

PROCESS AND PROPERTIES INDEX

Tautomeric conversions of some phosphorganic compounds. A. E. Arbuzov and A. I. Razuwov. J. Gen. Chem. (U. S. S. R.) 4, 834-41 (1934); cf. A. and Arbuzova, C. A. 25, 2414, 3018.—Previously it was shown (C. A. 23, 4444) that in the synthesis of the higher homologs of carboxy phosphatic compds. from the Na compd. of $(R'O)_2P(=O)CH_2COR''$ (I) $\frac{1}{2}$ of the initial materials reacts normally: $(R'O)_2P(=O)CH_2COR'' + R''Hal = (R'O)_2P(=O)CHR''COR'' + NaHal$ (1), while the other half gives the acid ester and alkyl halide. This could be explained only by the existence of a tautomeric form of the Na compd. of I, since the $(EtO)_2P(ONa)$ from which I is obtained, is known in 2 tautomeric forms (Strecker and Spitzer, C. A. 21, 1832; Stelling, C. A. 19, 3424). Hence, besides the normal reaction (1), one of the following reactions may be assumed: $(R'O)_2P(ONa):CHCOR'' + R''Hal \rightarrow (R'O)_2P(Hal)(ONa):CHR''COR'' \rightarrow R'OP(=O)(ONa)CHR''COR'' + R''Hal$ (2); $(R'O)_2P(=O)CH:COR''ONa + R''Hal \rightarrow (R'O)_2P(=O)CHR''CHHal(OH)ONa \rightarrow (R'O)_2P(=O)CHR''C(=O)ONa + R''Hal$ (3). A check could be made by using an ester with 2 different alkyl radicals.

d) 1.0212 (cf. loc. cit.; A. and Dunin, C. A. 8, 2551; 21, 1627) with MeI produced 50% $(iso-BuO)_2P(=O)CHMeCO_2Et$, b.p. 105-8.5°, and 50% NaI (scheme 1), and 50% of the acid ester and unexpectedly a mixt. of MeI and iso-Bul. Thus, the reaction is highly complicated, which can be explained by tautomerism of the Na compd. of I, or by a simple exchange of the radicals, or both. Thus, the process shows a great similarity to the enol-ketonic tautomerism of the Na compd. of $CH_2(CN)CO_2H$ conditioned by the tautomeric grouping, and makes clear the entire course of the reaction between the Na compd. of I and alkyl halides according to the 1st, 2nd and 3rd schemes. It was of interest to study the formation of keto esters, which could be analogously obtained by the interaction of $(EtO)_2P(ONa)$ and halogen-substituted ketones. Nysten (*Studien über organische Phosphorverbindungen. Diss. Upsala 1930, 43, 69-70*) failed to obtain the normal compd. in the reaction: $(EtO)_2P(ONa) + BrCH_2COPh \rightarrow (EtO)_2P(=O)CH_2COPh + NaBr$. The authors obtained this compd. by this and the following reaction: $P(OEt)_3 + BrCH_2COPh \rightarrow EtBr + (EtO)_2P(=O)CH_2COPh$, b.p. 174-6°, d₄ 1.1704. This, converted into the Na compd. and then treated with MeI, gave a small yield of probably $(EtO)_2P(=O)CH_2MeCOPh$, b.p. 171-80°. Ph_3PCl with $iso-BuONa$ gave a good yield of Ph_2POBu , b.p. 188°, d₄ 1.0311. This with $AcCH_2Cl$ gave $Ph_2P(=O)CH_2Ac$, m. 73°; it gives no Na compd. Chas. Blaise

AS 35-51 A METALLURGICAL LITERATURE CLASSIFICATION

1934 519221A

1934 519221A

1934 519221A

PROCESSES AND PROPERTIES INDEX

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The methyl ester of benzene phosphinic acid. A. K. Arbuzov. *J. Gen. Chem.* (U. S. S. R.) 4, 808-900(1934).
 —PCl₂ and alcohols react to give as principal products alkyl phosphites (I) and inorg. halides. I are characterized by 2 reactions: (1) The formation of crystalline products with cuprous halides and (2) the catalytic isomerization by alkyl halides according to the equation: $P(OR)_2 + R'X \rightarrow P(OR)(R')X + RX$. The isomerization giving deriva. of quinquivalent P. The isomerization velocity depends on the temp., the quantity of R'X, the nature of X and the size and structure of R'. It would be of interest to study the behavior of R' P(OR)₂ with R'X where R' is alkyl or aryl. The present paper concerns the reaction between PhPCl₂ (II) and MeONa which yielded the expected PhP(OMe)₂ (III) and also PhMeP(:O)OMe (IV). Freshly distd. II was added dropwise to dry MeONa (from 10.9 g. Na) covered with 500 cc. dry Et₂O, giving a yellow mist, with the evolution of heat. The next day the Et₂O layer was poured off, the Et₂O distd. and the residual reaction mixt. reextrd. with the Et₂O. After several such extrns. 45 g. of residue (V) was obtained on distg. the Et₂O. Fractional distn. of V gave 10 g. crude III and 20 g. crude IV. III, bp 101-2°, d₄ 1.1022, d₄ 1.0810, n_D 1.5281, gave a cryst. (from anhyd. NaOH) addn. product with CuBr, m. 130.5-31°. IV, bp 130.5-40°, d₄ 1.1575, n_D 1.6280, on hydrolysis with dil. HCl gave the known PhMeP(O)H, m. 143° (from hot EtOH).
 Lewis W. Buta

A.S.D. S.L.A. METALLURGICAL LITERATURE CLASSIFICATION

11300 83M179

121. AN. THE. DATES		PROCESSES AND PROPERTIES INDEX	
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The preparation of furfural. A. E. Arbusov and H. P. Lagovska. <i>J. Applied Chem. U. S. S. R.</i> 7, 660-7(1954).			
—An almost theoretical yield of furfural is obtained from rye straw, with H_3PO_4 as catalyst at 8-10 atm. pressure, with 0.5-2% acid. The yield in the presence of H_3PO_4 is lower than with HCl and H_2SO_4 , when working under atm. pressure. The application of H_3PO_4 has the following advantages in comparison with the other acids: (1) The furfural is of a higher quality and its yield is higher; (2) the corrosion of the app. is less; (3) the distillates so obtained are characterized by a lower acidity, which is also true for the residue; (4) H_3PO_4 is not consumed in the process and it can be re-used. The highest furfural yield was 9.3% from a straw contg. 9% H_2O . The straw left after the process is not carbonized and retains its appearance, and it can, therefore, find other applications. H_3PO_4 may be used as a catalyst in the prepn. of furfural from other raw materials. A. A. R.			
ASS. S. LA METALLURGICAL LITERATURE CLASSIFICATION		ECON. BOWLING	
120000 22		121.127 Out Only 121	
120000 22		121.127 Out Only 121	

PROCESSED AND PROPERTIES INDEX

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ch

The methods of obtaining furfural. A. K. Arbusov and H. P. Lugovkin. *Trans. VI Mendeleev Conv. Theoret. Applied Chem.* 1933 2, Pt. 1, 811-7 (1935). A method of obtaining furfural from rye straw with H_2PO_4 as a catalyzer has been developed. At ordinary pressure the output is lower than with HCl and H_2SO_4 ; at elevated pressures (8-10 atms.) it approximates theory (up to 0.3%), the concn. of the acid being very low (0.5-2%). The use of H_2PO_4 leads to a higher quality of the products, to a low corrosion of the Cu walls of the autoclave, to a low acidity of the material obtained; the acid can be used repeatedly. The residual straw does not change its outer aspect and consistency and can be used for technical purposes. H_2PO_4 can be used also for obtaining furfural from other raw materials (bran, sawdust, etc.).

R. E. Stefanovsky

METALLURGICAL LITERATURE CLASSIFICATION

PROCESSES AND PROPERTIES INDEX

ca

10

Action of dihalo hydrocarbons on ethyl phosphite and the salts of diethyl phosphite. A. B. Arbuzov and N. P. Kushkova. *J. Gen. Chem.* (U. S. S. R.) 6, 283-R(1930).— CH₂I₂ with P(OEt)₂ (I) reacts thus: CH₂I₂ + I → EtI + (CH₂PO(OEt)₂) (II), and not, as could be expected: CH₂I₂ + I → 2EtI + [(EtO)₂PO]CH₂ (III). Attempts to obtain III by interaction of II with (EtO)₂PONa have failed. II with (EtO)₂POK in 90% alc. gave HOCH₂-PO(OEt)₂ (IV). CH₂I₂ (24 g.) with 15 g. I was heated to 110°, and after the exothermic reaction was completed, the reaction product was redistd., giving 100% II, b_p 133°, d₄ 1.601, d₂₀ 1.6002. IV, b_p 72°, d₄ 1.0726, resulted in nearly 100% yield when 30 g. CH₂I₂ in 100% alc. was added to 15 g. (EtO)₂POH and 4.25 g. K in Et₂O. IV, sepand. by heating in a sealed tube at 160° for 4 hrs., gave HOCH₂PO(OEt)₂, m. 84.5-6°. C. H.

Translation DRB, Canada - T107 R OT/783

ASAC - S.A. METALLURGICAL LITERATURE CLASSIFICATION

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
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1ST AND 2ND CODES

PROCESSES AND PROPERTIES INDEX

d s

BC

Preparation of substituted indoles by catalytic decomposition of phenylhydrazones, A. E. ARBUZOV, L. A. ZAITSEV, and A. I. RAGUNOV (J. Gen. Chem. Russ., 1958, 6, 288-291).—The phenylhydrazone of COEtPr, b.p. 163°/12 mm., and CaCl at 200° yield 2:3-diethyl- and/or 3-methyl-2-propyl-indole, b.p. 167°/15 mm. (picrate, m.p. 144°). Similarly, NHPh·NCOEtBu affords 2-methyl-3-propylindole, b.p. 150–161°/11 mm. (picrate, m.p. 134°), and NHPPh·NCPHEt, m.p. 47°, gives 2-phenyl-3-methylindole, m.p. 112–5° (picrate, m.p. 139°). R. T.

ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION

SUBJECTS

SUBJECTS

SUBJECTS

SUBJECTS

1ST AND 2ND ORDERS PROCESSES AND PATENTABLES 3RD AND 4TH ORDERS

COMMON ELEMENTS

A58-51A METALLURGICAL LITERATURE CLASSIFICATION

427

10

The ethyl acetal of cyclohexanone and its conversion to the ether of cyclohexenol. A. E. Arbuзов and B. M. Mikhailova. *J. Gen. Chem.* (U. S. S. R.) 6, 3003 (1936).—Cyclohexanone (I) does not react with $\text{HC}(\text{OH})_2$ (II) in alc. without the addn. of a catalyst. The reaction starts with evolution of heat on the addn. of a few drops of concd. H_2SO_4 . The Et acetal of I (III) is best prepd. by mixing I, II and a few drops of H_2SO_4 without alc., since alc. gives rise to high-boiling products. I (80 g.), 120 g. II and 3 cc. $\text{HC}(\text{OH})_2$ did not react within 1 hr. Addn. of 1 drop H_2SO_4 initiated the reaction. Neutralization on the following day with EtONa and fractional distn. gave 53.2 g. III, b_p 64.5-5.5°, d₄²⁰ 0.9389, d₄²⁵ 0.9186. To eliminate EtOH from III, 40 g. P_2O_5 was added in small portions to a mixt. of 30 g. III and 65 g. pyridine. Refluxing on a water bath for 5 hrs., removal of the P_2O_5 and fractional distn. gave 30% of 1-cyclohexenyl Et ether, b_p 50-7.5°, d₄²⁰ 0.9230, d₄²⁵ 0.9060. Lewis W. Butz

PROCESSED AND PROPERTY INDEX

10

The action of primary aromatic amines on ethyl hypophosphate. A. R. Arbutov and H. P. Lugovkin. *J. Gen. Chem. (U. S. S. R.)* 6, 394-403 (1936). - Et hypophosphate, $(\text{EtO})_2\text{P}(\text{OH})$ (I) (*C. A.* 27, 1587) with PhNH_2 , $p\text{-MeC}_6\text{H}_4\text{NH}_2$, 1,3,4-xylydine and $\beta\text{-C}_6\text{H}_4\text{NH}_2$ gave liquid and cryst. products by a vigorous exothermic reaction. The colorless cryst. products are not the expected aryl amides of $(\text{EtO})_2\text{P}(\text{OH})$ since their properties differ and the product (II) from PhNH_2 is not identical with the $(\text{EtO})_2\text{P}(\text{OH})\text{NHPh}$ of Michaels and Schulze (*Ber.* 26, 2937; 27, 2572). II m. 70.5-1.5°; product from $p\text{-MeC}_6\text{H}_4\text{NH}_2$ (III), m. 74-5°; from 1,3,4-xylydine (IV), m. 91-5°; from $\beta\text{-C}_6\text{H}_4\text{NH}_2$ (V), m. 87-8°. II, III, IV and V are sol. in Et_2O , EtOH and PhH , dissolve in H_2O at ordinary temp. without decomp. to give acid solns., and are decomposed by the moisture of the air on long standing and become purple. Analysis for C gave variable results but the values for N and P were const. and agreed with the Michaels type formula. II is sapon. by 10% KOH and gives PhNH_2HCl with AcCl . The formula $(\text{EtO})_2\text{P}(\text{OH})\text{NR}$ is tentatively suggested for II-V. The liquid products were mixts. that contained Et_2HPO . *Exptl.* To 10.85 g. I (*C. A.* 25, 3618) was added 5.7 g. dry, freshly distd. PhNH_2 . The reaction mixt. after standing in *vacuo* overnight and cooling to -10° gave 6.0 g. II (recrystn. from Et_2O) and 14.8 g. liquid products. Lewis W. Butz

METALLURGICAL LITERATURE CLASSIFICATION

PROCESSES AND PROPERTIES INDEX

COMMON ELEMENTS

COMMON METALS INDEX

CA

10

Mechanism of the reaction of double decomposition of metal derivatives of tautomeric organic compounds. A. K. Arbuzov. *Trudy Sessii Akad. Nauk Org. Khim.* 1939, 211-40.—Since no satisfactory answer can be found in the literature on the structure of metal derivs. of keto-enols and other tautomeric compds., the mechanism of the double decompn. of metal derivs. of tautomers with alkyl or acyl halides remains unsolved. Proof of the existence of an equil. system of metal derivs. of tautomeric compds. would be very valuable. The author's own experiments indicate that the reaction of dialkyl phosphites (Me, Et, Pr, iso-Pr, iso-Bu) of metals (Ag, Cu, Na) with triaryl-methane halides or with chlorides of sodium malonic esters are very similar to the reactions of keto-enols and lactim-lactams. It is established that in the reaction between alkali dialkyl phosphites and triaryl bromomethanes there are formed free radicals (e. g., hexaphenylethane sepd. as peroxide) and also, probably, didialkyl phosphones according to the equation: $2(R'O)_2P(OR)Na + 2R_3CPh = [(R'O)_2PO]_2 + 2CPh + 2NaBr$. This fact cannot be explained on the basis of the present conception of the mechanism of double decompn. reactions. Complete details of the expts. will be published later. 64 references.

