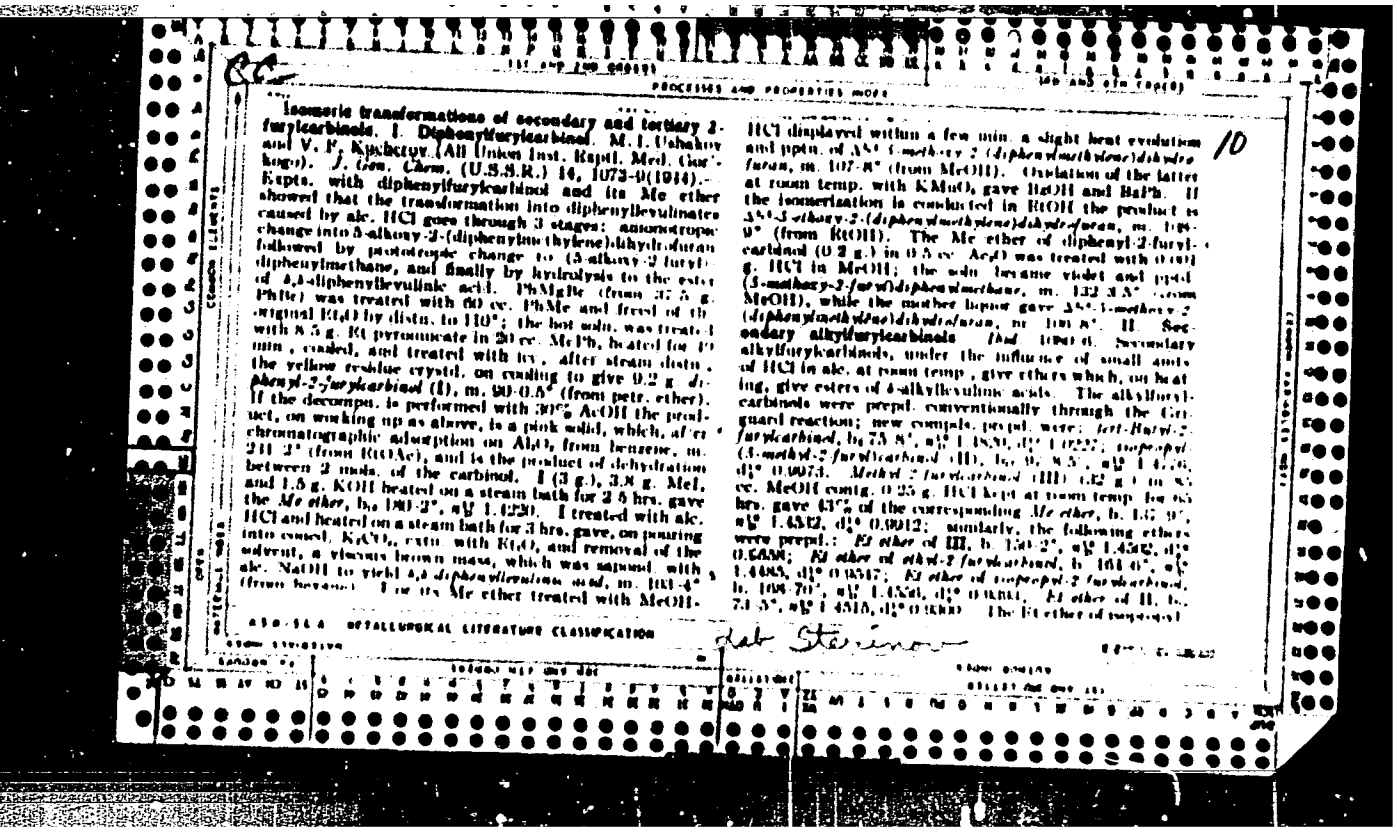
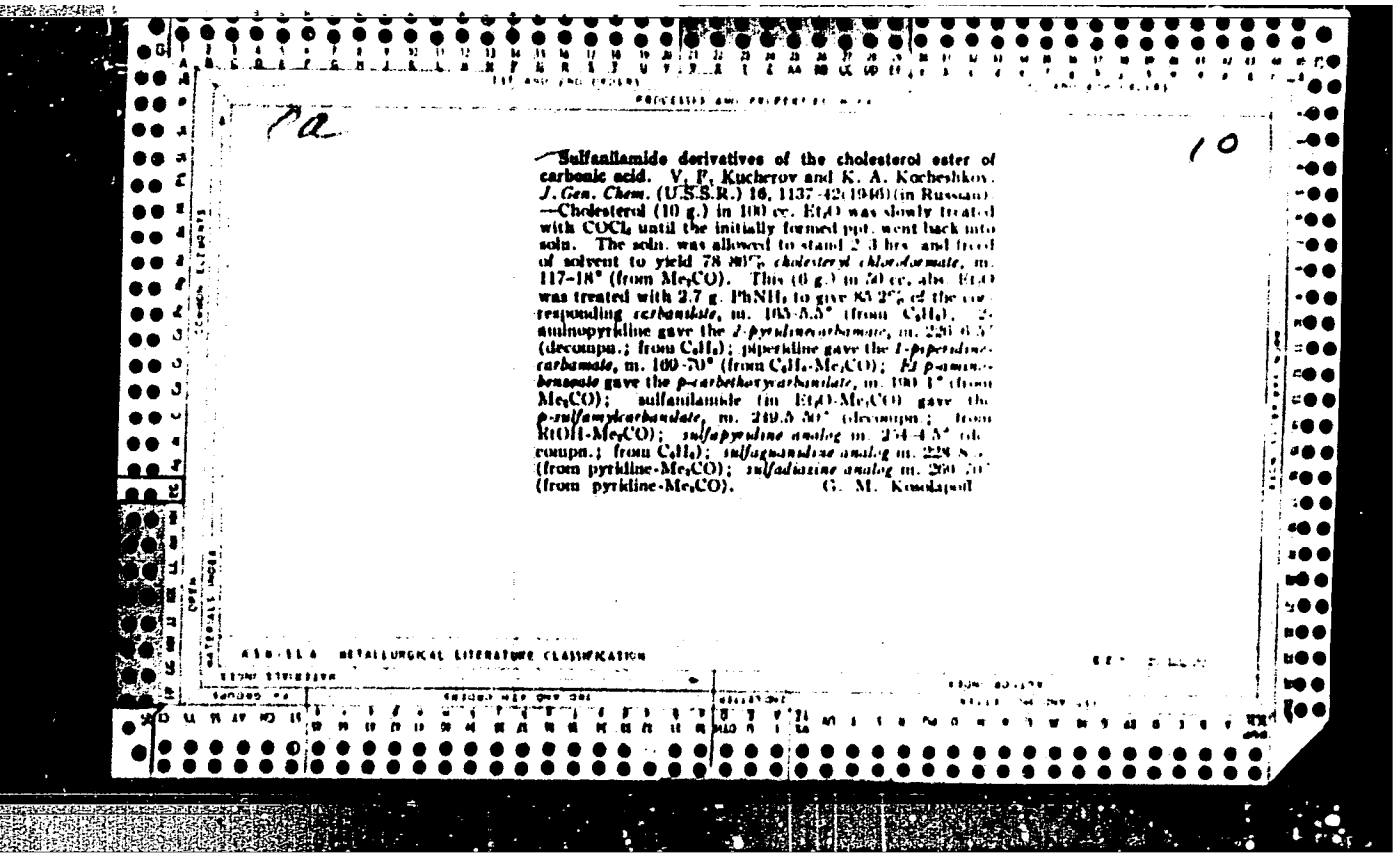
Reel # 271

Kucherov, V.F.



