1.2516, n_D^{20} 1.4830, Raman spectrum 295(1), 407(1), 503(3), 535(3), 927(2), 1208(1), 1293(5), 1376(4), 1411(4), 1438(4), 1640(7), 1662(8), 2239(1), 2994(3), 2916(6), 3016(4), 3080(2). Infrared spectrum shown. III also formed with the use of 65% HBr in the presence of Cu_2Br_2 . III treated 3 hrs. with alc. KOH lost 8.75% Br ion, while on refluxing 0.5 hr., 40% Br ion was

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...acted; decomposition gave CH_2O , AcOH , and a bromobutyric acid. Action of 30 g. $\text{PhSO}_2\text{NBr}_2$ on 17 g. I in MeOH gave 70% putative 1-bromo-2-methoxy-4-hexyne, bp 82-3°, n_D^{20} 1.3131, n_D^{25} 1.4830, infrared spectrum shows; the substance gave a weak test for a carbonyl group and formed an unpurifiable 2,4-dinitrophenylhydrazone. Refluxed 1 hr. with MeOH-KOH it gave a low yield of material, bp 67-8°, n_D^{20} 1.4815, approx. $\text{C}_8\text{H}_{10}\text{O}$, which with 5% H_2SO_4 gave a carbonyl test. Similar reaction of I with EtOH and $\text{PhSO}_2\text{NBr}_2$ gave mainly 65% 1-bromo-2-ethoxy-4-hexyne, bp 80-9.5°, n_D^{20} 1.3154, n_D^{25} 1.4830, infrared spectrum shown; alc. KOH gave a further unidentified product; bp 70.5-1.8°, n_D^{20} 1.4752. Thus, alkyl hypobromite addition takes place predominantly at the ethylenic link.

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Orientation of addition of bromine to alkenylacetylenes.
 A. A. Petrov and Yu. I. Fomin (Leningrad Univ. Chem. Dept.). *Doklady Akad. Nauk S.S.S.R.* III, 839-41 (1960). — Bromination of 18.2 g. $HC_7CCH:CHMe$ with 21.8 g. Br in $CHCl_3$ at -10° gave 84% dibromides, b_p 66-78°, d_4 1.7926, n_D^{20} 1.5742. This (9 g.) with 3 g. KOH in cold MeOH 2 hrs. gave 32% Br^- ions and 1.6 g. compd., C_8H_8Br , b_p 45-7°, d_4 1.8785, n_D^{20} 1.5210; the dibromide heated with Cu_2Br_2 in concd. HBr with Et_2O 5 hrs. gave some 60% 1,3-dibromo-1,3-pentadiene, b_p 60-2°, d_4 1.8079, n_D^{20} 1.5570, which failed to react with aq. KOH under above conditions. The bromination of 6.1 g. $HC_7CCH:CHEt$ with 7 g. Br in $CHCl_3$ as above gave 76% dibromides, b_p 85-95°, d_4 1.8937, n_D^{20} 1.5650, which with MeOH-KOH in the cold gave 42% Br^- ions. The results were discussed in the light of earlier work (cf. C.A. 48, 6373a; 50, 7713a). The infrared spectra of compds. described above were reproduced and were used for confirmation of the suggested structure. G. M. Kosolapoff

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Mikhail Vasil'evich Elkhosherstov. A. A. Petrov.
Zhur. Obshch. Nauch. 20, 1015-18 (1958). January 1962
60) with portrait, bibliography, and summary of work;
principally on methods of org. halogenation. G. M. K.

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