Bruno C. Metzner

COMMON METALS INDEX

A.S.B.-S.L.A. METALLURGICAL LITERATURE CLASSIFICATION

1ST AND 4TH EDITIONS		
PROCESS AND PROPERTIES INDEX		
<p style="text-align: center;"><i>ca</i></p>	<p style="text-align: right;">10</p>	<p>IDENTIFICATION OF 1940N: A. N. ARDUZOV. <i>Bull. acad. sci. U. R. S. S., Classe sci. chim.</i> 1940, 83-84 (in English, 194).—With the aim to establish the structure of isatin (I) the trityl deriv. has been prepd. To 1.02 g. Ph₃CCl (II) in 15 cc. dry C₆H₆ is added 0.845 g. Na salt of I and the mixt. warmed for 30 min. on the water bath. Crystals sep. from the filtered soln. which, together with the residue, are extd. with ether. The 1st fractions yield yellow needles (III) whereas red crystals (IV) are obtained from the last fractions. Both forms of tritylisatin m. 232-3°. IV turns yellow shortly before melting. Ether (1 cc.) dissolves 0.001 g. of IV and 0.0032 g. of III. Analogous results are obtained when II or Ph₂CCl reacts with Ag deriv. of I. III and IV give with PhNHNH₂ at 100° the phenylhydrazones of tritylisatin, m. 231-2°. Hydrolysis of III and IV with aq. alc. KOH yields I and Ph₂COH.</p> <p style="text-align: right;">G. Herbold</p>
<p><i>S. M. Kirov Chem. and Tech. Inst., Kazan, Lab. Organic Chem., -1940.</i></p>		
MATERIALS INDEX		ESTABLISHED
A.S.M.-I.S.A. METALLURGICAL LITERATURE CLASSIFICATION		FROM SOURCE
FROM SOURCE	SECONDARY SOURCE	REFERENCE
<p style="text-align: center;">S T C O N T A I N S</p>	<p style="text-align: center;">S T C O N T A I N S</p>	<p style="text-align: center;">S T C O N T A I N S</p>

PROCESSING AND PROPERTIES INDEX

10

C: Alkyl pyrocatechol esters of phosphorous acid. A. N. Arbusov and P. G. Valtova. *Bull. acad. sci. U. S. S. R., Classe sci. chim.* 1940, 520-43 (in English, 543-4); *cf. C. A.* 35, 2485. —The reaction of pyrocatechol and PCl₃ with the formation of C₆H₃O₂PCl (I) takes place in several stages, one of which is the formation of *o*-phenylene phosphite. I was obtained by the following procedure: a mixt. of 200 g. pyrocatechol (1 mol.) and 374 g. PCl₃ (1.5 mols.) was heated slowly on a glycerol bath in a flask equipped with a reflux condenser and CaCl₂ tube. The bath temp. was increased slowly to 70-80° as more HCl was evolved. The HCl evolution stopped after 5-6 hrs. The bath temp. was then raised for a short period to 100-110°. No crystals sep'd. on cooling the dark reaction mass to room temp. The reaction product was usually transferred, while still hot, to tubes which were half filled and sealed. The tubes were then heated to 170-80° for 4-5 hrs. The reaction product was now distd. The excess of PCl₃ was distd. under atm. pressure, and I was distd. under 10 mm. at 80° in perfectly pure form. It crystd. to needles, m. 30°, on cooling or often merely on transferring from the receiver to a flask. In sealed containers the product kept well for an indefinite period. The yield of I was 265 g. or 80% of theory. The alkyl pyrocatechol esters C₆H₃O₂POR (II) of H₂PO were obtained by the action of I on dry alcoholates in a dry ether medium, while the mixt. was vigorously stirred. The settled clear ether soln. was poured off the next morning and the residue extd. 5-8 times with ether. The combined ether solns. were distd. and the residual product was vacuum-distd. The pure product of II varied with the alkyl radical from 14-21% of theory. They were all colorless liquids and easily gave characteristic monohalogen salts of Cu. The Me ester was also highly refractive. The main phys. consts. of II are: R = Me, b. 73°, d₄²⁰ 1.2608, n_D²⁰ 1.5200; CuBr salt m. 130.4° with partial decompn.; R, b. 80°, d₄²⁰ 1.2420, n_D²⁰ 1.5085; CuBr salt, m. 142.5°; R, b. 97°, d₄²⁰ 1.1206, n_D²⁰ 1.4841; CuI salt, m. 138°; Iso-Pr, b. 73.4°, d₄²⁰ 1.1171, n_D²⁰ 1.4724; CuCl salt, m. 143°; CuI salt, m. 178.9°; Bu, b. 116°, d₄²⁰ 1.1255, n_D²⁰ 1.5053; CuCl salt, began to sinter at 180°, m. 202°; Iso-Bu, b. 105°, d₄²⁰ 1.1208, n_D²⁰ 1.4650, d₄²⁰ 1.0007; CuCl salt, sintered at 158°, m. 208.10°. The Me and Et esters formed isomeric esters of phosphinic acid when heated with MeI and EtI, resp., in closed tubes at 180° for 4-5 hrs. The isomers are cryst. solids. These isomers combined with 1 mol. of H₂O with liberation of a very large amt. of heat and formed heavy colorless liquids. Me and Et esters reacted with PhC₆H₄Br, yielding in all cases the same pyrocatechol ester of benzylphosphinic acid. James I. Lublin.

J. Lublin
Chem. 1940

S. M. K. Chem. and Tech. Inst.

12

ca

Preparation of pyrocatechol phosphorus monochloride.
 A. B. Arbutov and F. G. Valtova. *Trans. Kazan Inst. Chem. Tech. Kazan* No. 8, 12-15(1940).—The mixt. of 1 mol. of pyrocatechol and 1.5 mols. of PCl₃ (freshly distd., b. 76°) was refluxed at 70-80° for 6 hrs. in a glycerol bath. The HCl evolved was removed by absorption in water. At the end of the reaction the temp. was raised to 100-10°. After termination of the HCl evolution, the reaction mixt. was heated in half-full sealed glass tubes at 175-80° for 5 hrs. The yield of *pyrocatechol phosphorus monochloride*, O,C₆H₄,O.PCl₂, b₇₈₀ 80° and b₇₈₀ 80° after vacuum distn., was 90%.

A. A. Podgorny

ASSOCIATED METALLURGICAL LITERATURE CLASSIFICATION

117 AND 118 (OPTIONAL) PROCESSES AND PROPERTIES INDEX

BC

A-3

Synthesis of *trans*-1,2-diphenyl-1,2-dichloroethane, N.P.
 Graduated by *trans*-1,2-diphenyl-1,2-dichloroethane, N.P.
 1941, *trans*-1,2-diphenyl-1,2-dichloroethane, N.P.
trans-1,2-diphenyl-1,2-dichloroethane, N.P. Similarly obtained
 are *cis*-1,2-diphenyl-1,2-dichloroethane, m.p. 100-104°, and *cis*-1,2-
 dimethyl-1,2-diphenyl-1,2-dichloroethane, m.p. 84-86° (8% yield). F. R. S.

*Lab. of Organic Chemistry, S. M. Kurov
 Chem. Sect. Inst. Kargin, c. 1941-*

ASTM-A METALLURGICAL LITERATURE CLASSIFICATION

FROM NOMINITY

SELECT ONE OR MORE

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	00
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100 AND 4TH (587) 23

1ST AND 2ND SERIES PROCESSES AND PROPERTIES INDEX

2

Ca

Life and scientific achievements of Nikolai Nikolaevich Zinin. (1812-1880). A. E. Arbusov. *Voprosy Khim.* 12, No. 2, 81-93 (1943).—Biography with portrait on the hundredth anniversary of Zinin's discovery of the reduction of aromatic nitro compts. to the amine deriva. (1842). Scientific and technical significance of the work of N. N. Zinin on the reduction of the aromatic nitro compounds. A. E. Poral-Koshits. *Ibid.* 64-108. The works of N. N. Zinin. A. E. Arbusov. *Ibid.* 109-33.—Three papers of Zinin published in German in 1842-5 are translated into Russian and reproduced here. Development of the chemistry of the organic dyestuffs and their intermediate products in the U. S. S. R. during the past 25 years (1917-1942): A. E. Poral-Koshits. *Ibid.* 134-64.—Review About 200 references to the Russian literature on dyestuffs and intermediates. F. H. Rathmann

A.S.S.S.R. METALLURGICAL LITERATURE CLASSIFICATION

E-177.272.12872

1ST AND 2ND SERIES

BULLETIN

1ST AND 2ND SERIES

1ST AND 2ND SECTIONS PROCESSES AND PROPERTIES INDEX

2

CS

Georgi Vasil'evich Loboder, 1876-1934. Tenth anniversary of his death. A. E. Arbutov. *Uspekhi Khim.* 13, 253-264 (1944).—Special emphasis is given to the development of the industrial production of synthetic rubber. E. H. Rathmann

ASH-SLA METALLURGICAL LITERATURE CLASSIFICATION

SECTION #	SECTION M	SECTION O	SECTION I	SECTION J	SECTION K	SECTION L	SECTION M	SECTION N	SECTION O	SECTION P	SECTION Q	SECTION R	SECTION S	SECTION T	SECTION U	SECTION V	SECTION W	SECTION X	SECTION Y	SECTION Z

CA

1ST AND 2ND ORDERS PROCESSES AND PROPERTIES INDEX 1ST AND 2ND ORDERS

2

The Academy of Sciences of the U.S.S.R. and the development of organic chemistry. A. E. Arbuzov. *Vestnik Akad. Nauk S.S.S.R.*, 1945, 103-25 (in Russian). Historical review.

ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION

OPEN

MATERIALS INDEX

COMMON INDEX

1ST AND 2ND ORDERS

1ST AND 2ND ORDERS

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
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CA

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Certain Esters of Phenylphosphonic and Phosphinic acids. A. E. Arburg and A. I. Razumov (Org. Chem. Lab., Chem. Tech. Inst., Kazan). *Bull. Acad. Sci. U.R.S.S., Classe sci. chim.* 1945, 1074. —The esters were prepd. by direct action of PhPCl_2 on the appropriate alc. in dry ether and in the presence of PhNMe_2 . MeOH (33.0 g.), 90 g. PhPCl_2 , and 90 g. PhNMe_2 in dry ether gave 90 g. (70.5%) of *Me ester* (I) of phenylphosphonic acid, b_p 94.5°, d_4^{20} 1.0073, d_4^{25} 1.0732, n_D^{20} 1.5180. Some *Me ester* (II), b_p 137.2-8.2°, of methylphenylphosphinic acid (isomerized product) was also obtained. From 19 g. of pure I in a 100-cc. flask with 1 cc. of MeI was obtained 17.5 g. of the isomerized ester (92.5%), b_p 141.75°, d_4^{20} 1.1009, d_4^{25} 1.1436, n_D^{20} 1.4908, n_D^{25} 1.5229. PrOH (82 g.), 122.0 g. PhPCl_2 , and 146.0 g. PhNMe_2 , after fractional distn., gave the *Pr ester* (III) of phenylphosphonic acid, b_p 137°, yield 75%. No isomerized ester was found. The III is a colorless liquid, sol. in most org. solvents, d_4^{20} 1.0123, d_4^{25} 0.9925, n_D^{20} 1.4939. III (55 g.) and an equimol. amt. of PrI , heated for 2-3 hrs. at 80-90° and then subjected to fractional distn., gave 45 g. *Pr ester* (IV) of phenylpropylphosphinic acid (80%), b_p 163°, d_4^{20} 1.0501, d_4^{25} 1.0463, n_D^{20} 1.4979, colorless liquid with a pleasant odor. *Et ester* (V) of phenylphosphonic acid (40 g.) (prepared like III) and 21.7 g. of EtOCH_2Cl heated at 80-85° for about 1 hr. gave 40 g. (84%) *Et ester* (V) of phenyl(ethoxymethyl)phosphinic acid, b_p 149.5°, d_4^{20} 1.1017, d_4^{25} 1.0811, n_D^{20} 1.4910, colorless liquid, having an odor of rose. VI (39.0 g.) and 16 g. of MeOCH_2Cl were heated to 70° to start the reaction, and, after completion of the reaction, heated 45 min. at 120° and then subjected to fractional distn. to give *Et ester* of phenyl(methoxymethyl)phosphinic acid, b_p 138-9°, d_4^{20} 1.1543, n_D^{20} 1.4801, colorless liquid with a pleasant odor.

G. Lebedeff

ASB-SLA METALLURGICA

1ST AND 2ND ORDERS PROCESSES AND PROPERTIES INDEX 3RD AND 4TH ORDERS

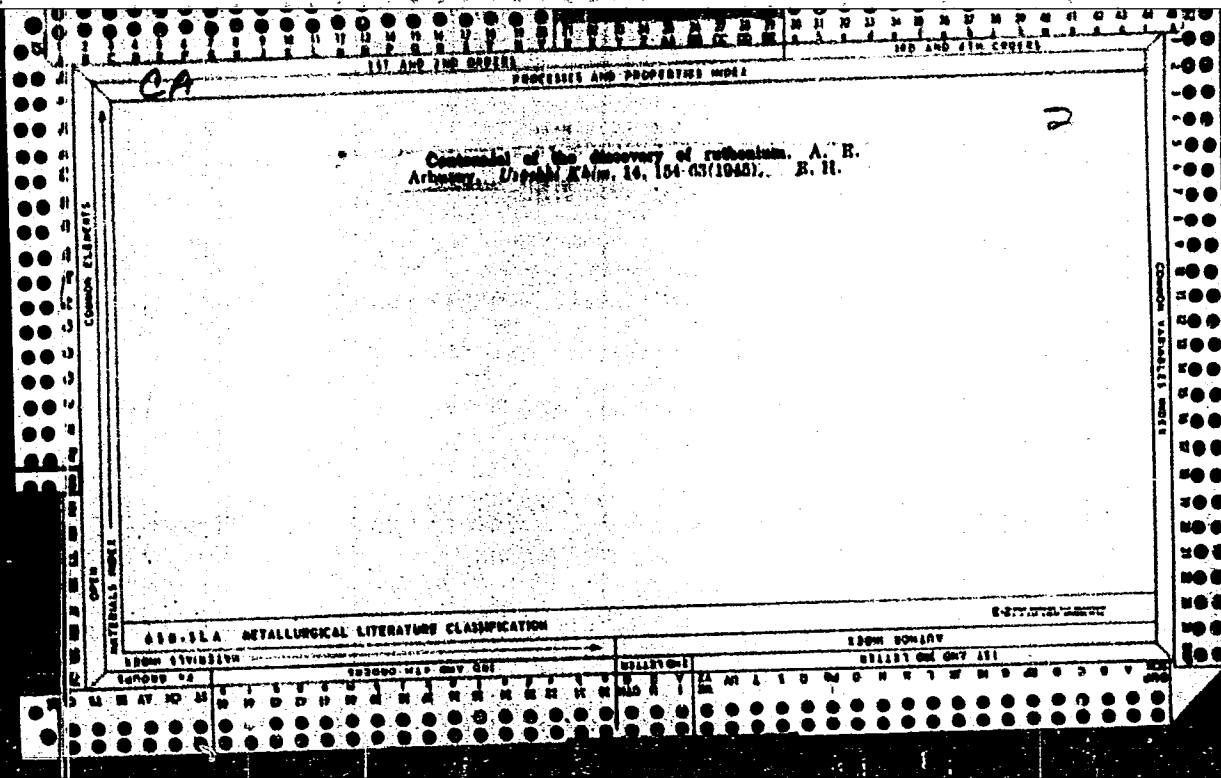
ca / 8

Preparation of 4,4'-bipyridine. A. B. Arbutov. *Bull. Acad. Sci. U.R.S.S., Classe Sci. Chim.* 1945, 451-5.—An improved method of prep. 4,4'-bipyridine is described. Powd. Zn (80 g., dried at 120°) is added to a stirred mixt. of dry C₂H₅N (50 ml.) and Ac₂O (150-250 ml., free from AcOH) during 3-4 hrs. at 25-30°. After a further 20 min., the mixt. is warmed to 85-90° (bath) and rapidly filtered. Crystals of 1,1-diacetyltetrahydro-4,4'-bipyridine (I) (10 g., m. 130-1°) sep. overnight. A thin layer (<1.5 cm., thick) of I (2 g.) is placed in a closed vessel also contg. 70% AcOH (1.3 g.) and a stream of O is passed in 6 hrs. at 50°; treatment of the product with AcOH or HCl, then NaOH, yields unchanged I (0.3 g.) and bipyridine dihydrate (1 g., m. 111-12°), and thence 4,4'-bipyridine, m. 73°. B. A.

*Lab. of Org. Chem., Kasen Chem. Inst.
Inst. -1945-
Mbr., Editorial Board, Dok. A.N., 1945*

ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION

GROUP 1ST AND 2ND ORDERS 3RD AND 4TH ORDERS



ANDREY, A. YE., Kamay, G. Kh., Belorossova, O. N.

"On the Isopropyl Ester of Phenyl-Phosphinic Acid," Zhur. Obshch. Khim., 1945.
Mbr., Lab. Organic Chemistry, Kazan Chhmmico-Technological Inst. im. S.M. Kirov, -1944-.

ARBUZOV, A. YE.