Isomeric transformations of secondary and tertiary 2-furylcarbinols. I. Diphenylfurylcarbinol. M. I. Ushakov and V. F. Kucherov. (All Union Inst. Rapid. Med. Chemicals). *J. Gen. Chem.* (U.S.S.R.) 16, 1073-9(1944).—Reacts. with diphenylfurylcarbinol and its Me ether showed that the transformation into diphenyllevulinates caused by alc. HCl goes through 3 stages: anomeotropic change into 5-ethoxy-2-(diphenylmethylene)-dihydrofuran followed by prototropic change to (5-ethoxy-2-furyl)-diphenylmethane, and finally by hydrolysis to the ester of 4,4-diphenylevulinic acid. PhMgBr (from 37.5 g. PhBr) was treated with 60 cc. PhMe and freed of the original Et$_2$O by distn. to 110°; the hot soln. was treated with 8.5 g. 2-furoylacetic acid in 20 cc. MePh, heated for 10 min., cooled, and treated with ice, after steam distn. the yellow residue crystd. on cooling to give 9.2 g. *diphenyl-2-furylcarbinol* (I), m. 99-0.5° (from petr. ether). If the decompn. is performed with 30% AcOH the product, on working up as above, is a pink solid, which, after chromatographic adsorption on Al$_2$O$_3$ from benzene, m. 211.2° (from EtOAc), and is the product of dehydration between 2 mols. of the carbinol. I (3 g.), 3.8 g. MeI, and 1.5 g. KOH heated on a steam bath for 2.5 hrs. gave the *Me ether*, b$_6$ 180-2°, n_D^{25} 1.6220. I treated with alc. HCl and heated on a steam bath for 3 hrs. gave, on pouring into concd. K$_2$CO$_3$, ppts. with Et$_2$O, and removal of the solvent, a viscous brown mass, which was aspirated with alc. NaOH to yield 4,4-*diphenylevulinic acid*, m. 103-4° (from benzene). For its Me ether treated with MeOH-HCl dissolved within a few min. a slight heat evolution and ppts. of 5-*methoxy-2-(diphenylmethylene)-dihydrofuran*, m. 107-8° (from MeOH). Oxidation of the latter at room temp. with KMnO$_4$ gave MeOH and BzPh. If the isomerization is conducted in MeOH the product is 5-*ethoxy-2-(diphenylmethylene)-dihydrofuran*, m. 129-9° (from MeOH). The Me ether of diphenyl-2-furylcarbinol (0.2 g.) in 0.5 cc. AcOH was treated with 0.01 g. HCl in MeOH; the soln. became violet and ppted. (5-*methoxy-2-furyl*)*diphenylmethane*, m. 132-3.5° (from MeOH), while the mother liquor gave 5-*methoxy-2-(diphenylmethylene)-dihydrofuran*, m. 108-9°. II. **Secondary alkylfurylcarbinols** *Ibid* 1080-6. Secondary alkylfurylcarbinols, under the influence of small amts. of HCl in alc. at room temp., give ethers which, on heating, give esters of 4-alkylevulinic acids. The alkylfurylcarbinols were prepd. conventionally through the Grignard reaction; new compds. prepd. were: *tert-Butyl-2-furylcarbinol*, b$_{12}$ 75.8°, n_D^{25} 1.4830, d_4^{25} 1.0227; *isopropyl-(5-methyl-2-furyl)carbinol* (II), b$_{12}$ 90, 93.5°, n_D^{25} 1.4766, d_4^{25} 0.9973. *Methyl-2-furylcarbinol* (III) (82 g.) in 85 cc. MeOH contg. 0.25 g. HCl kept at room temp. for 65 hrs. gave 43% of the corresponding *Me ether*, b. 137.9°, n_D^{25} 1.4532, d_4^{25} 0.9912; similarly, the following ethers were prepd.: *Et ether of* III, b. 150.2°, n_D^{25} 1.4532, d_4^{25} 0.9458; *Et ether of ethyl-2-furylcarbinol*, b. 161.6°, n_D^{25} 1.4485, d_4^{25} 0.9567; *Et ether of isopropyl-2-furylcarbinol*, b. 168-70°, n_D^{25} 1.4521, d_4^{25} 0.9311; *Et ether of* II, b. 73.5°, n_D^{25} 1.4510, d_4^{25} 0.9369. The Et ether of isopropyl



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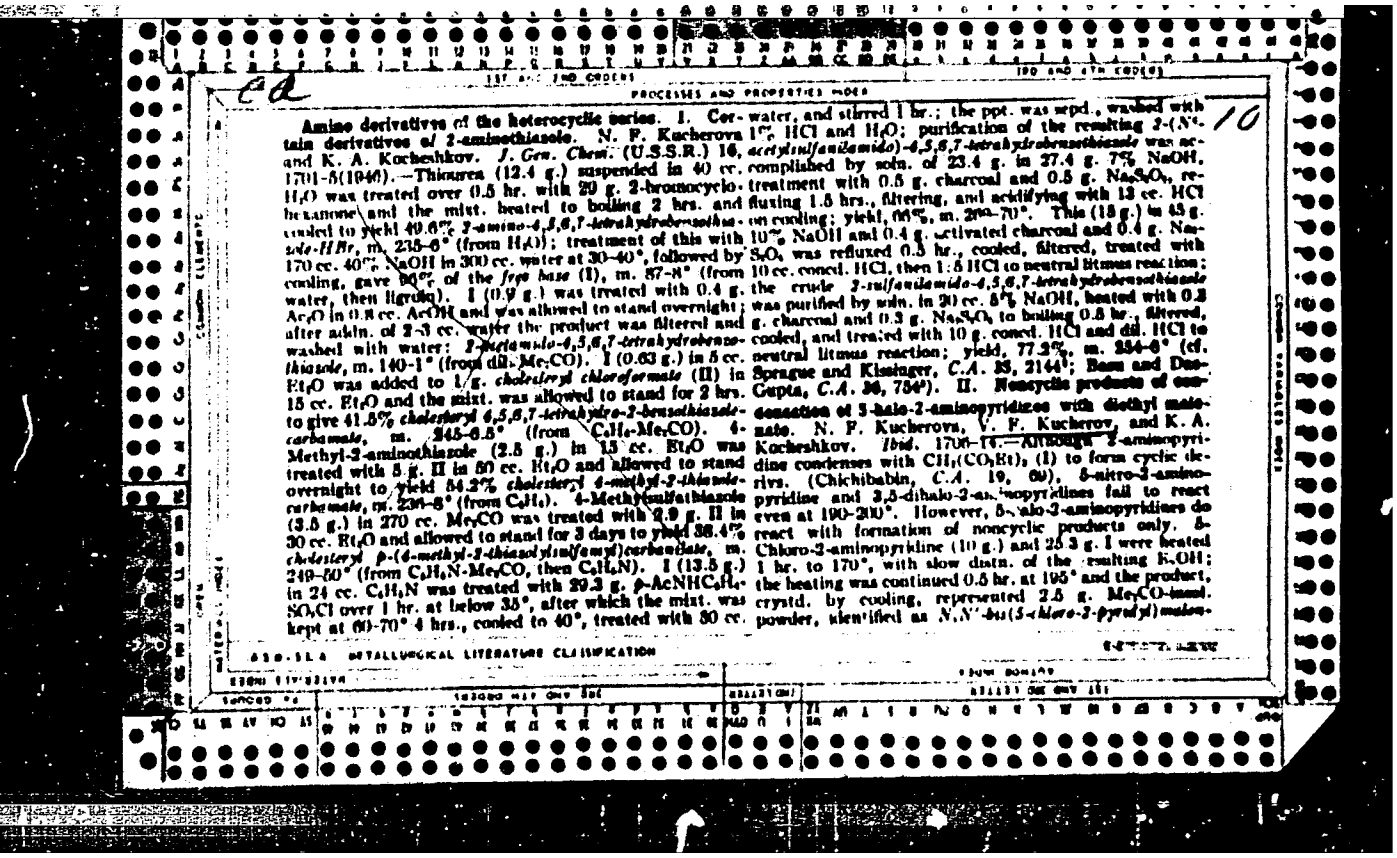
Sulfanilamide derivatives of the cholesterol ester of carbonic acid. V. F. Kucherov and K. A. Kocheshkov. *J. Gen. Chem.* (U.S.S.R.) 16, 1137-42 (1946) (in Russian). —Cholesterol (10 g.) in 100 cc. Et_2O was slowly treated with $COCl_2$ until the initially formed ppt. went back into soln. The soln. was allowed to stand 2-3 hrs. and freed of solvent to yield 78 80% *cholesteryl chloroformate*, m. 117–18° (from Me_2CO). This (6 g.) in 50 cc. abs. Et_2O was treated with 2.7 g. $PhNH_2$ to give 85.2% of the corresponding *carbanilate*, m. 165–5.5° (from C_6H_6). 2-Aminopyridine gave the *2-pyridinecarbamate*, m. 250–6.5° (decompn.; from C_6H_6); piperidine gave the *1-piperidinecarbamate*, m. 100–70° (from C_6H_6-Me_2CO); *Et p-aminobenzoate* gave the *p-carbethoxyanilate*, m. 190–1° (from Me_2CO); sulfanilamide (in Et_2O-Me_2CO) gave the *p-sulfamylcarbanilate*, m. 249.5–50° (decompn.; from ROH-Me_2CO); *sulfapyridine analog* m. 214–4.5° (decompn.; from C_6H_6); *sulfaguanidine analog* m. 228–8.5° (from pyridine-Me_2CO); *sulfadiazine analog* m. 260–70° (from pyridine-Me_2CO). G. M. Kosolapoff



Amino derivatives of the heterocyclic series. I. Certain derivatives of 2-aminothiazole. N. F. Kucherova and K. A. Kocheshkov. *J. Gen. Chem.* (U.S.S.R.) 16, 1701-5(1946).—Thiourea (12.4 g.) suspended in 40 cc. H_2O was treated over 0.5 hr. with 20 g. 2-bromocyclohexanone and the mixt. heated to boiling 2 hrs. and cooled to yield 49.6% *2-amino-4,5,6,7-tetrahydrobenzothiazole-HBr*, m. 235–6° (from H_2O); treatment of this with 170 cc. 40% NaOH in 300 cc. water at 30–40°, followed by cooling, gave 90% of the *free base* (I), m. 87–8° (from water, then ligroin). I (0.9 g.) was treated with 0.4 g. Ac_2O in 0.8 cc. AcOH and was allowed to stand overnight; after addn. of 2–3 cc. water the product was filtered and washed with water: *2-acetamido-4,5,6,7-tetrahydrobenzothiazole*, m. 140–1° (from dil. Me_2CO). I (0.63 g.) in 5 cc. Et_2O was added to 1 g. *cholesteryl chloroformate* (II) in 15 cc. Et_2O and the mixt. was allowed to stand for 2 hrs. to give 41.5% *cholesteryl 4,5,6,7-tetrahydro-2-benzothiazolecarbamate*, m. 245–6.5° (from C_5H_5N-Me_2CO). 4-Methyl-2-aminothiazole (2.8 g.) in 15 cc. Et_2O was treated with 5 g. II in 50 cc. Et_2O and allowed to stand overnight to yield 54.2% *cholesteryl 4-methyl-2-thiazolecarbamate*, m. 236–8° (from C_5H_5N). 4-Methylsulfathiazole (3.5 g.) in 270 cc. Me_2CO was treated with 2.9 g. II in 30 cc. Et_2O and allowed to stand for 3 days to yield 38.4% *cholesteryl p-(4-methyl-2-thiazolylsulfamyl)carbanilate*, m. 249–50° (from C_5H_5N-Me_2CO, then C_5H_5N). I (13.5 g.) in 24 cc. C_5H_5N was treated with 29.3 g. *p*-$AcNHC_6H_4SO_2Cl$ over 1 hr. at below 35°, after which the mixt. was kept at 60–70° 4 hrs., cooled to 40°, treated with 30 cc. water, and stirred 1 hr.; the ppt. was wshd., washed with 1% HCl and H_2O; purification of the resulting *2-(N⁴-acetylsulfanilamido)-4,5,6,7-tetrahydrobenzothiazole* was accomplished by soln. of 23.4 g. in 27.4 g. 7% NaOH, treatment with 0.5 g. charcoal and 0.5 g. $Na_2S_2O_4$, refluxing 1.5 hrs., filtering, and acidifying with 13 cc. HCl on cooling; yield, 66%, m. 200–70°. This (15 g.) in 45 g. 10% NaOH and 0.4 g. activated charcoal and 0.4 g. $Na_2S_2O_4$ was refluxed 0.5 hr., cooled, filtered, treated with 10 cc. concd. HCl, then 1:5 HCl to neutral litmus reaction; the crude *2-sulfanilamido-4,5,6,7-tetrahydrobenzothiazole* was purified by soln. in 20 cc. 5% NaOH, heated with 0.3 g. charcoal and 0.3 g. $Na_2S_2O_4$ to boiling 0.5 hr., filtered, cooled, and treated with 10 g. concd. HCl and dil. HCl to neutral litmus reaction; yield, 77.2%, m. 254–6° (cf. Sprague and Kissinger, *C.A.* 38, 2144⁵; Basu and Dasgupta, *C.A.* 36, 754⁴). II. **Noncyclic products of condensation of 5-halo-2-aminopyridines with diethyl malonate.** N. F. Kucherova, V. F. Kucherov, and K. A. Kocheshkov. *Ibid.* 1706–16.—Although 2-aminopyridine condenses with $CH_2(CO_2Et)_2$ (I) to form cyclic derivs. (Chichibabin, *C.A.* 19, 6u), 5-nitro-2-aminopyridine and 3,5-dihalo-2-aminopyridines fail to react even at 190–200°. However, 5-halo-2-aminopyridines do react with formation of noncyclic products only. 5-Chloro-2-aminopyridine (10 g.) and 25.3 g. I were heated 1 hr. to 170°, with slow distn. of the resulting EtOH; the heating was continued 0.5 hr. at 195° and the product, crystd. by cooling, represented 2.5 g. Me_2CO-insol. powder, identified as *N,N'-bis(5-chloro-2-pyridyl)malon-*