The isopropyl ester of benzenephosphonous acid. V. A. E. Arhuzov, G. Kh. Kamaev, and O. N. Belorossova (Kazan Chem.-Tech. Inst.). *J. Gen. Chem. (U.S.S.R.)* 15, 766-9 (1945).—When iso-PrOH and PhNMe₂ in dry Et₂O are cooled and treated with PhPCl₂ in a CO₂ atm., they form a distillate, 60% of which is *di-iso-Pr benzenephosphonite* (I), b_p 121-2°, d₄²⁰ 1.0103, d₄²⁵ 0.9952, n_D²⁰ 1.5021, and 15% *iso-Pr phenylisopropylphosphinate* (II), b_p 146-7°, d₄²⁰ 1.0057, d₄²⁵ 1.0813, n_D²⁰ 1.4929, formed by isomerization of I. When I is heated to 150° in the presence of iso-PrI (III) it liberates MeCH₂Cl, and forms *phenylisopropylphosphinic acid*, m. 61-2°, which gives cryst. Na, K, Ca, and Ba salts. When I and III are allowed to stand 10 days at room temp., 44.1% isomerization to II occurs. Addn. of a little PhNMe₂ increases the isomerization to 95%.
H. M. Leicester

ARBUZOV, A. Ye.

Preparation of α -phosphonopropionic acid, by A. Ye. Arbuzov, T. Konstantinova, and T. Antsyferova. Izvest Ak Nauk SSSR, Otdel khim nauk 1946, 179-84.

The preparation of $\text{HO}_2\text{CCH}_2\text{CH}_2\text{PO}_3\text{H}_2$, both by the $(\text{RO})_3\text{P}$ and $(\text{RO})_3\text{PONa}$ routes in their reaction with $\text{XCH}_2\text{CH}_2\text{CO}_2\text{Et}$, was investigated in detail. To 85 g. $(\text{EtO})_3\text{P}$ was added dropwise 70 g. $\text{ICH}_2\text{CH}_2\text{CO}_2\text{Et}$ at $120-50^\circ$; after the EtI distn., the product was distd. in vacuo to give 33.5 g. (45.8%) $(\text{EtO})_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{CO}_2\text{Et}$ (I), $b_{10} 151^\circ$, $b_{773} 287-8^\circ$, $d_4^0 1.1172$; hydrolysis with HCl in a sealed tube 4 hrs. at 120° gave the free acid (II), m. 170° . The difference in m.p. between this and Nylen's prepn. (m. $178-80^\circ$, C.A. 18, 3167) is unexplainable. The free acid may be also obtained from the tri-Et ester by heating per se to 280° , when 3 moles of C_2H_4 are split off in 4 hrs. and the residual oil solidifies on cooling to give nearly 100% of the acid, m. 170° ; the acid is stable even to 360° . An unspecified amt. of a by-product, $b_{11-5} 86.5-8^\circ$, was obtained; this substance contains 32% iodine and does not wet glass; its identity is unknown. $(\text{EtO})_2\text{POH}$ (36.5g.) was added dropwise to 18.5 g. EtONa suspended in dry Et_2O , with cooling, the resulting $(\text{EtO})_2\text{PONa}$ treated with an equiv. amt. of $\text{ICH}_2\text{CH}_2\text{CO}_2\text{Et}$ dild. with Et_2O , the mixt. heated 0.5 hr. on a steam bath, filtered from the NaI (17.4 g., 40.7%), and the filtrate distd. to give 23.5 g. I, $b_{10} 151^\circ$, $d_4^0 1.1162$, $d_4^{17} 1.1015$, and 33.2 g. residual oil. The latter was dissolved in H_2O , extd. 4 times with Et_2O (the ext. on evapn. gave only 2.35 g. oil, which was free of halogen and which on hydrolysis by HCl gave an acid m. $148-58^\circ$), and the aq. layer acidified by H_2SO_4 and thoroughly extd. with Et_2O to give 24 g. viscous oil; on attempted distn. in vacuo this yielded 10 g. EtOH , after which the distn. stopped even at 250° bath temp., at

(over)

which point decompn. set in; hydrolysis of the residual oil by HCl, as described above, gave 13.35 g. II; thus the total yield of II was 69%. $(\text{EtO})_2\text{POH}$ (37.5 g.) and 12.5 g. EtOH in 300-400 ml. Et_2O were treated slowly with 10.5 g. K in thin slices, and the resulting microcryst. suspension of $(\text{EtO})_2\text{-POK}$ treated dropwise with 62 g. $\text{ICH}_2\text{CH}_2\text{CO}_2\text{Et}$; a mild heat evolution took place and the reaction was completed by warming 1 hr. on a steam bath. Filtration gave 100% KI and distn. of the filtrate gave 54 g. pure I (85%). The distn. residue on hydrolysis gave an addnl. amt. of II (amt. not specified). The distn. residue in the prepn. using $(\text{EtO})_2\text{P(ONa)}$ was evidently a mono-Et ester of II (either C- or P- ester). Such a product may be visualized by an "abnormal" cleavage of the hypothetical intermediate $(\text{EtO})_2\text{P(ONa)}$ ($\text{CH}_2\text{CH}_2\text{CO}_2\text{Et}$)I, so that EtI, rather than NaI, splits off on heating. The same product may be also formed by interaction of NaI with I on heating, resulting in displacement of Et by Na.

G.M.K.

Lab. Org. Chem., Kazan Univ. - 1946
Stalin Prize 1946

ARBUZOV, A. Ye.

"On the Reactions of Halofen Derivatives of Triphenylmethane with Silver-Salts of Dialkyl-phosphorous Acids," Iz. Ak. Nauk SSSR, Otdel Khim. Nauk, NO. 2, 1946.

Laboratory of Organic Chemistry, Kazan State University. -1946-.

Won 1946 Stalin Prize.

PROCESSES AND PROPERTIES INDEX

10

Action of chloro- and bromomalonic ester on salts of diethylphosphorous acid. A. E. Arbutov and V. S. Abramov. *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1946, 223-4. -- To $(EtO)_2PONa$ (from 0.4 g. Na and 2.4 g. $(EtO)_2POH$ in 50 ml. Et_2O) was added slowly 4 g. $(EtO)_2CHCl$ in Et_2O ; a vigorous action ensued and rapid pptn. of $NaBr$ took place; after the addn. the mixt. was heated 15 min. on a water bath, the cooled mixt. treated with H_2O , and the org. layer evapd., giving 4 g. crude (1.95 g. pure) $[CH(CO_2Et)_2]$ (I) (73% yield). Use of $(EtO)_2POK$ in a similar expt. gave 86% I. When $(EtO)_2CHCl$ was used, however, $(EtO)_2PONa$ reacted slowly and required 3 hrs. boiling until 2.75 g. $NaCl$ pptd.; in 1 expt. the org. filtrate gave 7% I, in other expts. I could not be isolated at all. The same result was obtained with $(EtO)_2POK$. No other identifiable substances were isolated. In an attempt to det. whether the formation of free radicals of $(EtO)_2C$ and Ph_2C (previously observed in similar reactions of Ph_2CH (*J. Russ. Phys.-Chem. Soc.* 61, 1923(1929)) precedes the formation of the dimeric products or the former arise from dimerization of the latter, the following expt. was performed. To $(EtO)_2PONa$ (from 0.6 g. Na and 3.7 g. $(EtO)_2POH$) in Et_2O was added a mixt. of 3 g. $(EtO)_2CHCl$ and 4.2 g. Ph_2CH ; immediately the golden color of Ph_2C became visible; after brief standing in contact with air, an abundant pptn. of $(Ph_2C)_2O_2$, m. 180° (from $EtOH$), took place. Distn. of the filtrate gave a small amt. of I, m. 74.5-8.5° (from dil. $EtOH$). Since no $Ph_2CCH(CO_2Et)_2$ was found, it was concluded that the course of the reaction is more complex than mere pptn. of NaX and formation of free radicals. G. M. K.

E. M. K.

ASB. 114 METALLURGICAL LITER.

SIGN: 80-117

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Cl

Study of the structure of the dialkylphosphoric acids by the method of the combination scattering of light. A. F. Arbizov, M. I. Batsnev, and V. N. Vinogradova. *Compt. rend. Acad. Sci. P.R.S.S.* 54, 580 (1911010) (in French)

These acids may take two tautomeric forms

$$R-O-P(OR)-O \rightleftharpoons R-O-P(OR)-OH$$

(I) and (II). In the liquid acids studied, (Me-, Et-, Pr-, iso-Pr-, Bu-, and iso-Bu-) a wide and very intense band was observed centering at about 2435 cm⁻¹. Yost and Anderson (C. I. 28, 7101²), using liquid PH₃, found the frequency of P-H to be 2300 cm⁻¹. Thus the P-H group of these acids undergoes an intense internal action, probably through the H bond, of the type P-H...P or P-H...O. The P-H band obtained is narrower and less diffuse than the O-H band in the polymeric formation of water, alcohols, and phenols but is more like the O-H band in ring associates. A band was also observed for P=O at about 1200 cm⁻¹. It is weaker and more diffuse than the 1205 cm⁻¹ band observed in POCl₃. This diminution can be caused by the participation of P=O in P-H...O, analogous to the diminution of the C=O frequency in fatty acids when the C=O group takes part in the formation of the hydrogenated band (cf. M. I. Batsnev, C. I. 41, 2065³). In di-propyl- and dibutylphosphoric acids, a narrow band was observed at about 3150 cm⁻¹. This is less than the normal O-H frequency, but this type of band and shift are characteristic of dimeric rings. Thus these acids probably form a dimeric or a trimeric ring through the H...O of the two possible forms. I clearly predominates.

mlc of MS for 1946-

Paul F. Clark

ASB-114 METALLURGICAL LITERATURE

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
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PROCESS AND PROPERTIES INDEX

10

CA

Action of 1-bromo-1-nitro hydrocarbons on triethyl phosphite. A. E. Arbusov, B. A. Arbusov, and B. P. Lugovkin. *Bull. acad. sci. U.R.S.S., Class. sci. chim.* 1947, 835-8 (in Russian). --RCHBrNO₂ react with (EtO)₃P not along the lines of expected formation of RCH(NO₂)P(O)(OEt)₂, but anomalously with formation of Et₃PO, as the only identifiable product, evidently by a mechanism of the type presented by Allen and Wilson (*C.A.* 34, 3265^a) for the thermal decomn. of bromonitro derivs. through a biradical mechanism. The over-all reaction may be given by: $CH_3BrNO_2 \rightarrow CH_3 + Br + NO_2 + P(OEt)_3$

unsatd. and presumed to be C₁₁H₁₁. Similar treatment of Et₃PO₂ with an equimol. amt. of MeC(CH₃)BrNO₂ gave 47% Et₃PO₂. Heating Et₃PO₂ with MeNO₂ gave no reaction. To 28.4 g. Et₃PO₂ at 4° was added slowly 22 g. PhCBrNO₂; spontaneous reaction raised the temp. to 92° and EtBr began to distil; the mass was heated to 180° when EtBr distn. ceased for a total yield of 74%. Distn. gave 15.5 g. crude Et₃PO₂ and an unidentified product (2.6 g.), b. 78-81°, n_D²⁰ 1.5049, which on standing deposited crystals, m. 237-9° (from EtOAc), free from P and Br and analyzed as C₁₁H₁₁N₂O. G. M. K.

ASB-55A METALLURGICAL LITERATURE CLASSIFICATION

ARBUZOV, A. E.

FM 53T2

USSR/Chemistry - Phosphoric Acid
Chemistry - Ethers, Ethyl

Sep/Oct 1947

"The Action of α -Bromonitrohydrocarbons on the Ethyl Ether of Phosphorous Acid," A. E. Arbuzov, B. A. Arbuzov; B. P. Lugovkin, Chem Sci Res Inst imeni A. M. Butlerov, Kazan State U, 3 pp

"Izv Akad Nauk SSSR, Otd Khim Nauk" No 5

Contains experimental data and results, and shows that in each case where bromonitromethane, α -bromonitroethane and α, α -dibromophenylnitromethane acts on the ethyl ether of phosphorous acid, the result is triethylphosphate.

53T2

PROCESSES AND PROPERTIES INDEX

10

Some esters of triarylmethanephosphonic acids. A. B. Arbuзов and K. V. Nikonov (Kazan Chem. Tech. Inst.). *J. Gen. Chem. (U.S.S.R.)* 17, 2139-48 (1947) (in Russian).—The Arbuzov reaction was used to prep. a no. of new esters of triarylmethanephosphonic acids. $\text{Ph}_2(\text{p-PhC}_6\text{H}_4)_2\text{CBr}$ (9 g.) and 3.6 g. $(\text{MeO})_2\text{P}$ were slowly heated to 130° (a spontaneous reaction begins at 70°) with distn. of MeBr; on cooling there was obtained 72.0% *di-Me diphenyl(p-biphenyl)methanephosphonate*, colorless, m. 124-6° (from benzene-petr. ether, then Bu_2O). Similarly, $(\text{EtO})_2\text{P}$ gave 83.15% of the *di-Et ester* (I), m. 147-8° (from petr. ether), yellow needles; while $(\text{PrO})_2\text{P}$ gave 82.6% of the *di-Pr ester*, m. 132-3°, pale yellow. A mixt. of 3.2 g. $(\text{iso-PrO})_2\text{P}$ and 6 g. $\text{Ph}_2(\text{p-PhC}_6\text{H}_4)_2\text{CBr}$ and the cooled mixt. treated with petr. ether, gave 5.8 g. *di-iso-Pr diphenyl(p-biphenyl)methanephosphonate*, m. 194-5° (from benzene-petr. ether); the yield was raised to 95.4% if the original reaction was conducted in PhMe; the product (II) in this case is purer and m. 196-6.5° (from benzene-petr. ether). $\text{Ph}_2(\text{p-PhC}_6\text{H}_4)_2\text{CBr}$ (4 g.) and 3 g. $(\text{BuO})_2\text{P}$ in 1.5 ml. PhMe heated to 95° until soln. occurred, part of the solvent removed, and a few drops of petr. ether added, gave 72.54% of the corresponding *di-Bu ester* (III), m. 90-1°, colorless (from petr. ether). Heating I, II, or III in a sealed tube with 1:6 HCl 4-5 hrs. to 180-220° gave essentially quant. yields of $\text{Ph}_2(\text{p-PhC}_6\text{H}_4)_2\text{CPO}_2\text{H}_2$, m. 271-2° (from EtOH). Heating 5 g. $\text{Ph}_2(\text{p-PhC}_6\text{H}_4)_2\text{CBr}$ and 4 g. $(\text{iso-BuO})_2\text{P}$ in 1.5 ml. PhMe to 145° gave 74.8% of the corresponding *di-iso-Bu ester*, yellowish, m. 93-4° (from petr. ether). Similar reaction using $\text{Ph}_2(\text{p-PhC}_6\text{H}_4)_2\text{CBr}$ gave the corresponding esters: *di-Me*, m. 159° (from Bu_2O), 81.7%; *di-Et*, m. 140-1° (from Bu_2O), 76.89%; *di-Pr*, m. 110-11° (from Bu_2O), 69.44%; *di-iso-Pr*, m. 159-60° (from Bu_2O), 68.73%; *di-Bu*, m. 87-9° (from Bu_2O), 74.53%; *di-iso-Bu*, m. 118-20° (from Bu_2O), 68.32%; hydrolysis of these esters under the conditions given above gave $\text{Ph}_2(\text{p-PhC}_6\text{H}_4)_2\text{CPO}_2\text{H}_2$, m. 163-4°. *Tri-p-biphenylmethyl bromide* gave the corresponding esters: *di-Me*, m. 200-1° (from Bu_2O), 85.85%; *di-Et*, m. 144-5° (from benzene), 84.59%; *di-Pr*, m. 148-9° (from Bu_2O), 77.89%; *di-iso-Pr*, m. 177-8° (from Bu_2O), 80.65%; *di-Bu*, m. 132-3° (from Bu_2O), 83%; *di-iso-Bu*, m. 120-1°, 74.58%; hydrolysis of these in sealed tubes as described above gave *tri-(p-biphenyl)methanephosphonic acid*, m. 292-4° (from EtOH).

G. M. Kosolapoff

Lab. Dry. Chem.