amide, m. 236–7° (from EtOH-C_5H_5N); the mother liquor with 10 parts H_2O and a little EtOH gave 8 g. *Et N-(5-chloro-3-pyridyl)malonamate*, m. 108–9° (from petr. ether). Similarly, 14 g. 5-bromo-2-aminopyridine and 29 g. I gave after 2.5 hrs. at 195° 3.2 g. *N,N'-bis(5-bromo-3-pyridyl)malonamide*, m. 238–9° (from pyridine-Me_2CO), and 8.5 g. *Et N-(5-bromo-3-pyridyl)malonamate*, m. 106–7° (from dil. Me_2CO); 6 g. 5-iodo-2-aminopyridine and 1 g. (?) I gave after 2.5 hrs. at 195° 1.4 g. *N,N'-bis(5-iodo-3-pyridyl)malonamide*, m. 244–5° (from EtOH-C_5H_5N), and 4.5 g. *Et N-(5-iodo-3-pyridyl)malonamate* (II), m. 117–18° (from dil. Me_2CO). When 1.2 g. II and 1 g. 5-iodo-2-aminopyridine were heated to 180–200° 0.5 hr. there was obtained 83.5% of the corresponding diamide. The Br malonamate similarly heated with 5-bromo-2-aminopyridine gave 92% of the disubstituted malonamide. Et *N*-(5-iodo-3-pyridyl)malonamate (1 g.) and 0.8 g. 5-bromo-2-aminopyridine heated 45 min. to 190–200° yielded 76.9% *N-(5-iodo-3-pyridyl)-N'-(5-bromo-3-pyridyl)malonamide*, m. 238–9° (from EtOH-C_5H_5N), while 2.5 g. Et *N*-(5-chloro-2-pyridyl)malonamate and 1.7 g. 5-bromo-2-aminopyridine similarly gave 60.6% *N-(5-chloro-3-pyridyl)-N'-(5-bromo-3-pyridyl)-malonamide*, m. 215–6° (from EtOH-C_5H_5N) (the latter product is obtained also by the interaction of 5-chloro-2-aminopyridine with the corresponding Br-substituted malonamate). Et *N*-(5-chloro-2-pyridyl)malonamate (4 g.) in 17 cc. cold concd. H_2SO_4 allowed to stand 2 days and, after dilu. with cold H_2O, neutralized with 30% NaOH, gave 2.7 g. *N-(5-chloro-3-pyridyl)malonamic acid*, m. 185–5.5° (from EtOH), which loses CO_2 on heating above the m.p. to yield *5-chloro-3-acetamidopyridine*, m. 171° (from EtOH); similarly, there were prepd. *N-(5-bromo-3-pyridyl)malonamic acid*, m. 152–3° (from Me-OH-Me_2CO) (70.7%); *5-bromo-3-acetamidopyridine* m. 175–6° (from EtOH); *N-(5-iodo-3-pyridyl)malonamic acid* m. 144–5° (from Me_2CO) (65.5%); *5-iodo-3-acetamidopyridine* m. 154–5° (from EtOH). G. M. K.

KUCHEROV, V. F.

58/49T37

USSR/Chemistry - Phosphoric Acid Jan 49
Chemistry - Esters

"Amino-Derived Arylphosphoric Esters,"
V. F. Kucherov, 4 pp

"Zhur Obshch Khim" Vol XIX, No 1

Obtains the diarylaminophosphonate types $(C_6H_5O)_2$ POHRN and $(o\text{-}CHO_3.\ C_6H_4O)_2$ PONHR, where R is an aromatic or sulfamide radical These, during saponification or catalytic reduction, give diaryl esters of phosphoric acid. Submitted 18 Mar 47.

58/49T37

USSR/Chemistry - Benzothiazole
Sulfides

Apr 49

"The Oxidation of Several Sulfides of the Benzothiazole Series," V. F. Kucherov, Chem Div, Lab of Experimental Chemotherapy, Min of Med Ind USSR, 6½ pp

"Zhur Obshch Khim" Vol XIX, No 4

Describes the general method of oxidizing alkylbenzothiazolylsulfides into their corresponding sulfones and shows that the derivatives of mercaptobenzothiazole, containing the sulfide groups - S - CH_2 - COR and - S - CH_2 - CH_2OH, during oxidation by H_2O_2 in glacial acetic

65/49731

USSR/Chemistry - Benzothiazole (Contd) Apr 49

acid give 2-oxybenzothiazole. The intermediate stage of oxidation of mercaptobenzothiazolyl-2-acetone to 2-oxybenzothiazole may be the formation of the corresponding sulfoxide. Submitted 18 Mar 48

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KUCHEROV, V. F.

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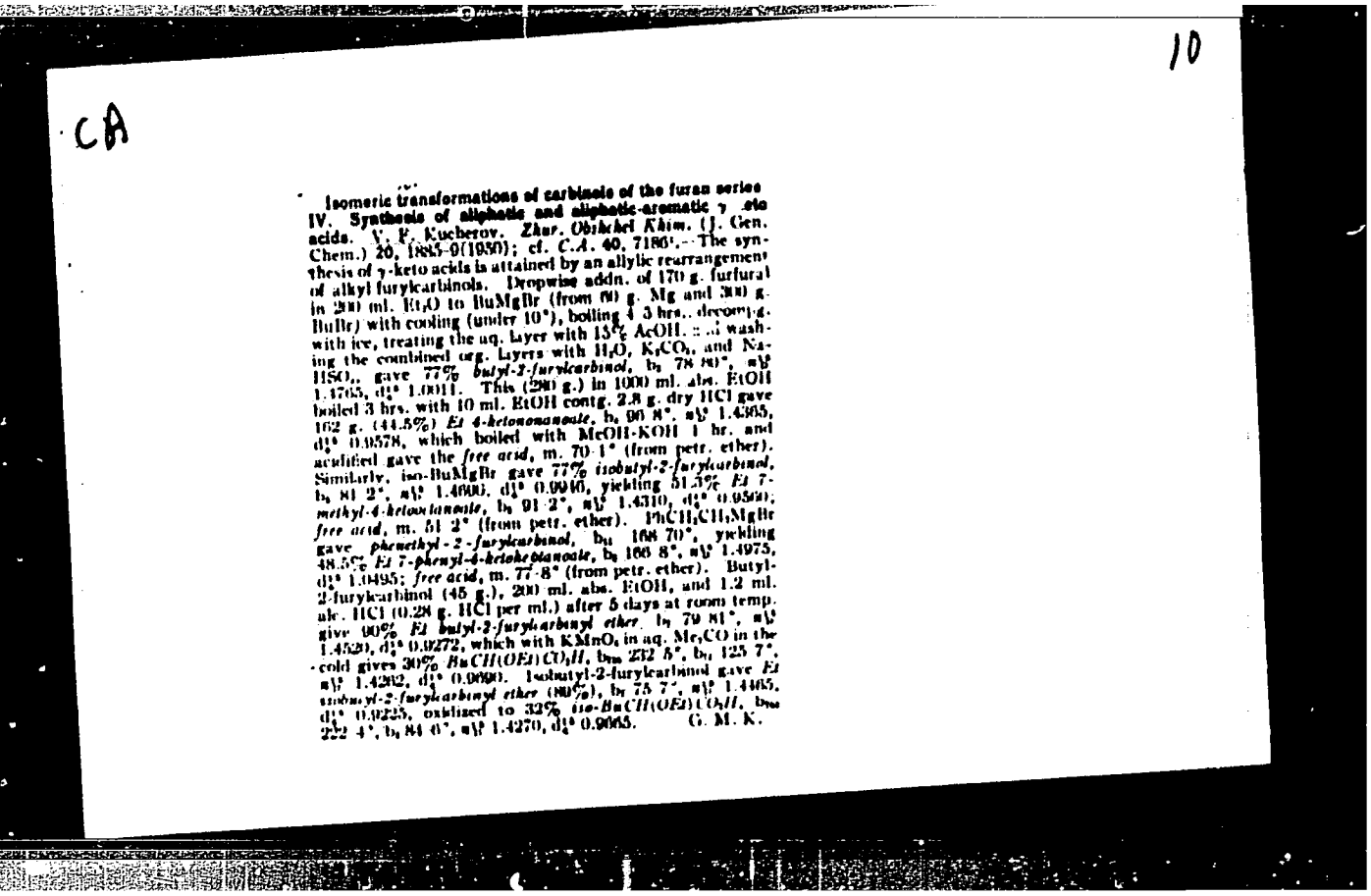
Amino derivatives of the heterocyclic series. III. Polycyclic analogs of aminothiazole. V. F. Kucherov. *Zhur. Obshchei Khim.* (J. Gen. Chem.) 20, 1653-61(1950); cf. C.A. 41, 6242d.—Slow addn. of 15 g. 2-bromo-1-keto-1,2,3,4-tetrahydronaphthalene to 5.8 g. $(H_2N)_2CS$ in 60 ml. H_2O at 60-70°, boiling until a clear soln. formed, and cooling, gave 70.2% 2-amino-4,5-dihydronaphtho[1,2]thiazole·HBr, m. 208-9° (from H_2O); addn. of NaOH yields the *free base*, m. 137-9° (crude), m. 140-1° (from dil. MeOH); standing overnight with Ac_2O-AcOH yielded the 2-acetamido analog, m. 225-6° (from MeOH). Stirring the free base in pyridine at 50-70° 6 hrs. with p-$AcNHC_6H_4SO_2Cl$ gave 50% of the 2-(N-acetylsulfanilamido) analog, decomp. 201-3° (from dil. pyridine). Boiling 1.35 g. $(H_2N)_2CS$ and 4.8 g. 3-bromo-4-keto-1,2,3,4-tetrahydrophenanthrene in dry MeOH 5 hrs. gave 80.5% 2-amino-4,5-dihydrophenanthro[4,3]thiazole·HBr, decomp. 303-4° (from 0.5% HBr); treatment with 20% NaOH, drying the pptd. violet free base in N, and allowing this to stand overnight in Ac_2O-AcOH gave the 2-acetamido analog, m. 245-6° (from dil. Me_2CO). **IV. Synthesis of alkyl derivatives of 3-hydroxypyridazine.** *Ibid.* 1662-6(1950).—Addn. of 21.6 g. semicarbazide·HCl and 18.5 g. NaOAc in 130 ml. 50% MeOH to 32 g. 4-ketononanoic acid in 60 ml. MeOH gave after 24 hrs. at room temp. 81% of the *semicarbazone*, m. 157-9° (decompn.; from EtOH); this pyrolyzed at 180-90° and extd. with Me_2CO gave insol. $(NHCONH_2)_2$, m. 245-6°, and 70% sol. 3-hydroxy-6-amyl-4,5-dihydropyridazine, b_5 150-2°; treatment with Br in AcOH gave 3-hydroxy-6-amylpyridazine, m. 82-3° (from H_2O or H_2O). 7-Methyl-4-ketooctanoic acid similarly yielded the semicarbazone, m. 141-2° (decompn.; from EtOH), which gave 3-hydroxy-6-isoamyl-4,5-dihydropyridazine, b_5 149-50°, and this gave 60.5% 3-hydroxy-6-isoamylpyridazine, m. 83-4° (from EtOH). Boiling 10 g. Et 4-ketononanoate and 5.4 g. $PhNHNH_2$ in EtOH 5 min. and permitting the soln. to stand overnight gave 84% phenylhydrazone, m. 85-7° (from EtOH), which heated 2 hrs. to 110-20° gave 76% 2-phenyl-3-keto-6-amyltetrahydropyridazine, b_5 186-7°. Et 7-methyl-4-ketooctanoate similarly gave the phenylhydrazone, m. 81-2°, which gave 71% 2-phenyl-3-keto-6-isoamyltetrahydropyridazine, b_5 181-4°.

G. M. Kosolapoff



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Isomeric transformations of carbinols of the furan series. IV. Synthesis of aliphatic and aliphatic-aromatic γ-keto acids. V. P. Kucherov. *Zhur. Obshchei Khim.* (J. Gen. Chem.) 20, 1885–9(1950); cf. *C.A.* 40, 7186⁶.—The synthesis of γ-keto acids is attained by an allylic rearrangement of alkyl furylcarbinols. Dropwise addn. of 170 g. furfural in 200 ml. Et_2O to BuMgBr (from 90 g. Mg and 300 g. BuBr) with cooling (under 10°), boiling 4 3 hrs., decompg. with ice, treating the aq. layer with 15% AcOH, washing the combined org. layers with H_2O, K_2CO_3, and $NaHSO_3$, gave 77% *butyl-2-furylcarbinol*, b_{15} 78–80°, n_D^{20} 1.4765, d_4^{20} 1.0011. This (280 g.) in 1000 ml. abs. EtOH boiled 3 hrs. with 10 ml. EtOH contg. 2.8 g. dry HCl gave 162 g. (44.5%) *Et 4-ketononanoate*, b_6 96.8°, n_D^{20} 1.4365, d_4^{20} 0.9578, which boiled with MeOH-KOH 1 hr. and acidified gave the *free acid*, m. 70–1° (from petr. ether). Similarly, iso-BuMgBr gave 77% *isobutyl-2-furylcarbinol*, b_6 81.2°, n_D^{20} 1.4600, d_4^{20} 0.9940, yielding 51.5% *Et 7-methyl-4-ketooctanoate*, b_6 91.2°, n_D^{20} 1.4310, d_4^{20} 0.9560; *free acid*, m. 51.2° (from petr. ether). $PhCH_2CH_2MgBr$ gave *phenethyl-2-furylcarbinol*, b_{11} 168.70°, yielding 48.5% *Et 7-phenyl-4-ketoheptanoate*, b_6 166.8°, n_D^{20} 1.4975, d_4^{20} 1.0495; *free acid*, m. 77–8° (from petr. ether). Butyl-2-furylcarbinol (45 g.), 200 ml. abs. EtOH, and 1.2 ml. alc. HCl (0.28 g. HCl per ml.) after 5 days at room temp. give 90% *Et butyl-2-furylcarbinyl ether*, b_6 79.81°, n_D^{20} 1.4520, d_4^{20} 0.9272, which with $KMnO_4$ in aq. Me_2CO in the cold gives 30% $BuCH(OEt)CO_2H$, b_{760} 232.5°, b_{11} 125.7°, n_D^{20} 1.4282, d_4^{20} 0.9690. Isobutyl-2-furylcarbinol gave *Et isobutyl-2-furylcarbinyl ether* (80%), b_7 75.7°, n_D^{20} 1.4465, d_4^{20} 0.9225, oxidized to 32% *iso*-$BuCH(OEt)CO_2H$, b_{760} 222.4°, b_6 84.6°, n_D^{20} 1.4270, d_4^{20} 0.9065. G. M. K.

KUCHEROV, V.F.; VOLODINA, Z.V.

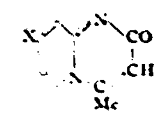
Amino derivatives of the heterocyclic series. V. Condensation products of 5-halogeno-2-aminopyridines with acetoacetic ester. J. gen. Chem. USSR, '50, 20, 1890-1897 [U.S. transl., 1957-1964]. (MLRA 3:9)
(BA - A II Ja '53:83)

KUCHEROV, V. F.