A 59-11 A METALLURGICAL LITERATURE CLASSIFICATION

The reaction of the preparation of phosphonomalic esters. A. E. Arbusov and G. Karnal (Kazan Sect., Acad. Sci.). *J. Gen. Chem. (U.S.S.R.)* 17, 2149-57 (1947).—The previously reported prepn. of $\text{EtO}_2\text{CCH}_2\text{PO}(\text{OEt})_2$ from $(\text{EtO})_2\text{CCH}_2\text{Cl}$ and $\text{NaOP}(\text{OEt})_2$ in EtOH (C.A. 23, 4443) was repeated in view of results of Kosolapoff (C.A. 40, 4658) who obtained lower yields of the product in EtOH than in inert solvents. Na (11.5 g.) in 250 ml. abs. EtOH , treated with 69 g. $(\text{EtO})_2\text{POH}$ dropwise, heated 2 hrs. on a steam bath, treated, dropwise with stirring and cooling, with 63 g. $\text{ClCH}_2\text{CO}_2\text{Et}$, boiled 3 hrs. with charcoal, allowed to stand overnight, filtered, and distd., gave 90.1 g. (80.5%) $\text{EtO}_2\text{CCH}_2\text{PO}(\text{OEt})_2$, b_p 141-3°. To 8.8 g. Na in EtOH was added 23.5 g. PhOH and the EtOH removed *in vacuo*, giving colorless dry PhONa , a white mass; to this, suspended in 200 ml. dry Et_2O , was added 34.5 g. $(\text{EtO})_2\text{POH}$, followed by heating 1 hr. on a steam bath; the soln. was treated, with stirring and cooling, with 31 g. $\text{ClCH}_2\text{CO}_2\text{Et}$, then boiled 3 hrs. with charcoal, allowed to stand overnight, filtered, and the filtrate distd., giving 31.8 g. (57%) $\text{EtO}_2\text{CCH}_2\text{PO}(\text{OEt})_2$. The small drop in yield (57 instead of 59%) on the exchange of EtOH by PhOH in Et_2O is cited as evidence of the rapid rate of reaction of $(\text{EtO})_2\text{PONA}$ with the chloroacetate, which explains the high yields obtained in this reaction when EtOH is used as the solvent. The reaction of $\text{ClCH}_2\text{CO}_2\text{Et}$ with RONa is a relatively slow one. Na (6.4 g.) in 175 ml. abs. EtOH and 31.5 g. $\text{ClCH}_2\text{CO}_2\text{Et}$ boiled 3 hrs. as above gave 19.3 g. (53%) *Et ethoxycetate*, b_p 61-2°, d_4^{20} 0.9886, n_D^{20} 1.4020. A similar reaction using ClCO_2Et gave different results in EtOH , because in this case the acyl chloride reacted preferentially with EtONa and the acyl phosphonate ester was formed at all; in petr. ether, however, 55% $\text{EtO}_2\text{CPO}(\text{OEt})_2$, b_p 130-1°.

11 AND PROPERTIES (CONT.)
 —WERE OBTAINED. The reaction in EtOH yielded as the only identifiable products $(\text{EtO})_2\text{POH}$ and $(\text{EtO})_2\text{CO}$. The lack of phosphonation in this case is not due to alcoholysis of the phosphonofumarate, as the latter is unchanged on boiling 5 hrs. with EtOH . Following the prepn. of phosphonomalic esters reported by Kosolapoff (see above), the following were prepd. in good degree of purity: $(\text{MeO})_2\text{POCH}(\text{CO}_2\text{Et})_2$, b_p 153-4°, d_4^{20} 1.2332, d_4^{25} 1.2184, n_D^{20} 1.4525 (from 22.6 g. $(\text{MeO})_2\text{P}$ treated slowly with 43.5 g. $\text{BrHC}(\text{CO}_2\text{Et})_2$ and heated 1 hr. on steam bath), 80%; $(\text{EtO})_2\text{POCH}(\text{CO}_2\text{Et})_2$, (I), b_p 154-6°, d_4^{20} 1.1719, d_4^{25} 1.1550, n_D^{20} 1.4450 (from 10.0 g. $(\text{EtO})_2\text{P}$ and 23.9 g. $\text{BrHC}(\text{CO}_2\text{Et})_2$, on the steam bath), 70%; $(\text{PrO})_2\text{POCH}(\text{CO}_2\text{Et})_2$, b_p 169-70°, d_4^{20} 1.1230, d_4^{25} 1.1117, n_D^{20} 1.4430 (from 21 g. $(\text{PrO})_2\text{P}$ and 24 g. $\text{BrHC}(\text{CO}_2\text{Et})_2$, heated 2 hrs. on a steam bath), 64.7%; $(\text{BuO})_2\text{POCH}(\text{CO}_2\text{Et})_2$, b_p 185-90° (substantial decompn.), n_D^{20} 1.4405 (from 20 g. $(\text{BuO})_2\text{P}$ and 20 g. $\text{BrHC}(\text{CO}_2\text{Et})_2$, after 3 hrs. heating in a CO_2 atm.), 40% (mostly due to loss during distn.). Although phosphonomalonates apparently were formed on heating $\text{BrHC}(\text{CO}_2\text{Et})_2$ with $(\text{iso-BuO})_2\text{P}$ or $\text{PhP}(\text{OPr})_2$, the products could not be isolated because of decompn. on attempted distn. When 27.5 g. I was treated with 1.8 g. Na in 150 ml. Et_2O a brisk reaction ensued and the Na deriv. was formed in soln.; treatment with MeI, however, gave not the expected Me deriv. of I, but $\text{MePO}(\text{OEt})_2$, b_p 80.5-1°, d_4^{20} 1.0725, n_D^{20} 1.4062. Similarly, $(\text{PrO})_2\text{POCH}(\text{CO}_2\text{Et})_2$ gave $\text{MePO}(\text{OPr})_2$, b_p 68-70°, b_p 105-6°, d_4^{20} 1.0683, n_D^{20} 1.4082. This result is interpreted by a possibility of tautomerism of the Na deriv. in which is formed an enolic PONA compd. which adds MeI across the enolic double bond and the adduct breaks to give $\text{MePO}(\text{OR})_2$. The phosphonomalic esters were yellow liquids which on hydrolysis with HCl gave inorg. P acids and malonic acid only, thus confirming the earlier work of K. G. M. K.

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ARBUZOV, A. E.

USSR/Chemistry - Carbon Tetrachloride
Chemistry - Phosphinic Acids

Jan 1947

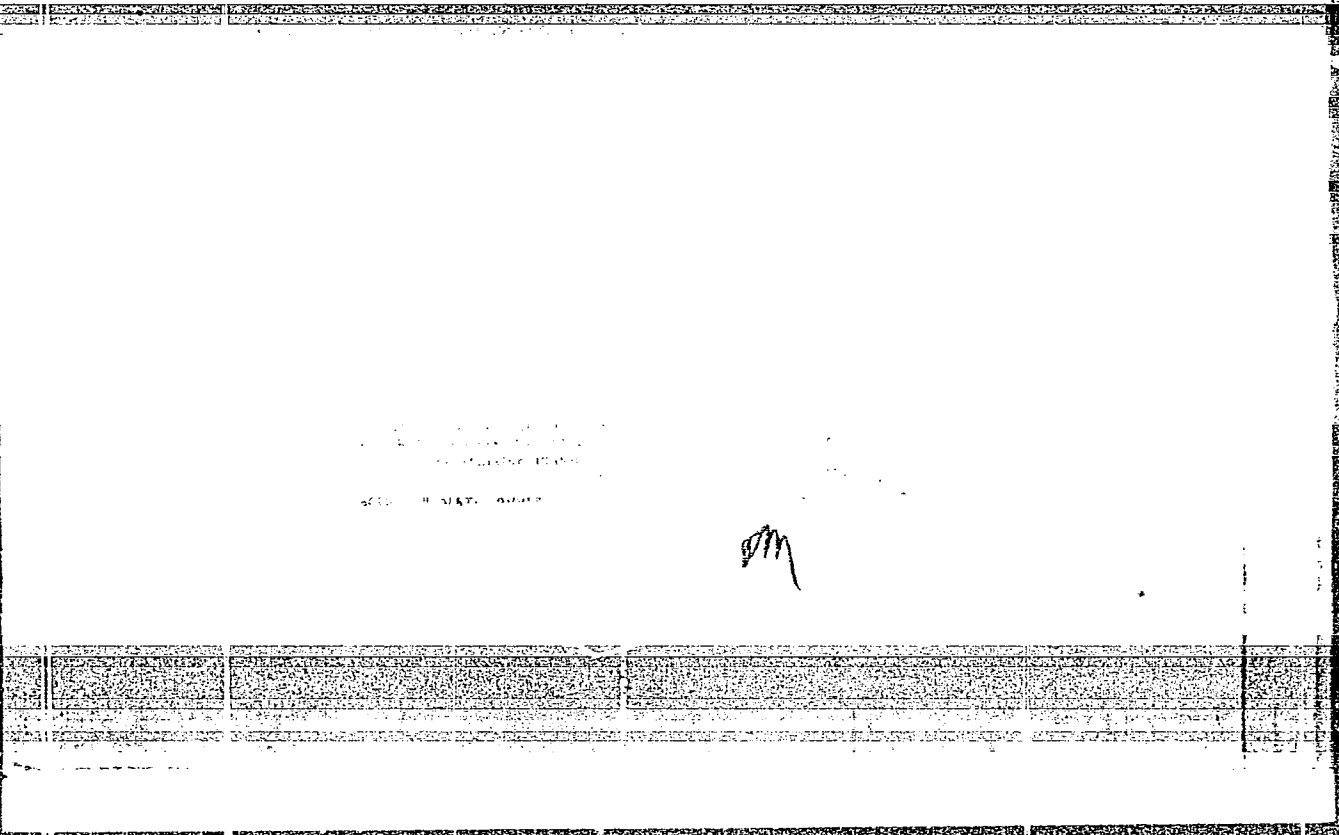
"The Effect of Carbon Tetrachloride on Ester Phosphite and Phenylphosphinic Acid,"
Gil'm Kamay, 3 pp

"Dok Ak Nauk SSSR" Vol LV, No 3

Submitted by A. E. Arbuzov, Institute of Chemistry, Kazan Branch, Academy of Sciences of the USSR. Experiments were conducted to determine the interaction between chlorine and bromine ethyl and n-propyl on the middle esters and salts of oxidized ester phosphite acid. O. N. Belorossion and L. F. Egorov assisted on the experimental part.

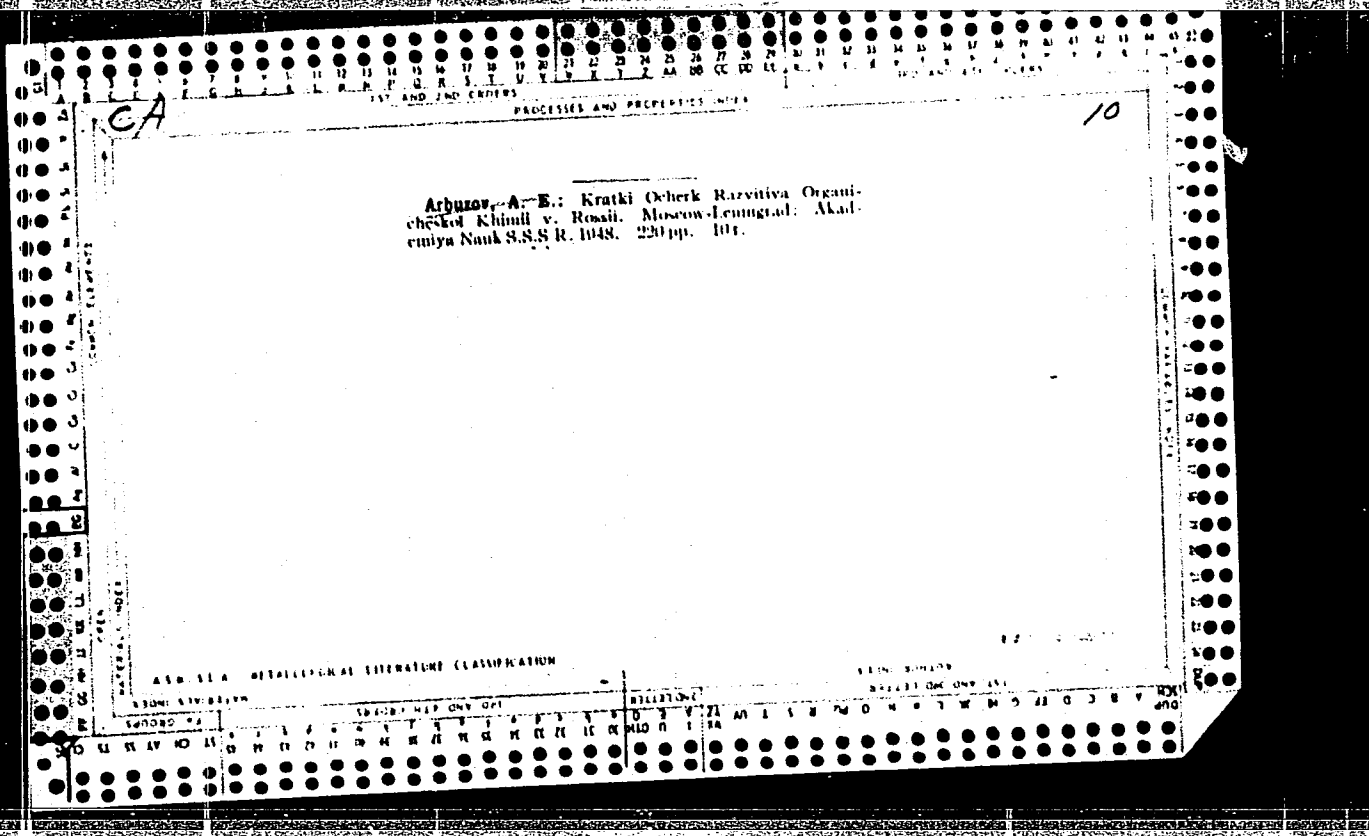
FA 21T7

ARKH 7 27 ALE



KIRSANOV, N.V.; ABBUZOV, A.Ye., glavnyy redaktor, akademik; MIROPOL'SKIY,
L.M., otvetstvennyy redaktor, professor.

[Pliocene clays in the Tatar A.S.S.R.] Pliotsenovye gliny v Tatar-
skoi A.S.S.R. Izd-vo Kazanskogo Filiala Akademii Nauk SSSR, 1948.
154 p. (Akademia nauk SSSR. Kazanskiy filial, Kazan, Trudy, no.1)
(Tatar A.S.S.R.--Clay) (MLRA 9:12)



"Obtaining Certain Esters of Diphenylphosphinous Acid." Zhur. Obshch. Khim. 18, No. 11
1948.
Cjem. Inst. Kazan Affiliate of USSR Acad. Sci. -c1948-.

ARBUZOV, A. Ye.

USSR/Chemistry - Phosphorous Acid, Mar/Apr 1948
Esters of

Chemistry - Synthesis

① "Methods for Obtaining and Properties of Some Cyclic Esters of Phosphorous Acid," A. Ye. Arbuzov, V. M. Zorostrova, N. I. Rizpolozhenskiy, Chem Res Investigation Inst imeni A. M. Butlerov, Kazan State U, 10½ pp

"Izvest Akad Nauk SSSR, Otd Khim Nauk" No 2

Methods for obtaining chlorine anhydrate from glycol phosphate acid, and ethyl and methyl esters of glycol phosphate acid. Description of some properties and process of conversion. Submitted 15 Aug 1947.

63713

TA 9/49T22

ARBUSOV, A. YE.

USSR/Chemistry - Alcoholates Jun 48
Chemistry - Phosphinic Acid, Triarylmethyl,
Ester of

"The Action of Boyd's Chloranhydride Analogues on
Alcoholates," A. Ye. Arbusov, K. V. Nikonov,
Lab of Org Chem, Kazan Chem Tech Inst, 7 3/4 pp

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

Alcoholates react with analogues of Boyd's chloran-
hydride to form chloresters (I) or diesters of cor-
responding triarylmethylphosphinic acids (II); II
can be formed from I by saponification. Submitted
12 Jul 1947.