"Synthesis of a-amino acid derivatives. I. N^a-benzene sulphosubstituted l- and d-lysine." by V. F. Kucherov and A. I. Ivanov. (p.1139)

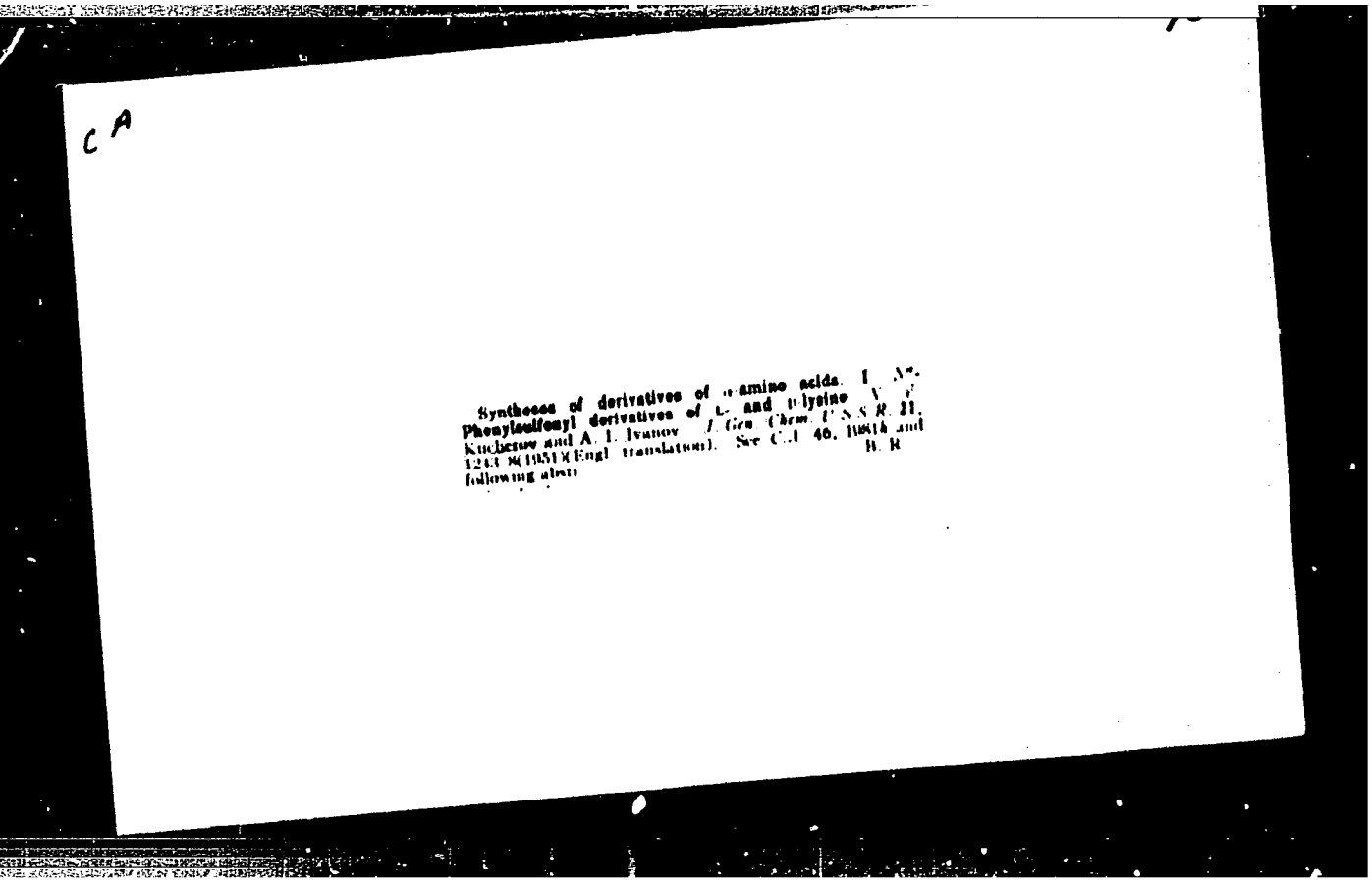
SO: Journal of General Chemistry (Zhurnal Obshchei Khimii) 1951, Volume 21, No. 6

Amino derivatives of the heterocyclic series. VI. Derivatives of 5-halo-2-pyridonimine. V. F. Kucherov. *Zhur. Obshchei Khim.* (J. Gen. Chem.) 21, 1145-50(1951); cf. *C.A.* 45, 2951f.—5-Iodo-2-aminopyridine (5.5 g.) in 10 ml. abs. EtOH and 8 g. $AcCH_2CO_2Et$ contg. 1 drop concd. H_2SO_4 refluxed 6 hrs. gave on cooling 37.5% *Et 1,2-dihydro-5-iodo-β-methyl-1-pyridineacrylate*, m. 83-4°, did not depress the m.p. of the product of fusion of 5-iodo-2-aminopyridine with EtO_2CCH_2Ac. Similarly prepd., the *5-Br analog* m. 89-90° (from EtOH); *5-Cl analog*, m. 84-5°. Boiling the Br deriv. 4 hrs. with H_2O gave *1,2-(3-bromodiriniylene)-6-methyl-4-pyrimidone* (8-bromo-4-methyl-2H-pyrimido[1,2-a]pyrimidin-2-one), m. 169-71° (from EtOH); the same product forms after 2 days at room temp. in cold concd. H_2SO_4 or after 15 min. at 100°. On boiling with 50% KOH it decomp. and evolves NH_3. Refluxing 1 g. 5-bromo-2-(acetoacetamido)pyridine and 0.7 g. 5-bromo-2-aminopyridine in 10 ml. abs. EtOH and 1 drop H_2SO_4 3 hrs. gave 55.5% *N-(5-bromo-2-pyridyl)-β-(5-bromo-2-pyridylamino)crotonamide*, m. 240-1°. 5-Chloro-2-aminopyridine gave 56% *N-(5-bromo-2-pyridyl)-β-(5-chloro-2-pyridylamino)crotonamide*, m. 230-3°; substitution of 5-chloro-2-(acetoacetamido)pyridine and 5-bromo-2-aminopyridine similarly gave 52% *N-(5-chloro-2-pyridyl)-β-(5-bromo-2-pyridylamino)crotonamide*, m. 241-2°. Similar methods gave 46% *N-(5-chloro-2-pyridyl)-β-(5-chloro-2-pyridylamino)crotonamide* (I), m. 241-2°, and 42.5% *N-(5-chloro-2-pyridyl)-β-(5-iodo-2-pyridylamino)crotonamide*, m. 271-2°. Heating I with concd. H_2SO_4 to 100° 15 min. gave on diln. and neutralization with NH_4OH *1,2-(3-chlorodiniylene)-6-methyl-4-pyrimidone*, m. 167-9° (from EtOH). Thus, the interaction of 5-halo-2-aminopyridines with EtO_2CCH_2Ac goes by the way of formation of the corresponding N-acetoacetyl deriv. (II) and the above described crotonates (III), both of which can form cyclic products of type IV, also obtainable



(IV)

from the pyridylamides of the corresponding pyridyl-substituted crotonic acids which arise from II. G. M. K.