9/49T22

PROCESSES AND PROPERTIES INDEX

10

CA

The action of analogs of Boyd's chloride on sodium alcoholates. A. E. Arbutov and K. V. Nikonorov. *Zhur. Obshchei Khim.* (J. Gen. Chem.) 18, 1137-44 (1948); cf. *C.A.* 42, 4540g.—In the reaction of Ar_2CPOCl_2 with $RONa$ it was possible, in 8 cases out of 18, to isolate dialkyl phosphonate esters, which were identical with the products of reaction of Ar_2CX with $(RO)_2P$ (cf. A. and N., *C.A.* 42, 4546b). $Pb_2(p-PhC_6H_4)_2CPOCl_2$ (1.8 g.) and dry $MeONa$ (from 0.24 g. Na) in 10 ml. benzene at 100° gave an orange-colored soln.; after washing with water, no pure products could be isolated; similar reaction with $EtONa$ at 95° gave $Pb_2(p-PhC_6H_4)_2CPO(OEt)_2$, m. $115-6^\circ$ (73.2%), yellow needles; $NaOPr$ gave 80% corresponding *di-Pr ester*, m. $131-2^\circ$; *iso-PrONa* gave 31.0% $Pb_2(p-PhC_6H_4)_2CPOCl_2(OPr-iso)$, m. $118-20^\circ$ (from Bu_2O); $BuONa$ gave the *di-Bu ester*, m. $90-1^\circ$ (from Bu_2O) (59%); the use of *iso-BuONa* gave 61.5% *di-iso-Bu ester*, m. $93-4^\circ$. $Pb_2(p-PhC_6H_4)_2CPOCl_2$ (1.5 g.) and $MeONa$ (from 0.17 g. Na) in dry benzene also failed to give a definite product; $EtONa$ gave the *di-Et ester*, m. $130-41^\circ$ (from Bu_2O) (51.4%); $NaOPr$ failed to give a definite product; *iso-PrONa* gave the *Pr ester chloride*, m. $133-4^\circ$ (from Bu_2O) (38.8%); $BuONa$ failed to give a clean-cut product, while *iso-BuONa* gave the *di-iso-Bu ester*, m. $118.5-20^\circ$ (from Bu_2O) (33%). $(p-PhC_6H_4)_2CPOCl_2$ with 2 mols. dry $MeONa$ in benzene again failed to give a definite product; $NaOEt$ gave 72.7% *di-Et ester*, m. $143-5^\circ$ (from Bu_2O); $PrONa$ gave the *Pr ester chloride*, m. $139-11^\circ$ (from Bu_2O) (41.3%); *iso-PrONa* gave the *iso-Pr ester chloride*, m. $170-3^\circ$ (from Bu_2O) (39.9%); $BuONa$ gave 51% *di-Bu ester*, m. $130-2^\circ$ (from Bu_2O); *iso-BuONa* failed to give a definite product. Hydrolysis of the esters or the ester chlorides by water in a sealed tube 5 hrs. at $170-80^\circ$ gave the corresponding previously described $Ar_2CPO(OH)_2$. Hydrolysis of the crude products from $MeONa$ also gave the same result.

G. M. Kosolapoff

ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION

PREPARATION AND PROPERTIES INDEX

/0

Preparation of some esters of diphenylphosphinous acid.
 A. R. Arbutov and K. V. Nikonov. *Zhur. Obshchei Khim.* (1. Gen. Chem.) 18, 2008-15(1948).—Earlier attempts to prep. Ph₂PO₂R, where R = Me or PhCH₂, using RONA and Ph₂PCl, gave only the corresponding Ph₂P(O)R, due to easy isomerization of the esters (A., Thesis, Kazan, 1914). Addn. of 11 g. Ph₂PCl (I), b.p. 175-6°, to 1.6 g. MeOH, 3.0 g. pyridine, and 50 ml. dry azoxy deriv., m. 186-7.5°. Similar results may be obtained by oxidizing the corresponding bromoazobenzene. The formation of V from IV and KOEt and the reaction of p-C₆H₄(NO₂)₂ with Na₂S to give 4,4'-dinitroazobenzene were observed. A 5% yield of bis(2,4-dinitrophenyl) sulfone was obtained upon oxidation of [2,4-(O₂N)₂C₆H₃]₂S₂ prepd. from Na₂S₂ and 2,4-(O₂N)₂C₆H₃Cl (VI); 2-O₂N(MeO₂C)C₆H₄Cl (VII) may also be used. Bis(2-nitro-4-carboxyphenyl) disulfide, m. 140-50°, when oxidized gave 8% of the sulfone, m. 205-6°. Under proper conditions I will undergo sulfurization, a reaction which appears new in type. The disulfides prepd. from VI and VII with Na₂S₂ appeared to be contaminated with the corresponding monosulfides. G. T. Boykin

Preparation of N,N-dimethylaniline-m-sulfonic acid.
 A. N. Kurakin. *Zhur. Obshchei Khim.* (1. Gen. Chem.) 18, 2060-91(1948).—Sulfonation of Me₂NPh according to Melau and Bucherer (*Pract. Manual of Chem. of Dyestuffs*, 1927) gives approx. equal amts. of m- and p-sulfonic acids; the use of the amine sulfate failed to change the proportions. The best sepn. is by soly. of the Ca salts; the p-salt is less sol. and seps. first on evapn. In a typical expt. 20 ml. Me₂NPh and 1300 g. 30% oleum gave 105 g. 11A METALLURGICAL LITERATURE CLASSIFICATION

m. 102-3°, which is also obtained by addn. of a trace of iodine to the ester; heating with CCl₄ gives Ph₂P(O)CCl₂, while Ph₂CBr spontaneously gives Ph₂CP(O)Ph. Addn. of 11 g. Ph₂PCl to 0.2 g. PhCH₂SH and 4 g. pyridine in Et₂O with cooling, stirring 0.5 hr., and filtration gave presumably Ph₂P(S)CH₂Ph, which on attempted distn. or merely standing overnight gives Ph₂P(S)CH₂Ph, m. 144-7°, does not react with CuCl, CCl₄, MeI, or Ph₂CBr. Addn. of 11 g. Ph₂PCl to 2.0 g. CH₂:CHCH₂OH and 4 g. pyridine in Et₂O, filtration after 40 min., and attempted distn. resulted in vigorous action at 160° which gave Ph₂P(O)-CH₂:CH:CH₂, m. 94-5°, b.p. 200-2°; use of PhNMe₂ in place of pyridine gave the same result; undistd. Ph₂P(O)-CH₂:CH:CH₂ gives the CuCl salt, m. 101-3°, reacts with a trace of iodine giving Ph₂P(O)CH₂:CH:CH₂, while MeI gives Ph₂MePO and Ph₂CBr gives Ph₂CP(O)Ph. Use of CH₂:CHCH₂SH in the above prepn. gives Ph₂P(S)CH₂:CH:CH₂, which isomerizes on distn. (b.p. 184-5°), yielding Ph₂P(S)CH₂:CH:CH₂, m. 49-50°; this isomerization occurs spontaneously on standing 2 days; the same phosphine sulfide was obtained from K₂S₂O₈ and Ph₂PCl in Et₂O. G. M. Kosolapoff

1ST AND 2ND ORDERS PROCESSES AND PROPERTIES INDEX

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CA

Synthesis and the study of properties of mixed thio esters of phosphorous acid. A. E. Arbutov and K. V. Nikonov. *Doklady Akad. Nauk. S.S.S.R.* 62, 75-8 (1948); cf. Divinski, *et al.*, *C.A.* 43, 509c.—Esters of the general type $(RO)_2PSR$ and $RPO(SR)_2$ were prepd. and their isomerization with halogen derivs. was investigated. The prepn. was according to the scheme $(RO)_2PCl + NaSR \rightarrow (RO)_2PSR + NaCl$, and $ROPCl_2 + 2NaSR \rightarrow 2NaCl + ROP(SR)_2$; $(EIO)_2PSEt$ (61%), b_p 75-7°, n_D^{20} 1.4592, d_4^{20} 1.0213; $(EIO)(SEt)_2$ (80%), b_p 108-11°, n_D^{20} 1.5226, d_4^{20} 1.0381; $(PrO)_2PSEt$ (36%), b_p 120-4°, n_D^{20} 1.5241, d_4^{20} 1.0502; $(PrO)(SEt)_2$ (85%), b_p 128°, n_D^{20} 1.5278, d_4^{20} 1.0487. All the esters are evil-smelling, unstable substances, easily oxidized in air; the tri-Rt ester (1st example) is especially sensitive to O₂ and on bubbling of a few ml. of air, its temp. rises to over 100°. All are decompd. by water, alkali, or strong acids; HNO₃ leads to explosive decompn. They give characteristic CuX salts (no data) and add S. They react with halogen compds.: Ph₂CH₂, Ph₂CCl, BzCl, PhCH₂Cl, AcCl, AcBr, and EtO₂CCl. However, these esters, in addn. to the possible Arbutov reaction at the P atom, may undergo a similar isomerization at the S atom, which would result in formation of $(RO)_2PX$ and $R-S-R$ in the case of $(RO)_2PSR$ and RX . Expts. indicate that both reactions take place. Thus, EtI acting on $(EtO)_2PSBt$ or $RPO(SBt)_2$ yields not only the $(EtO)(OEt)(SBt)$ type, but also gives some Et₂SI, which forms from the unstable $(RO)_2PI$ (from the 2nd reaction scheme) and RI. No exptl. data.

G. M. Kosolapoff

E-2

ARBUZOV, A. Ye., Acad

USSR/Chemistry - Phosphoric Acid, Sep 48
Thioesters

Chemistry - Synthesis

"Synthesis and Studies of the Properties of Mixed Thioesters of Phosphoric Acid," Acad A. Ye. Arbutov, K. V. Nikonov, Chem Inst Imeni A. Ye. Arbutov, Kazan Affiliate, Acad Sci USSR, 4 pp

"Dok Ak Nauk SSSR" Vol IXII, No 1

The compounds $(C_6H_5O)_2PSC_2H_5$, $C_2H_5OP(SO_2C_2H_5)_2$, $(C_3H_7O)_2PSC_2H_5$, and $C_3H_7OP(SO_2C_2H_5)_2$ were synthesized in yields of 61, 89, 36, and 85% respectively. It follows: $(RO)_2PCl + RNa \rightarrow (RO)_2PSR + NaCl$;

35/4919

USSR/Chemistry - Phosphoric Acid, Sep 48
Thioesters (Contd)

$ROPCl_2 + 2RNa \rightarrow ROP(SR)_2 + 2NaCl$. They are unstable compounds oxidizing rapidly in air, and boil between 75° and 128° under 10 - 15 mm pressure. Briefly describes their chemical properties. Submitted 9 Jul 48.

35/4919

ARBUZOV, A. YI

BARANOV, V.I., professor; ARBUZOV, A.Ye., akademik, glavnyy redaktor; LIVANOV, N.A., professor, otvetstvennyy redaktor; RASSTRIGIN, M.A., tekhnicheskyy redaktor.

[Kuligash] Kuligash. Izd-vo Kazanskogo filiala Akademii nauk SSSR, 1948. 72 p. (Akademiia nauk SSSR. Kazanskii filial, Kazan. Trudy. Seriya biologicheskikh i sel'skokhoziaistvennykh nauk, no.1)
(MLBA 10:2)

(Aktanysh District--Swamps)

CA

13

- Preparation and properties of esters of tetramethylene glycol phosphorous acid. A. E. Arhuzov and M. M. Azanovskaya. *Invest. Akad. Nauk S.S.S.R., Dokl. Khim. Nauk* 1949, 473-9. - Slow addn. of 13.6 g. $\text{P}(\text{O})_2\text{O} \cdot \text{O} \cdot \text{CMe}_2 \cdot \text{CMe}_2 \cdot \text{O} \cdot \text{P}(\text{O})_2\text{O}$ to 11.8 g. $[\text{Me}_2\text{C}(\text{OH})_2]$ (I), 15.8 g. pyridine, and 80 ml. Et_2O with ice cooling, heating 0.5 hr. on a steam bath, and filtration gave 47% $\text{O} \cdot \text{CMe}_2 \cdot \text{CMe}_2 \cdot \text{O} \cdot \text{P}(\text{O})_2\text{O}$, b_p 81.5-82°, d_4^{20} 1.1502, d_4^{25} 1.1580, n_D^{20} 1.4720, with some 50% undistillable residue (contains some real P if distn. is attempted), which on cooling deposits on standing some $\text{O} \cdot \text{CMe}_2 \cdot \text{CMe}_2 \cdot \text{O} \cdot \text{POH}$ (II), also formed on exposure of the chloride to moisture. A similar reaction with 14.6 g. I, 19.5 g. pyridine, and 10.5 g. MeOPCl_2 in 100 ml. Et_2O gave 51.4% $\text{O} \cdot \text{CMe}_2 \cdot \text{CMe}_2 \cdot \text{O} \cdot \text{POMe}$, b_p 91-2.5°, d_4^{20} 1.0022, d_4^{25} 1.0449, d_4^{30} 1.0469, n_D^{20} 1.4417, and 3 g. II as residue; the ester reacts vigorously with H_2O , yielding II, while mixing 0.5 g. with 0.9 g. Ph_2CBr in C_6H_6 and refluxing 5 min., gave on evapn. $\text{Ph}_2\text{CP}(\text{O}) \cdot \text{O} \cdot \text{CMe}_2 \cdot \text{CMe}_2 \cdot \text{O}$, m. 229.5-31.5° (from C_6H_6); reaction of 2 g. of the ester with 1.6 g. BzCl , completed by 0.5 hr. at 60-80°, gave 2.0 g. $\text{BzP}(\text{O}) \cdot \text{O} \cdot \text{CMe}_2 \cdot \text{CMe}_2 \cdot \text{O}$, m. 80-90° (from ligroin), which forms a 1,4(11)-dinitrophenylhydrazone, m. 104.5-5.5° (from MeOH). Similarly, 11.5 g. $\text{O} \cdot \text{CMe}_2 \cdot \text{CMe}_2 \cdot \text{O} \cdot \text{P}(\text{O})_2\text{O}$ and 4.0 g. pyridine in Et_2O gave, on addn. of 2.0 g. EtOH with ice cooling and warming 30

min. on a steam bath, 46.7% $\text{O} \cdot \text{CMe}_2 \cdot \text{CMe}_2 \cdot \text{O} \cdot \text{POEt}$, b_p 75-6°, d_4^{20} 1.0322, d_4^{25} 1.0136, d_4^{30} 1.0156, n_D^{20} 1.4302 (and 1.5 g. II), which with BzCl at 60-80° gave $\text{BzP}(\text{O}) \cdot \text{O} \cdot \text{CMe}_2 \cdot \text{CMe}_2 \cdot \text{O}$, identical with the above. The use of I (14.6 g.), 19.6 g. pyridine, and 20 g. PropCl in Et_2O gave 44.9% $\text{O} \cdot \text{CMe}_2 \cdot \text{CMe}_2 \cdot \text{O} \cdot \text{POPr}$, b_p 84.5-80°, d_4^{20} 1.0133, d_4^{25} 0.9901, d_4^{30} 0.9981, n_D^{20} 1.4400, which on heating with BzCl 4 hrs. at 90-110° and evapn. gave hygroscopic $\text{BzP}(\text{O}) \cdot \text{O} \cdot \text{CMe}_2 \cdot \text{CMe}_2 \cdot \text{O}$, m. 90-1° (from ligroin). Similarly, 27.7 g. I, 41 g. BuOPCl_2 , and 37.2 g. pyridine in Et_2O gave 68.5% $\text{O} \cdot \text{CMe}_2 \cdot \text{CMe}_2 \cdot \text{O} \cdot \text{POBu}$, b_p 105-6.5°, d_4^{20} 1.0076, d_4^{25} 0.9901, d_4^{30} 0.9780, n_D^{20} 1.4413; the latter (4.4 g.) and 0.36 g. H_2O slightly acidified with HCl react vigorously and on cooling yield II, m. 100.5-8° (from petr. ether), hygroscopic, insol. in Et_2O or C_6H_6 , giving a monomeric mol. wt. in dioxane; the Bu ester (1 g.) with 1.45 g. Ph_2CBr in hot C_6H_6 gave $\text{Ph}_2\text{CP}(\text{O}) \cdot \text{O} \cdot \text{CMe}_2 \cdot \text{CMe}_2 \cdot \text{O}$, m. 211-1.5° (from C_6H_6), giving $\text{Ph}_2\text{CPO}(\text{OH})_2$ on hydrolysis with HCl ; heating 5.2 g. Bu ester with 3 g. PhCl_2Cl 4 hrs. to 100° in a sealed tube gave some BuCl and $\text{PhCl}_2\text{P}(\text{O}) \cdot \text{O} \cdot \text{CMe}_2 \cdot \text{CMe}_2 \cdot \text{O}$, m. 115-16.3° (from Et_2O); although heating the Bu ester with BzBr or BzCl 3-4 hrs. to 150-80° gave 71-91% BuBr or BuCl , the main reaction products could not be distd. without decompos. G. M. Kosolapoff

Chem. Sci. Res. Inst. in. A. M. Butlerov Kazan State Univ. Ul'yanov - Lenin. 1949

ARBUZOV, A. Ye.

TRUFANOV, A.A.; ARBUZOV, A. Ye., akademik, glavnyy redaktor; MIROPOL'SKIY,
L.M., professor, otvetstvennyy redaktor.

[Cross circulation in free flowing channels (working hypothesis
of the theory of circulation)] O poperechnoi tsirkulatsii v
svobodnom ruslovom potoke (opyt rabochei gipotezy teorii tsirkulatsii).
Kazan', Izd-vo Kazanskogo filiala AN SSSR, 1950. 86 p. (Academia
nauk SSSR. Kazanskiy filial. Trudy, seriia vodokhoziaistvennykh
problem no.1) (MLRA 10:4)

(Hydraulics)

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Dipole moments of esters of phosphoric, phosphorous, and phosphinic acids. A. B. Arbusov and P. I. Rakov (Kazant State Univ.). *Dokl. Akad. Nauk S.S.S.R.* (Dokl. Akad. Nauk) 1968, 237-40. From dielectric constant measurements in soln. in CCl_4 , the following dipole moments were detd. by the formula of deVries (J. Chem. Phys. 33, 2782): phosphites $\text{P}(\text{OR})_3$, R = Me 1.83, Et 1.90, Pr 1.90, iso-Pr 1.88, Bu 1.92, Ph 1.50; the latter value differs very considerably from that detd. by Lewis and Murph (C. d. 36, 4014). Phosphates have considerably higher dipole moments than phosphites; the values detd. for $\text{PO}(\text{OR})_3$ are, R = Me 3.03, Et 3.07, Pr 3.00, iso-Pr 2.85, Bu 3.05, Ph 2.80. Esters of alkylphosphinic acids have, on the whole, dipole moments by about 0.1 debye lower than the corresponding phosphates; and about 1.0 higher than the corresponding phosphites; thus, for $\text{RPO}(\text{OR})_2$, R = Me 2.80, Et 2.91, Pr 2.92, iso-Pr 2.91, Bu 2.80. Dialkyl phosphites $(\text{RO})_2\text{POH}$, R = Me 2.94, Et 3.06, Pr 3.15, iso-Pr 3.08, Bu 3.17. The high values of the dipole moments indicate that the tautomeric equil. $\text{OHP}(\text{OR})_2 \rightleftharpoons \text{OPH}(\text{OR})_2$, i.e. the shift is, however, influenced by the nature of the solvent, but is, however, influenced by the nature of the solvent, shift is, however, influenced by the nature of the solvent, betwe the dipole moment varies to some extent with the solvent. Thus, for $(\text{RO})_2\text{POH}$, the dipole moments in CCl_4 , decalin, C_6H_6 , and cyclohexane, are 3.06, 3.04, 3.17, and 2.85, resp. In cyclohexane soln., the dipole moment of $(\text{RO})_2\text{PO}$ is found 2.84, again distinctly lower than in CCl_4 3.07. N. Thom

Allyl esters of ethylene-, trimethylene-, and 1-methyltri-methylene glycol phosphorous acid and their transformations.
 A. B. Arbutov and V. M. Zorostrova (A. M. Butlerov Inst., Kazan State Univ.). *Izv. Akad. Nauk S.S.S.R., Otdel Khim. Nauk* 1950, 357-60; cf. C. I. 42, 4032g. $(CH_2O)_2PCl$ (43.8 g.) was added, with ice cooling, to 20.1 g. allyl alc., 27.4 g. dry pyridine, and 200 ml. Et_2O ; after filtration, there was obtained 58.6% $(CH_2O)_2POCH_2CH:CH_2$, b_p 69.5-70.0°, d_4^{20} 1.1553, n_D^{20} 1.4635, which yields a $CuBr$ adduct, m. 107-8° (from CaH_2), and evolved much heat on contact with H_2O . Addn. of S causes spontaneous reaction and yields $(CH_2O)_2P(S)OCH_2CH:CH_2$ (40% pure), b_p 130-2°, n_D^{20} 1.5025, d_4^{20} 1.2610. Heating the phosphite (10.5 g.) and 4.9 g. $CH_2=C(CH_3)OP(O)(CH_2CH:CH_2)OC-CH_2CH:CH_2$, b_p 132-3°, n_D^{20} 1.4708, d_4^{20} 1.1725. Similarly $PhCH_2Cl$ (4 hrs. at 155-60°) gave a moderate yield of liquid, b_p 172-7°, which on standing deposited crystals, m. 122-3° (from CaH_2), appearing by analysis to be $(CH_2O)_2P(O)CH_2Ph$; the liquid portion on further distn. gave an unstated yield of $PhCH_2P(O)(OCH_2CH_2)OCH_2CH:CH_2$, b_p 175-7°, d_4^{20} 1.2061, n_D^{20} 1.5210. Reaction with $AcBr$, run in Et_2O to moderate the action, yielded a liquid, b_p 125-9.5°, n_D^{20} 1.4740, d_4^{20} 1.4348, which could not be obtained in pure state, as much polymer was formed during

distn.; the product was $C_{11}H_{18}O_2PBr$, although Br analyses were quite low; a similar reaction with $AcCl$ gave largely a polymer on distn. and only a small amt. of distillable $C_{11}H_{18}O_2PCl$ (very crude), b_p 139-42°, d_4^{20} 1.2530, n_D^{20} 1.4600. Addn. of 0.6 g. cold H_2O to 5.2 g. phosphite caused a vigorous reaction, yielding 0.6 g. allyl alc. and a small amt. of liquid, b_p 132-41°. Addn. of 28.1 g. $CH_2=C(CH_3)OPCl$ to 11.6 g. allyl alc., 15.8 g. pyridine, and 180 ml. Et_2O with ice cooling gave 52.7% $CH_2=C(CH_3)OP(O)CH_2CH:CH_2$, b_p 82-2.5°, d_4^{20} 1.1214, n_D^{20} 1.4625, which reacts vigorously with CuI ; the adduct, m. about 70°, decomp. rapidly in air. Heating the product with allyl chloride 1 hr. to 100° in a sealed tube, followed by distn. of the allyl iside, gave 74.3% $CH_2=C(CH_3)P(O)(CH_2CH:CH_2)$, m. 78° (from CaH_2); similarly, $PhCH_2Cl$ (5.5 hrs. at 140-50°) gave $CH_2=C(CH_3)P(O)CH_2Ph$, m. 138-9°, which on hydrolysis with HCl gave $PhCH_2P(O)(OH)_2$, m. 170-1°; $PhCBr$ in boiling CaH_2 (10 min.) gave $CH_2=C(CH_3)P(O)CPh_2$, m. 228-9° (from CaH_2 -

ligroin). Addn. of 22.59 g. allyl alc. to 60 g. $CHMeCH_2CH_2O.PClO$, 31 g. pyridine, and 250 ml. Et_2O with cooling gave 62.6% $MeCH_2CH_2CH_2O.P(O)CH_2CH:CH_2$, b_p 102-3°, n_D^{20} 1.4580, d_4^{20} 1.0777. 1 (9.4 g.) heated with 9 g.

allyl iodide 2 hrs. at 50° after 15 hrs. at room temp., gave

74.4% $\text{MeCH}_2\text{CH}_2\text{CH}_2\text{O.P(O)(CH}_2\text{CH:CH}_2\text{)O}$, b₁ 130-1°, d₄²⁰ 1.1540, n_D²⁰ 1.4680. PbCl_2Cl (7 hrs. at 140-50°)

gave 43.6% crude $\text{MeCH}_2\text{CH}_2\text{CH}_2\text{O.P(O)(CH}_2\text{Ph)O}$, b₁ 180-3°, n_D²⁰ 1.5210, d₄²⁰ 1.1828; on standing the product deposited crystals of the pure product, m. 120° (from C₁₁H₁₂). Addn. of 3.35 g. AcBr in Et₂O to 4.8 g. I in Et₂O with ice cooling gave 51% product, b₁ 142-3°, n_D²⁰ 1.4590, d₄²⁰

1.2544, which appeared to be $\text{MeCH}_2\text{CH}_2\text{CH}_2\text{O.P(O)(Ac)O}$, contaminated with some Br deriv. Addn. of 1 mole S to I

gave a spontaneous reaction and yielded 43% $\text{MeCH}_2\text{CH}_2\text{-}$

$\text{CH}_2\text{O.P(S)(OCH}_2\text{CH:CH}_2\text{)O}$, b₁ 158-60°, n_D²⁰ 1.5025, d₄²⁰ 1.2111. Heating I with EtO₂CCl to 50° 2 hrs. gave a dark, undistillable, halogen-free oil. Addn. of 0.51 g. H₂O to 5 g. I gave a spontaneous reaction and distn. yielded

$\text{MeCH}_2\text{CH}_2\text{CH}_2\text{O.P(OH)O}$, b₁ 130-7°, m. 48-50°, a very hygroscopic solid. G. M. Kosolapoff

ARBUZOV, A. Ye.

From the history of chemistry of phosphorus-organic compounds.
Izv. Kazan. fil. AN SSSR Ser. khim. nauk no. 1:5-20 '50. (MLRA 10:5)
(Chemistry, Organic) (Phosphorus organic compounds)

ARBUZOV, A.Ye.; ALIMOV, P.I.

Condensation products of pyrophosphorous acid esters with
aldehydes. Izv.Kazan.fil.AN SSSR Ser.khim.nauk no.1:21-30

'50.

(MLRA 10:5)

(Pyrophosphorous acid) (Aldehydes)

~~ARBUZOV, A.Ye.~~ ALIMOV, P.I.

Effect of strong mineral acids on certain phosphorus acid esters.
Izv.Kazan.fil.AN SSSR Ser.khim.nauk no.1:39-44 '50. (MLRA 10:5)
(Phosphorus acids)

ARBUZOV, A.Ye.; RAZUMOV, A.I.

Certain esters of allylphosphinic acid. Trudy KKHTI no.15:
3-6 '50 [publ. '51] (MIRA 12:12)
(Phosphinic acid)

CA

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Action of strong mineral acids on some esters of acids of phosphorus A. E. Arbutov and P. I. Alimov (Kazan Univ., U.S.S.R.) *Zh. Fiz. Khim. Akad. Nauk S.S.S.R., Otdel Khim. Nauk* 1951, 268-72. Addn. of 11.76 g. H_2SO_4 to 19.0 g. $(EtO)_2P_2O_5$, with occasional cooling yielded 18.6 g. distillable liquid (SO₂ odor present), which gave unstated amts. of $(EtO)_2POH$, b. 70-15°, n_D^{20} 1.4086, and $(EtO)_3P_2O_5$, b. 88-9°, n_D^{20} 1.4011; the latter probably formed during the heating from $(EtO)_2P_2O_5$; the results are the same when the molar proportions are 2:1. Addn. of 3.14 g. H_2SO_4 to 8.20 g. $(EtO)_2P_2O_5$, with cooling, gave 6.7 g. distillable products and 3.5 g. residue; distn. of the former gave 3.5 g. pure $(EtO)_2POH$ and 1.5 g. $(EtO)_3P_2O_5$. Pure $(EtO)_2PO_3$ (4.9 g.) added to 8.3 g. $(EtO)_2P_2O_5$ did not visibly react, but after short heating to 120° distn. gave 5.1 g. product, b. 45°, identified as $(EtO)_2POH$; extrn. of the residue with H_2O and evapn. of the residual H_2O gave 2.7 g. viscous liquid, whose analysis approximated $(EtO)_2P_2O_5$. Passage of 1.4 g. dry HCl into 9.5 g. $(EtO)_2P_2O_5$ gave 9.8 g. distillable product, sepl. into unstated amts. of $(EtO)_2P_2O_5$, b. 37-8°, n_D^{20} 1.4349, d_4^{20} 1.0816, and $(EtO)_2POH$, b. 70-1°. Passage of 1.7 g. dry HCl into 12 g. $(EtO)_2P_2O_5$ gave 1.7 g. $(EtO)_2P_2O_5$, b. 37-9°, n_D^{20} 1.4346, 1.5 g. $(EtO)_2POH$, b. 69-70°, and 1.5 g. $(EtO)_2P_2O_5$ (l. b. 135-7°, n_D^{20} 1.4108. Addn. of 1.35 ml. H_2O to 25.8 g. $(EtO)_2P_2O_5$ with ice cooling, removal of the HCl by evacuation, at first with ice cooling, finally with slow heating to 85°, gave some unreacted chloride and 8.5 g. l. b. 130-5° (crude), b. 135-7° (pure), n_D^{20} 1.420, d_4^{20} 1.1909, and 3.2 g. undistillable residue. This reaction probably explains the formation of the pyrophosphate in the reaction of HCl with the subphosphate.

G. M. Kosolapoff

ARBUZOV, A. E.

USSR

Mixed anhydrides of carboxylic acids and diethylphosphoric acid. A. E. Arbuzov and P. I. Alimov (Chem. Inst., Kazan). *Izvest. Akad. Nauk. S.S.S.R., Otdel Khim. Nauk* 1951, 409-10.—Addn. of acids to $(EtO)_2P=O$ (I), after an initial temp. rise and further heating at 100-200° for 10 min., gave $(EtO)_2P(OH)$ (II) and mixed anhydrides of the type $RCO_2P(OEt)_2$ (III) which were isolated by vacuum distn. The acid deriv., wts. (g.), of acid, I, and III, and b.p./mm., n_D^{20} , and d_4^{20} of III are: isobutyric, 2.6, 7.5, 1.1, 86-70°/12, 1.4212, 1.0233; butyric (IV), 3.4, 0.8, 2.0; 93.5-4.0°/11, 1.4253, 1.0289; isovaleric (V), 3.8, 9.7, 2.5, 100-1°/11, 1.4268, 1.0078; caproic (VI), 3.6, 7.7, 2.5, 118-10°/11, 1.4310, 0.9917; crotonic, 3.3, 0.4, 103-4°/10, 1.4974, 1.0375; benzoic (VII), 4, 8.8, 0.7, 124-17°/4, 1.4974 (after redistg. b. 102-3°), 1.1193; *o*-toluic, 4.3, 8.2, 3.5, 116°/1, 1.5029, 1.1001. Hydrolysis of the III was highly exothermic; V gave a 1:1 max. azeotropic mixt. of iso-BuCO₂H and II over a range of pressures. Similarly hydrolysis of IV gave PrCO₂H and II which formed a 1:1 max. azeotrope mixt., b., 78-0.5°, n_D^{20} 1.4055. Synthetic equimolar mixts. gave the same const. The hydrolysis product of VII did not form an azeotrope. Addn. of 0.30 g. S to 2.7 g. VI and heating at 120° until all the S dissolved gave $C_6H_5CO_2P(S)(OEt)_2$, b., 109-13°, n_D^{20} 1.4508. The mixed anhydride of AcOH, which was not isolated because of its closeness in b.p. to II (b. 70-1°) was shown to be present in the prepn. mixt. by the exothermic reaction with water and the formation, when warmed with S at 120° of $AcOP(S)(OEt)_2$, b., 93-0°, n_D^{20} 1.4511. Abs. EtOH (1.2 g.) and 0.3 g. VII exothermally deposited crystals of EtOH; distn. of liquid yielded 3.3 g. $(EtO)_2P$, b., 50-3°. CuCl (0.35 g.) partially dissolved in 0.9 g. of V at 163° and from the decanted liquid slowly sepd. crystals of $C_6H_5O_2PCuCl$ which, pressed dry, m. 105-6°. V (0.8 g.) heated with 1 ml. EtI at 135-42° 3 hrs. in a sealed tube gave unchanged EtI; 2.5 g. $C_6H_5CO_2P(O)(OEt)Et$, b., 90-130°, which upon redistg. b. 120-2°, n_D^{20} 1.4312, d_4^{20} 1.0385 (Arbuzov isomerization); and 2.5 g. unidentified product, b., 130-63° (redistd., b. 150-4°, n_D^{20} 1.4382, d_4^{20} 1.0974). C. M. S.