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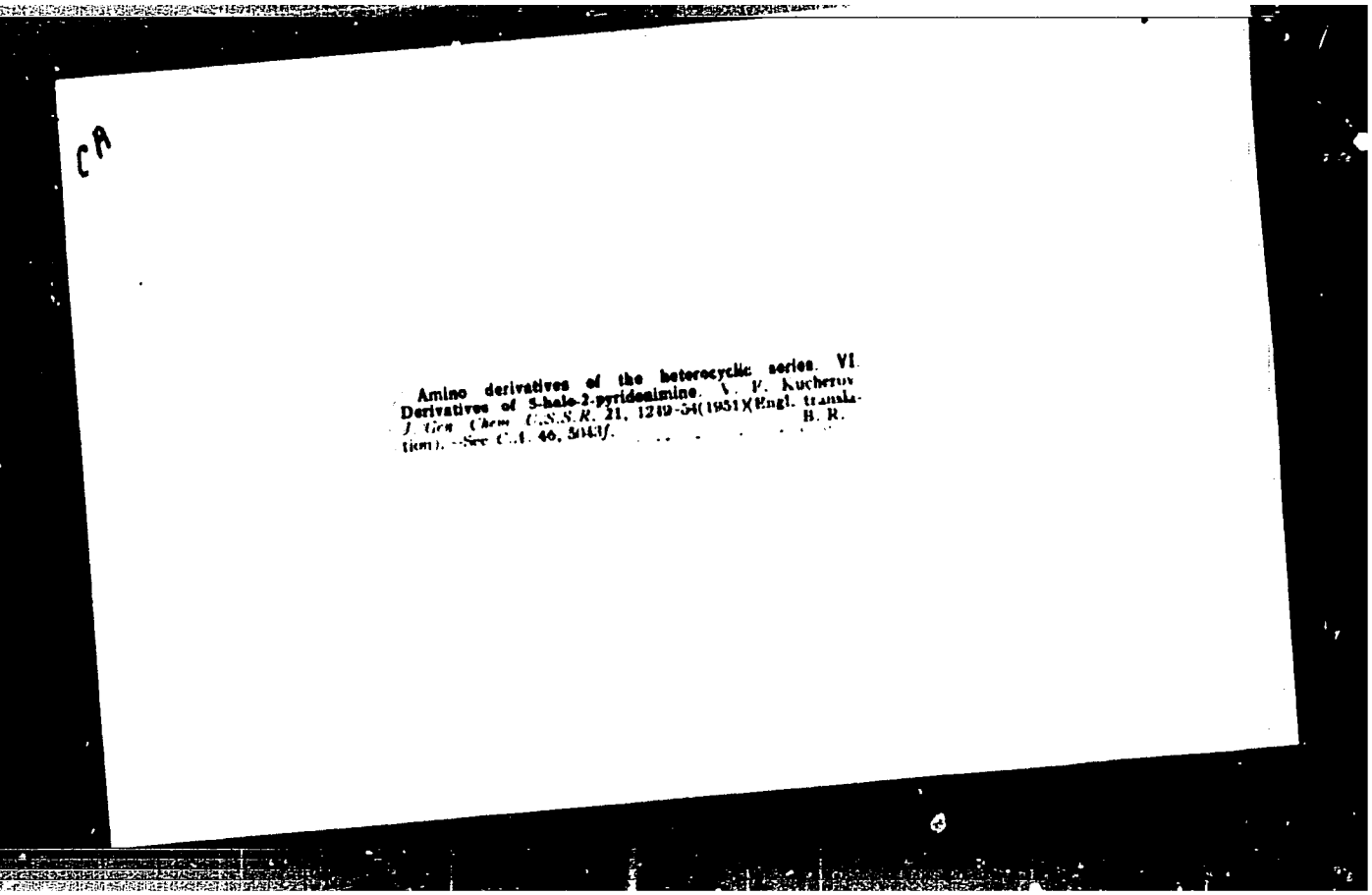
Syntheses of derivatives of α-amino acids. I. N-Phenylsulfonyl derivatives of L- and D-lysine. V. [illegible] Kucherov and A. I. Ivanov. J. Gen. Chem. U.S.S.R. 21, 1241-9(1951)(Engl. translation). See C.A. 46, 11814 and following abstr.



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Amino derivatives of the heterocyclic series. VI. Derivatives of 5-halo-2-pyridoximine. V. V. Kucherov (Inst. Org. Chem. Acad. Sci. U.S.S.R., Moscow). *J. Gen. Chem. U.S.S.R.* 21, 1219-34 (1951) (Engl. translation). See *C.A.* 46, 5443f.

CA

Syntheses of derivatives of α-amino acids. II. New method of synthesis of amides of α-amino acids. V. V. Kurbatov and M. I. Dorokhova. Zhur. Obshchei Khim. (J. Gen. Chem.) 21, 1488-91(1951); J. Gen. Chem. U.S.S.R. 21, 1621-5, 1627-30 (Eng. Translation); cf. Bergmann and Zervas, C.A. 20, 3672; preceding abstr. 3-Alkyl-2,5-diketooxazolidines are prepd. from α-(carbobenzyloxyamino) acids with PCl_5; the products with NH_3 yield amides of α-amino acids. The following *N-carbobenzyloxy derivs.* of α-*amino acids* were prepd. conventionally from 10% excess of $PhCH_2OCOCl$ in alk. soln. at 0-3°: DL-*valine* (I), 73.3%, m. 73-5° (from petr. ether); DL-*norvaline* (II), 71%, m. 85-7° (from CCl_4-petr. ether); DL-*leucine* (III), 70%, m. 54-6°; DL-*norleucine* (IV), 74%, m. 105-6° (from CCl_4-petr. ether). To 9 g. I in dry Et_2O was added at −3 to 0° 8.3 g. powd. PCl_5, and the mixt. stirred 15 min. at 0° and 1 hr. at room temp., filtered, and evapd. in vacuo with addn. of petr. ether, yielding 90% *3-isopropyl-2,5-diketooxazolidine*, decomp. 90-1° (from Et_2O); on standing in air or on heating it loses CO_2 and forms a high-melting *polymer*, $(C_5H_9ON)_x$. Similarly, II yields *3-propyl-2,5-diketooxazolidine* (V), 84.3%, decomp. 67-9° (from Et_2O), while III gives 80% *3-iso-Bu analog*, m. 48-50°, and IV gives 85% *3-Bu analog*, decomp. 78-80°. Similarly, DL-N-(carbobenzyloxy)phenylalanine and PCl_5 in dry Et_2O at 0° gave 72% DL-*N-(carbobenzyloxy)phenylalanyl chloride*, isolated by diln. with petr. ether in the cold; refluxing in Et_2O 1 hr. yields *3-benzyl-2,5-diketooxazolidine*, decomp. 123-6° (from $CHCl_3$). Addn. with cooling of 3.5 g. V to 30 ml. MeOH satd. with

NH_3 at 0°, gives 3.2 g. crude *NH_4 salt of* DL-*α-(carboxyamino)valeramide*, decomp. 100-4°, which, boiled until dissolved in C_6H_6, loses CO_2 and NH_3, yielding 60% DL-*norvalinamide*, m. 67-9°. Similarly were obtained: DL-*valinamide*, 81.5%, m. 77-9°; DL-*norleucinamide*, 83%, m. 60-1° (*NH_4 salt of α-(carboxyamino)caproamide*, decomp. 103-7°), DL-*leucinamide*, 60%, m. 105-8°; DL-*phenylalanamide*, 65%, m. 137-9°. III. **Synthesis of decarboxydipeptides.** *Ibid.* 1491-4. Extension of the reaction described in paper II of the series showed that amines may be substituted for NH_3 in the reactions with the oxazolidines. Thus, addn. to 3-4 moles of the amine in dry MeOH at about 0° of the 3-alkyl-2,5-diketooxazolidine, followed by 0.5 hr. at 0°, yields on evapn. in vacuo, the amine salt of the amide of the corresponding α-(carboxyamino) acid, which, boiled 1 hr. in MeOH, then allowed to stand 1 hr., yields the desired decarboxydipeptide in 80.5% yields. Such a treatment of 3-isopropyl-2,5-diketooxazolidine (I) (3.3 g.) and 20 ml. 20% $MeNH_2$ in MeOH gave the *$MeNH_3$ salt of* DL-*α-(carboxyamino)-N-methylisovaleramide*, decomp. 98-102°.