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Organic Chemistry 10

Products of condensation of esters of pyrophosphorous acid with aldehydes. A. B. Arbutov and P. I. Alimov (A. F. Arbuzov Chem. Inst., Kazan). *Izv. Akad. Nauk S.S.S.R., (Dokl. Khim. Nauk 1951, 68) 5.*—Analogously to formation of diacyl derivatives from aldehydes with carboxylic anhydrides, aldehydes with $[(RO)_2P]_2O$ form compounds of the general type $(RO)_2P(O)CH(R)P(O)(OR)_2$. Thus, heating 4 g. AcH and 14.1 g. $[(EtO)_2P]_2O$ (I) in a sealed tube 1 hr. at 110° gave 8.2 g. $(EtO)_2P(O)CHMeP(O)(OEt)_2$ (II), b_p 109–110°, n_D^{20} 1.4381, d_4^{20} 1.091, sol. in org. solvents and H_2O . To 0.2 g. I and 1.73 g. $PrCHO$ was added 1 drop H_2SO_4 , which caused a temp. rise to 37° , and after 10 min. at 100° the mixt. gave 3 g. $(EtO)_2P(O)CHPrP(O)(OEt)_2$, b_p 134–5°, n_D^{20} 1.4390, d_4^{20} 1.0078. Heating 7.4 g. I with 2.75 g. n -butylal 40 min. at 120° gave after 2 distns. 1.3 g. $(EtO)_2P(O)CH(C_4H_9)P(O)(OEt)_2$, b_p 140–8°, n_D^{20} 1.4097, d_4^{20} 1.1090. Similarly 7.5 g. I with 3.1 g. BzH 1 hr. at 120° gave 4.7 g. $(EtO)_2P(O)CHPhP(O)(OEt)_2$, b_p 149–50°, n_D^{20} 1.4885, d_4^{20} 1.1316, sol. in slightly acidified H_2O . p - MeC_6H_4CHO gave the p -tolyl analog, b_p 159–60°, n_D^{20} 1.4890, d_4^{20} 1.1158. On slow addn. of 2.8 g. Cl_2CHCHO to 7.3 g. I heat was evolved (temp. rise to 65°) and after 10 min. at $100–20^\circ$ were obtained 2.5 g. (after several distns.) $(RO)_2P(Cl)CH_2P(O)(OR)_2$, b_p 41–3°, and 3.5 g. $(EtO)_2P(O)C(Cl)CHO$, b_p 127–8°, n_D^{20} 1.4480, d_4^{20}

1.2081, indicating an anomalous reaction course. The latter product was also obtained, a proof of its structure, in 7.2 g. yield by slow addn. of 7.4 g. $(RO)_2P$ to 0.6 g. Cl_2CHCHO , followed by heating 10 min. at $120–40^\circ$; the product b_p 120–7°, n_D^{20} 1.4490, d_4^{20} 1.2081. No reaction took place between this product and I. I also failed to react with $MgCO$. II boiled 6 hrs. with 10% HCl , then briefly with $HgCl_2$, gave 95.20% $HgCl_2$. Similarly the $(EtO)_2P(O)CHPhP(O)(OEt)_2$ (III) gave 90.4% $HgCl_2$; hydrolysis of the BzH deriv. 6 hrs. at reflux with 10% HCl , followed by repeated evapn. with H_2O , soln. of the residue in K_2CO_3 , evapn., and crystn. from $AcOH-C_6H_6$, gave $PhCH(OH)P(O)(OH)_2$, $m.$ 172–3°, confirming the structure. Heating II (5.1 g.) with 1 ml. HCl in a sealed tube 4 hrs. at 140° gave 3 g. $(EtO)_2P(O)CHMeOP(O)(OEt)_2$, b_p 132–3°, n_D^{20} 1.4890, d_4^{20} 1.1290, sol. in org. solvents and H_2O . Similarly III in 2 hrs. at $120–45^\circ$ gave $(EtO)_2P(O)CHPhOP(O)(OEt)_2$, b_p 176–7°, n_D^{20} 1.4894, d_4^{20} 1.1624, in almost 100% yield. II reacts with $(CuX)_2$ with evolution of heat, but the adducts could not be isolated. G. M. K.

Benzyl esters of ethylene glycol, trimethylene glycol, and 1-methyltrimethylene glycol phosphites and their transformations. A. S. Arbutov and V. M. Zornitsina (Kazan State Univ.) *Izv. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1951, 830-43; cf. *ibid.* 1946, 220; *C.I.* 42, 4032g. (C₁₁H₁₆O₄PCl) (52.3 g.), 50 g. PhNMe₂, 200 ml. 1:1 CCl₄-C₆H₆ and a few crystals of PhNMe₂·HCl were treated with stirring and ice-cooling with 44.68 g. PhCH₂OH over 1 hr.; nitration gave 40.5 g. O.C₁₁H₁₆O₄POC₆H₄Ph (I), viscous

oil, b_p 120-20.5°, d₄²⁰ 1.2122, n_D²⁰ 1.5315. I (11.7 g.) and 10.1 g. PhCH₂Br, heated 5 hrs. at 100° in a sealed tube and the unreacted RBr evapd., gave 5.3 g. (45.3%) O.C₁₁H₁₆O₄Ph.

O.C₁₁H₁₆O₄Ph, m. 123° (from C₆H₆-ligroine), which

with 20% HCl gave PhCH₂P(O)(OH)₂, m. 170-1°. Similarly 9 g. I and 2.25 g. PhCH₂Cl in 12 hrs. at 100° gave 1.8 g. (25%) product identical with the above, b_p 192°, m. 121°, and much material undistillable at 246° (bath temp.) and 3 mm., contg. halogen. Likewise, 0.92 g. I and 1.51 g. Ph₂CHBr in 3 ml. CCl₄ refluxed 0.5 hr. gave on evapn. and abdn. of ligroine 0.45 g. (27%) O.C₁₁H₁₆O₄P(O)CPh₂.

m. 201-4° (from C₆H₆-ligroine), hydrolyzed with 20% HCl in 5 hrs. at 100° to Ph₂CHP(O)(OH)₂, m. 274-5°; much undistillable halogen-contg. material remained after the reaction. Aqdn. of 0.9 g. slightly acidified H₂O to 9.0 g. I, with the temp. kept at 60-5° gave, on distn., 1.2 g. PhCH₂OH and 3.5 g. viscous product, b_p 110-3.5°, n_D²⁰ 1.4035, which on standing sepd. into viscous and mobile layers. I (7.4 g.) in 10 ml. Et₂O with A. Br gave after distn. only 3.2 g. (50.1%) PhCH₂Br and the residue decoupled, on attempted distn.; reaction of PhCH₂OH with CH₂CH₂O₄PCl, similar

to that described above gave 30% O.C₁₁H₁₆O₄Ph.

CH₂Ph (II), b_p 147-8°, d₄²⁰ 1.1873, n_D²⁰ 1.5270, which reacts with CuI and *explodes* on contact with HNO₃. II (0.6 g.) and 4 g. PhCH₂Cl after 4 hrs. in a sealed tube at 110-100° gave on cooling 2 g. (30.3%) O.C₁₁H₁₆O₄Ph.

O.C₁₁H₁₆O₄Ph, m. 138° (from C₆H₆-ligroine), identical with a specimen previously prepd. from O.C₁₁H₁₆O₄POMe;

the residue from the isolation of this polymerized to undistillable matter on attempted distn. Similarly Ph₂CHBr in hot CCl₄ gave PhCH₂Br, and on cooling and abdn. of ligroine, 37% O.C₁₁H₁₆O₄Ph; O.C₁₁H₁₆O₄Ph, m. 228° (from

C₆H₆-ligroine), identical with the product of a similar reaction with O.C₁₁H₁₆O₄P(O)CPh₂·H₂O (0.4 g.) re-

acted vigorously with 0.70 g. H₂O contg. a little HCl and on distn. gave 2.75 g. (57.5%) PhCH₂OH and 4.1 g. impure acid, b_p 130-6°, that had been obtained previously by hydrolysis of O.C₁₁H₁₆O₄POMe; the rest of the ma-

terial was an undistillable polymer. Similarly 26.85 g.

PhCH₂OH and 38.4 g. CH₂CH₂CHMe.O.PClO in the presence of PhNMe₂ gave 53.3% CH₂CH₂CHMe.O.P.

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Organic Chemistry - 10

Preparation and properties of esters of [bicyclohexyl]-1,1'-diol phosphorous acid. A. R. Arbatov and M. M. Aramovskaya (Kazan State Univ.). *Izvest. Akad. Nauk S.S.S.R., (Otdel. Khim. Nauk 1951, 544-50)*; cf. preceding abstr. To 10.7 g. [bicyclohexyl]-1,1'-diol (I), 1.01 g. PhNMe₂ and 20 ml. dry C₆H₆ was slowly added with cooling 7.4 g. PCl₃ and the mixt. was stirred 20 min. at 70°; after filtration and concn. *in vacuo*, distn. of the product was impossible because of decompn.; removal of the solvent causes the product to crystallize, yielding [bicyclohexyl]-1,1'-diol phosphonate, m. 65-75°, a very active compd. which could not be recrystd. Addn. of 8.9 g. MeOPCl₂ to 43.2 g. I and 10.5 g. pyridine in C₆H₆, filtration, and concn. gave Me [bicyclohexyl]-1,1'-diol phosphite (II), m. 55-65°, which has an odor similar to that of (MeO)₂P; it cannot be recrystd. as momentary exposure to air causes it to liquefy and to resolidify in a few min. because of hydrolysis. Similarly, 11.1 g. I, 8.8 g. pyridine, and 8.2 g. P(O)Cl₂ gave 3.8 g. (25%) Et [bicyclohexyl]-1,1'-diol phosphite (III), bp 163.5-5.0°, d₄²⁰ 1.0852, n_D²⁰ 1.4871, n_F²⁰ 1.4000. Similarly P(O)Cl₂ gave 25.0% Pr analog, bp 177.0°, d₄²⁰ 1.0802, d₄²⁰ 1.0711, d₄²⁰ 1.0730, n_D²⁰ 1.4870, n_F²⁰ 1.4000. Similarly MeOPCl₂ gave 20.5% Bu analog,

bp 186.8°, d₄²⁰ 1.0610, d₄²⁰ 1.0605, n_D²⁰ 1.4618. II (2.6 g. with 0.18 g. H₂O) evolved much heat and filtration after 2 hrs. gave [bicyclohexyl]-1,1'-diol II phosphite, m. 92-2.5° (from ligroine), sol. in the usual solvents; the Bu ester with slightly acidified H₂O hydrolyzed similarly. Boiling II (4 g.) in C₆H₆ with 1.2 g. Ph₃CBr 1.5 hrs. gave MeEt and concn. yielded [bicyclohexyl]-1,1'-diol triphenylmethoxyphosphonate, m. 105.5-0.5° (from ligroine), also formed from the Bu ester. II refluxed 1.5 hrs. with PhCH₂Br in C₆H₆, concn., and Et₂O added gave [bicyclohexyl]-1,1'-diol *o*-toluenephosphonate, m. 143.5-4.0° (from ligroine). Similarly BrCl gave the *o*-*ortho*-toluenic analog, m. 173.5-4.5° (from ligroine). In all the above reactions the cyclic structure of the ester is preserved. II (1 g.) with 0.13 g. S in hot C₆H₆ gave after 10 min. on a steam bath and concn., 72.7% Me [bicyclohexyl]-1,1'-diol thiophosphite, m. 145.5-10.2° (from MeOH); III gave the Et analog, m. 65.6° (from petr. ether), while the Pr analog, prepd. similarly, m. 50.5-2.0° (from petr. ether).

G. M. Kowaloff

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USSR/Chemistry - Organophosphorus Compounds May/June 51

"Action of Strong Inorganic Acids on Some Esters of Phosphorus Acids," A. Ye. Arbuzov, P. I. Alimov, Chem Inst Imeni Acad A. Ye. Arbuzov, Kazan' Affiliate, Acad Sci USSR

"Iz Ak Nauk SSSR, Otdel Khim Nauk," No 3, pp 268-272

Sulfuric or phosphoric acid, similarly to HCl, splits triethylphosphite into diethylphosphorous acid and ethyl ester of the inorganic acid. Action of HCl on tetraethyl pyrophosphite results in formation of diethylphosphorous acid and diethylphosphorous acid

LC

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USSR/Chemistry - Organophosphorus Compounds (Contd) May/June 51

chloride. Action of HCl on tetraethyl hypophosphate results either in formation of diethylphosphoric acid chloride (I) and diethylphosphorous acid (II) or of diethylphosphoric acid (III) and diethylphosphorous acid chloride (IV). Following products of this reaction were isolated: II, IV, and tetraethyl pyrophosphate (V). V is product of secondary reaction between I and III.

LC

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ARBUZOV, A. YE.

PA192T21

USSR/Chemistry - Organophosphorus Compounds Jul/Aug 51

"Combined Anhydrides of Carboxylic Acids and Diethylphosphorous Acid," A. Ye. Arbutov, P. I. Alimov, Chem Inst Imeni Acad A. Ye. Arbutov, Kazan' Affiliate, Acad Sci USSR

"Iz Ak Nauk SSSR, Otdel Khim Nauk" No 4, pp 409-416

Action of isobutyric, butyric, isovaleric, crotonic, capronic, benzoic, p-toluylic acids on (EtO)₂P-O-P(EtO)₂ yielded combined anhydrides of type RCOOP(OEt)₂ prepd for the 1st time, which

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USSR/Chemistry - Organophosphorus Compounds (Contd) Jul/Aug 51

react in the manner of acid anhydrides. Under action of EtI, they form by Arbutov reaction isomers contg P5+ atom (phosphonic acid-carboxylic acid anhydrides) and high-boiling substances of undetd structure.

192T21

PA 197T5

ARBUZOV, A. YE.

USSR/Chemistry - Organophosphorus Compounds Nov/Dec 51

"Regarding Some Esters of Allylphosphonic Acid,"
A. Ye. Arbutov, A. I. Razumov, Lab of Org Chem,
Kazan' Chem Technol Inst

"Iz Ak Nauk SSSR, Otdel Khim Nauk" No 6, pp 714-716

Synthesized for 1st time methyl and isopropyl esters of allylphosphonic acid. Established the best conditions for prep of the methyl ester. Found that method of prep allylphosphonic esters from salts of dialkylphosphorous acids by reacting them

197T5

USSR/Chemistry - Organophosphorus Compounds (Contd) Nov/Dec 51

with R'Hal is of no advantage as compared with the isomerization of trialkyl phosphites, e.g., trialkyl phosphite plus allyl chloride. The 1st method often does not lead to the desired products.

197T5

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APPROVED FOR RELEASE: 06/05/2000

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analysis of 12.3 g. Me_2P_2OPh gave 2 g. PhI and a liquid,
b.p. 186-220°, which solidified and m.p. 134°. In $MeOH$,
the undistillable part gave 2.45 g. Me_2P_2O (m.p. 151° from
 $EtOH-Et_2O$).

G. M. Kosolapoff

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ARBUZOV, A. Ye

191T9

USSR/Chemistry - Organophosphorus Sep/Oct 51
Compounds

"Organic Derivatives of the Acids of Phosphorus,"
A. Ye. Arbuzov, Kazan'

"Uspekhi Khim" Vol XX, No 5, pp 521-532

Gives general review of foreign and Russian
work on subject, with particular emphasis on
results of his own work. Discusses latest data
on Arbuzov rearrangement, the constitution of
Boyd's acid chloride, etc.

191T9

ARBUZOV A.

Reaction of diene hydrocarbons with nitroso compounds.
 Catalytic reduction of 2-phenyl-3,6-dihydro-1,2(2H)-oxazine
 and 4-phenylamino-2-buten-1-ol. Yu. A. Arbuзов.
 Doklady Akad. Nauk S.S.S.R. 76, 681-1 (1951); cf. C. I.
 43, 680c. —Passing 110 g. ($C_{11}H_{12}$) into 107.1 g. ice-
 cooled $PhNO$ in 1 l. $CHCl_3$, letting stand overnight, and
 distg. gave 164 g. 2-phenyl-3,6-dihydro-1,2(2H)-oxazine, b.
 108-9°, m. 50-1° (from MeOH); 32.2 g. of this, hydro-
 genated in cyclohexane over 3 g. Pt-C at room temp. took
 up 4600 ml. H_2 and gave 25.4 g. tetrahydro compd., b. 101-5°,
 d_4^{20} 1.0593, n_D^{20} 1.5550. This (10.3 g.) in 200 ml. AcOH was
 treated in 4 portions with 40 g. Zn, dust with shaking, 200
 ml. H_2O and 200 g. NaOH added, the mixt. steam-distd. and
 the filtered disto. residue extd. with CaH_2 ; the ext. yielded
 7.7 g. 4-phenylamino-1-butanol (I), b. 151-5°, d_4^{20} 1.0488,
 n_D^{20} 1.5636; acid oxalate, decomp. 124.5-5.0° (from MeOH).
 Hydrogenation of $PhNHCN=CH-CH_2OH$ in Et_2O at
 room temp. over Pt-C yielded BuOH, $PhNH_2$, $PhNH_2H_2$,
 b.p. 95-6°, d_4^{20} 0.9904, n_D^{20} 1.5393 (Bz deriv., m. 19-51°),
 and 17% I, identical with the above, b.p. 147.8°, d_4^{20}
 1.0101, n_D^{20} 1.5633.

G. M. Kosolupov

ANBUZOV, Aleksandr Yerminingel'Dovich.

Izbrannyye Trudy (Selected Works) Moskva, Izd-vo Akademii Nauk SSSR, 1952.
755 P. Diagr., Ports., Tables.
"Literatura" At End Of Chapters.
At Head of Title: Akademiya Nauk SSSR.

SO: N/5
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Ninety years of the theory of chemical structure (proposed by) A. M. Butlerov. A. E. Arbuzyov (Kazan State Univ.). *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1952, 3-13.—Historical review with Butlerov's portrait
G. M. Kosolapoff

ARBUZOV, A. E.

Chemical Abst.
Vol. 48 No. 9
May 10, 1954
Organic Chemistry

③ Chem
Tautomerism of isatin, M. E. Arbutov and M. Sh.
Babanova. *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.*
1952, 443-51 (Engl. translation).—See C.A. 47, 4876a.
H. L. H.

11-9-51

ARBUZOV, A. E.

Chemical Abst.
Vol. 48 No. 8
Apr. 25, 1954
Organic Chemistry

Substituted amides of cyclic esters of phosphorous acid. *(2) Chem*
A. E. Arbuзов and V. M. Zaslavskaya. Bull. acad. sci.
U.S.S.R. Div. Chem. Sci. 1952, 713-21 (Engl. translation).
See C.A. 47, 10461c.
H. L. H.

11-11-54
mly

ARBUZOV, *Chemical Abstr.*
A. E. Vol. 48 No. 8
Apr. 25, 1954
Organic Chemistry

Derivatives of phosphorous acid that contain the cyclo-
hexyl radical. A. B. Arbuзов and P. G. Valtova. *Bull.*
acad. sci. U.S.S.R., *Classif. sci. chim.* 1952, 722-B (Engl.
translation).—See C.A. 47, 10402c.
H. L. H.

(2) chem

11-11-54
ml

ARBUZOV, A. E.

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Chemical Abst.
Vol. 48 No. 8
Apr. 25, 1954
Organic Chemistry

@ chem

Complex compounds of esters of phosphorous acid. I.
Compounds with salts of copper, silver, and gold. A. E.
Arbuzov and V. M. Zornastroya, *Bull. acad. sci. U.S.S.R.,
Chem. ser. chim.* 1952, 729-35 (Engl. translation). See
C.A. 47, 9698a. II. Complex compounds with salts of
bivalent platinum. *Ibid.* 737-42. See C.A. 47, 9699a.
III. Complex compounds with mercury salts. *Ibid.* 743-
6. See C.A. 47, 9600a.
H. L. H.

11-11-54
MEF

HRBUDOV, A. E.

Chemical Abst.
Vol. 48 No. 8
Apr. 25, 1954
Organic Chemistry

The tautomerism of derivatives of carbonyl A. I.
Abstracts of the Journal of Biological Chemistry
1954, Vol. 194, No. 1, pp. 1-10
C.A. 47: 11106A H. L. H. L.

ARBUZOV, A. E.

Chemical Abst.
Vol. 48 No.8
Apr. 25, 1954
Organic Chemistry

4 11
Action of alkyl halides on the sodium, potassium, and silver salts of dialkyl phosphorous acids. A. E. Arbuзов and O. M. Shanshinskaya. Bull. acad. sci. U.S.S.R., Classe sci. chim. 1952, 765-8 (Engl. translation). See C.A. 48, 650d. H. L. H.

11-11-54
msf

ARBUZOV, A.Ye.; ZOROASTROVA, V.M.

Esters of glycol-phosphorous acids. I. Compounds containing 5-, 7-, and 8-member rings. Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk '52, 770-8. (CA 47 no.19:9900 '53) (MLRA 5:11)

1. Kazan State Univ.

ARBUZOV, A.Ye.; ZOROASTROVA, V.M.

Esters of glycol-phosphorous acids. II. Compounds with 6-member ring.
Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk '52, 779-88. (MLRA 5:11)
(CA 47 no.19:9901 '53)

ARBUZOV, A.Ye.; ZOROASTROVA, V.M.

Complex compounds of esters of phosphorus acid. I. Compounds with salts of copper, silver, and gold. Izvest. Akad. Nauk S.S.S.R., Otdel Khim. Nauk '52, 809-17. (MLRA 5:11)
(CA 47 no.19:9898 '53)

1. Kazan State Univ.

ARBUZOV, A.Ye.; ZOROASTROVA, V.M.

Complex compounds of esters of phosphorus acid. II. Complex compounds
with salts of bivalent platinum. Izvest. Akad. Nauk S.S.S.R., Otdel Khim.
Nauk '52, 818-25. (MLRA 5:11)
(CA 47 no.19:9899 '53)

ARBUZOV, A.Ye.; ZOBOASTROVA, V.M.

Complex compounds of esters of phosphorus acid. III. Complex compounds
with mercury salts. Izvest. Akad. Nauk S.S.S.R., Otdel Khim. Nauk '52,
826-30. (MLRA 5:11)
(CA 47 no.19:9900 '53)

ARBUZOV, A.Ye.; BASTANOVA, M.Sh.

Tautomerism of derivatives of carbostyryl. Izvest. Akad. Nauk S.S.S.R.,
Otdel Khim. Nauk '52, 831-41. (MIRA 5:11)
(CA 47 no.21:11196 '53).

1. S.M. Kirov Chem.-Technol. Inst., Kazan.

ARBUZOV, A.E.

Chem Abstr V48
1-25-54

Organic Chemistry

Action of alkyl halides on the sodium, potassium, and silver salts of dialkyl phosphorous acids. A. E. Arbuzov and M. Shamsaevskaya (S. M. Kirov Chem. Technol. Inst., Kazan). *Izv. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1952, 842-6; cf. *Trudy Kazansk. Khim. Tekh. Inst.* 1949, 10. — EtBr or EtI with $(EtO)_2P(S)ONa$ or the K or Ag salts yielded only $(EtO)_2PS$, although in different yields. (For prepn. of the above salts from $(RO)_2POM$ and S, cf. above ref.). No reaction took place in Et_2O between $(EtO)_2P(S)ONa$ and EtBr; $(EtO)_2P(S)OK$ and EtBr, and $(EtO)_2P(S)OAg$ and EtI. Addn. of 25 g. $(EtO)_2POH$ to 4.1 g. Na in Et_2O , warming until all the Na had reacted (2.5 g. ester had to be added in excess for this purpose), followed by 5 g. S in C_6H_6 , and the yellow mixt. let stand overnight, gave a white ppt.; addn. of 31.6 g. EtI in Et_2O , and the soln. refluxed for several hours,

K in Et_2O , warming until the soln. was complete, then addn. of 5.70 g. S in C_6H_6 , and the mixt. refluxed for an unstated period gave a colorless ppt.; this mixt. refluxed for unstated period with 28.2 g. EtI in C_6H_6 gave 43 g. ppt., while distn. of the filtrate gave 1.5 g. (4.2%) I, bp 115-16°, n_D 1.4523. The $(EtO)_2P(S)OK$ (43 g. isolated from a previous expt., above) taken up in abs. EtOH treated with EtI, a white ppt. formed, refluxed 4 hrs., and let stand overnight, yielded 14.5 g. KI, with 4.5 g. addnl. after concn.; addn. of Et_2O gave 3.2 g. unreacted $(EtO)_2P(S)OK$; the filtrate, distd., gave 17 g. (35.2%) I, bp 111°, n_D 1.4520. To 3.2 g. $(EtO)_2P(S)OK$ in abs. EtOH was added an excess of EtBr (white ppt. formed); the mixt. filtered, the filtrate, refluxed 4 hrs., gave 55.8% I, bp 118°, n_D 1.4520. Refluxing a suspension of 4.5 g. $(EtO)_2P(S)OAg$ two hrs., or more in Et_2O with 2.5 g. EtI gave no reaction. When enough abs. EtOH was added to the mixt. to dissolve the salt, reheating the brown soln. gave entirely different results; the soln. lost color and gave a yellow ppt. of AgI.

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ARBUZOV, A. YE.

USSR/Chemistry - Theory of Structure

Jan 52

"A. M. Butlerov's Theory of Chemical Structure,"
Acad A. Ye. Arbutov

"Priroda" No 1, pp 15-24

Reviews history of modern theories of org structure. Points out that Gerard's multiple formulas for every org compd, used depending on the type of action, were superseded by Butlerov's concept of a unique formula for every compd. States further that Butlerov emphasized the mutual influence of atoms in a mol and the effect which this influence

211736

has on reactivity. Criticizes resonance theory on the ground that it does not consider complete mols in interpreting complex chem phenomena, but relates these phenomena to the motion of elementary particles. In order to illustrate the futility of resonance theory, says that calcn of all resonance structures of one of the penta, hexa, or heptacyclic cancerogens of the type synthesized by USSR chemists would require a year's work by a special office organized for that purpose.

211736

USSR/Chemistry - Organo-Phosphorus Compounds May/June 52

"The Chloride of 1,2-dithiolethanephosphorous Acid and Its Derivatives," A. Ye. Arbutov, V. M. Zorostrova, Sci Res Inst of Chem Imeni A. M. Butlerov, Kazan State U Imeni V. I. Ulyanov-Lenin

"Tr Ak Nauk, Otdel Khim Nauk" No 3, pp 453-458

The cyclic chloride of dithiolethanephosphorous acid was synthesized by the action of PCl₃ on 1,2-dithioethane. Esters of this acid were synthesized both by the action of alc on the acid

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chloride in presence of pyridine, and by the action of Menshutkin's acid chloride on dithioethane. The esters react with allyl halides (methyl iodide, triphenylbromoethane). The structure of these reaction products was not established.

ARBUZOV, A. Ye.

22079

ISSR/Chemistry - Isatin

May/Jun 52

"The Question of Tautomerism of Isatin," A. Ye. Arbutov, M. Sh. Bastanova, Kazan' Chem-Techinol Inst Imeni S. M. Kirov

"Iz Ak Nauk, Otdel Khim Nauk" No 3, pp 459-469

Sodium and silver derivs of isatin when treated with bromo-, and chloro-methyl, -methylene, -methyl, and -methylpropyl ethers yield the corresponding isatin esters. All of them are easily saponified. In saponification of methoxymethyl, ethoxymethyl, and propoxymethyl isatin esters, isatin, formaldehyde, and the corresponding alcs are obtained in almost quant

220710

yields. Sodium and silver derivs of isatin, treated with p-benzhydryltetraphenyl bromomethane, benzyl bromide or chloride, or p-xylyl bromide, yield benzyl isatin, p-xylyl isatin, and diphenyl-p-tri-phenylmethylphenylmethyl isatin. Attempts to saponify these products were not successful; the reactions reversed themselves. The structure of the products was not detd. Methyl iodide and ethoxymethyl upon reacting with methoxymethyl products. Benzyl derivs of isatin form high-melting products. Benzyl isatin does not change in presence of methyl iodide and benzyl bromide.

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ARBUZOV, A. Ye.

ARBUZOV, A. Ye.

Chemists

"Butlerov." Reviewed by A. Ye. Arbuzov. Znan. sila. no. 4 (1952)

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9. Monthly List of Russian Accessions, Library of Congress, August 1954. Unclassified.

ARBUZOV, A.Ye.

Egor Egorovich Vagner. Trudy Inst.ist.est. 4:46-61 '52. (MLBA 6:7)
(Vagner, Egor Egorovich, 1849-1903)

1. A.YE. ARBUZOV

2. USSR (600)

4. Arbuzov, Aleksandr Erminingel' Dovich, 1877

7. General meeting of the Section of Chemical Sciences of the Academy of the U.S.S.R. dedicated to the 75th birthday of Acad. A. Ye. Arbuzov. Izv. AN SSSR, Otd. khim, nauk no. 6. 1952.

9. Monthly List of Russian Accessions, Library of Congress, April 1953, Uncl.

ARBUZOV, A.Ye., akademik; SHAPSHINSKAYA, O.M.

Some derivatives of isatin and instances of tautomerism.
Trudy KKhTI no.16:11-15 '51 [Publ. '52]. (MIRA 12:12)
(Isatin) (Tautomerism)

ARFUZOV, A. Ye., Acad.

Nikolay Nikolayevich Zinin. Nauka i zhizn' 19 no. 8, 1952.

SO: MLRA, November 1952

"Ninety years of the theory on chemical structure discussed by A. M. Butlerov. Tr. from the Russian."
Chemicke Zvesti, Bratislava, Vol 6, No 9/10, Nov./Dec. 1952, p. 597

SO: Eastern European Accessions List, Vol 3, No 10, Oct 1954, Lib. of Congress

232T14

ARBURZOV, A. Ye.

USSR/Chemistry - Organophosphorus Compounds Sep 52

"The Action of Triarylboromethanes on Alkylpyrocatechol Esters of Phosphorous Acid," A. Ye. Arburzov, F. G. Vallimov, Kazan' Chem-Tech Inst

"Zhur Obshch Khim" Vol 22, No 9, pp 1479-1483

By treating the ethylpyrocatechol ester of phosphorous acid with triphenylboromethane, diphenylbiphenylboromethane, phenyldibiphenylboromethane, phenylxanthylboromethane, and dimethane, phenylxanthylboromethane, the corresponding phenylmethylboromethane, the corresponding

232T14

pyrocatechol esters of triarylmethylphosphonic acids were obtained. Saponification of the pyrocatechol esters of triarylmethylphosphonic acids leads to the formation of the corresponding triarylmethylphosphonic acids. The above pyrocatechol esters of triarylmethylphosphonic acids are identical in physicochem properties with those obtained from Boyd's acid chloride.

232T14

ARBUZOV, Vol. 48 No. 8
A. E. Apr. 25, 1954
Organic Chemistry

(2) ~~Chem~~
Action of triaryl bromomethanes on alkyl pyrocatechyl
esters of phosphorus acid. A. E. Arbutov and P. G.
Valitova. *J. Gen. Chem. (U.S.S.R.)* 22, 1523-7 (1952)
(Engl. translation).—See *C.A.* 47, 9200a. H. L. H.

11-11-54
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1. ARBUSOV' A. Ye., Acad.
2. USSR (600)
4. Chemists
7. Outstanding Russian chemists (140th anniversary of N. N. Zinin's birth),
Priroda, 41, No. 12, 1952.

9. Monthly List of Russian Accessions, Library of Congress, March, 1953. Unclassified.

ARBUZOV, A. Ye.

USSR/Chemistry - Organophosphorus Com-
pounds 1 Apr 52

"Study of the Phosphorus-Containing Members of the
Products of the Reaction in Which Free Radicals Are
Obtained by the Method of A. Ye. and B. A. Arbutov,"
A. Ye. Arbutov, F. G. Valtova

"Dok Ak Nauk SSSR" Vol 83, No 4, pp 577-580

Among the products of the reaction of triphenylbromo-
methane with sodium diethylphosphite, the presence of
subphosphoric acid ester was established. Its pres-
ence was proved by converting it to benzylphosphonic

23419

and triphenylmethylphosphonic acids by means of ben-
zyl bromide and triphenylbromomethane. A cryst compd
of cuprous bromide with the ethyl ester of pyrophos-
phoric acid was obtained as a result of the reaction
of the copper salt on esters of subphosphoric acid.

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