which yielded 83% *N*-DL-*valyldecarboxyglycine* (DL-α-amino-
N-methylisovaleramide), b_{4} 109-10°, n_D^{20} 1.4712, d_4^{20} 0.9040.
Similarly, the 3-Pr analog of I gave 56.5% DL-α-amino-*N*-
methylvaleramide, b_4 110-11°, n_D^{20} 1.4702, d_4^{20} 0.9094. The 3-
iso-Bu analog of I gave the *MeNH*$_3$ *salt* of DL-α-(carboxy-
amino)-*N-methylisocapronamide*, decomp. 98-104°, which
gave 60% DL-α-amino-*N-methylisocapronamide*, b_4 131°, n_D^{20}
1.4670, d_4^{20} 0.9060. The 3-Bu analog of I gave 60% DL-α-
amino-N-methylcapronamide, b_4 120-1°, n_D^{20} 1.4685, d_4^{20}
0.9174, which crystallizes on prolonged standing. The 3-
benzyl analog of I gave 48% DL-α-amino-*N-methyl-β-*
phenylpropionamide, b_4 163-7°, low-melting solid. Simi-
larly, iso-$AmNH_2$ gave with the corresponding oxazolidines:
DL-α-*amino-N-isoamylisovaleramide*, 80%, b_4 140-2°, n_D^{20}
1.4620, d_4^{20} 0.9273; *isocapronamide analog*, 84.3%, b_4 150-1°,
n_D^{20} 1.4608, d_4^{20} 0.9161. $PhCH_2CH_2NH_2$ similarly gave:
DL-α-*amino-N-phenethylisovaleramide*, 85%, b_4 190-1°, n_D^{20}
1.5275, d_4^{20} 1.0376; *isocapronamide analog*, 85%, b_4 170-1°,
n_D^{20} 1.5212, d_4^{20} 1.0175 (*HCl salt*, m. 202-3°), and *capro-
amide analog*, 82%, b_4 175-6°, cryst. on cooling.

G. M. Kosolapoff

KUCHEROV, V. F.

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

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Synthesis of polycyclic compounds related to steroids. XI. Stereochemistry of cyclic compounds. I. Condensation of bivinyl with citraconic and mesaconic acid and their esters. Cis-trans isomerism of 1-methylcyclohexene-1,2-dicarboxylic acids and their esters. I. N. Nazarov and V. F. Kucherov. *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.* 1952, 301-7(Engl. translation).—See *C.A.* 47, 5362c. XII. Condensation of cyclic β-diketones with vinyl ketones and the transformation of the products. I. N. Nazarov and S. I. Zavyalov. *Ibid.* 309-18.—See *C.A.* 47, 5364b.

H. L. H.

KUCHEROV, V. F.

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

Acetylene derivatives. CXXVI. Synthesis of polycyclic compounds related to steroids. 14. Synthesis of tetracyclic ketones with a methylcyclopentane B ring. I. N. Nazarov, V. F. Kucherov, and L. N. Terekhova. *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.* 1952, 427-35 (Engl. translation).—See *C.A.* 47, 5306*c*. CXXVII. Synthesis of polycyclic compounds related to steroids. 15. Structure of products of condensation of 2-methoxy-1,3-butadiene with 2-methyl-2-cyclohexen-1-one and methyl methacrylate. I. N. Nazarov and S. I. Zavyalov. *Ibid.* 643-7.—See *C.A.* 47, 10515*d*. CXXVIII. Heterocyclic compounds. 27. Action of primary aromatic amines and 2-aminopyridine on vinyl alkyl ketones. Synthesis of aryl substituted 4-piperidones and 1-(2-pyridyl)-4-piperidones. I. N. Nazarov, S. G. Matsoyan, and V. A. Rudenko. *Ibid.* 923-32.—See *C.A.* 48, 13872*d*. CXXIX. Heterocyclic compounds. 24. Transformations of 1-phenyl-2,5-dimethyl-4-piperidone. *Ibid.* 933-7.—See *C.A.* 48, 1355*e*. H. L. H.

USSR/Chemistry - Acetylene May/Jun 52
Derivatives

"Acetylene Derivatives. Report No 126. Synthesis of Polycyclic Compounds Related to Steroids. XIV. Synthesis of Tetracyclic Ketones With a Methylcyclopentane B-Ring," I. N. Nazarov, V. F. Kucherov, L. N. Terekhova, Inst of Org Chem, Acad Sci USSR

"Iz Ak Nauk, Otdel Khim Nauk" No 3, pp 442-452

The following reactions were carried out in the course of this investigation: Condensation of 2-methoxy-1, 3-butadiene with 1, 3-dimethyl-Δ^1-cyclopentenone, hydrolysis of (1) 220T8

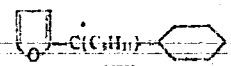
5-methoxy-3, 8-dimethyl-Δ^5-hydrindene-1-ol; condensation of 5-methoxy-3, 8-dimethyl-Δ^5-hydrindene-1-one with acetylene; condensation of 1-vinyl-3,8-dimethyl-5-keto-Δ^1- hydrindene with 1-methyl-Δ^1-cyclopentenone, with 1-methyl-Δ^1-cyclohexenone, and with benzoquinone; selective hydrogenation of 1-ethyl-3,8-dimethyl-6-ketohydrindane-1-ol; dehydrogenation of 1-vinyl-3,8-dimethyl-6-ketohydrindane-1-ol; condensation of 1-vinyl-3,5-dimethyl-6-keto-Δ^1-hydrindene with maleic anhydride; hydrogenation of 5-methoxy-3,8-dimethyl-Δ^5-hydrindene-1-one; condensation of 5-methoxy-3,8-dimethyl-hydrindene-1-one with acetylene; hydrogenation of 1-ethinyl-3,0-dimethyl-5-methoxy-hydrindane-1-ol; (2) 220T8

dehydrogenation of 1-vinyl-3,8-dimethyl-5-methoxyhydrindan-1-ol; condensation of 1-vinyl-3,8-dimethyl-5-methoxy-Δ^1-hydrindene with maleic acid; condensation of 1-vinyl-3, 8-dimethyl-5-methoxy-Δ^1-hydrindene with p-benzoquinone; and with 1-methyl-Δ^1-cyclohexanone. 220T8

KUCHEROV, V. F.

Isomeric transformations of carbinols of the furan series. V. Transformations of dicyclohexylfurylcarbinol. V. P. Kucherov (Inst. Org. Chem., Acad. Sci. U.S.S.R., [illegible]). *[illegible] Sbornik Statei Obshchei Khim., Akad. Nauk S.S.S.R.* 1, 681-6(1953); cf. *C.A.* 46, 10116e.—To RMgX from 205 g. $C_6H_{11}Br$ was added slowly 70 g. Et pyromucate and the mixt. was refluxed 20 hrs., yielding, after treatment with [illegible] and NH_4Cl, 42.5% *dicyclohexyl-2-furylcarbinol* (I), b_2 147-9°, m. 58-61°. To 15 g. I in 20 ml. abs. EtOH was added 0.25 ml. EtOH-HCl satd. at 0° and the mixt. allowed to stand at 20° 3 days, yielding 0.5 g. II, m. 161-2°, which oxidized with CrO_3 in AcOH to *dicyclohexyl ketone*, b_{15} 130-157 (crude) (*oxime*, m. 157-9°); the alc. mother liquor slowly deposited 3.5 g. product, m. 80-2°; further addn. of EtOH-HCl and allowing the mixt. to remain 24 hrs. longer at room temp., after a brief heating, gave a total of 35% yield of this substance, m. [illegible], [illegible] $(C_6H_{11})_2CHCOCH_2CH_2CO_2Et$, which hydrolyzed with KOH-MeOH in 2 hrs. to the free *acid*, m. 162-2.5° (from MeOH). Passage of dry HCl into 20 g. I in 35 ml. AcOH, followed by letting the soln. stand at room temp. 24 hrs. gave 10 g. ppt., m. 148-51°, and an addnl. 2.3 g. by pptn. with [illegible] recrystd. from C_6H_6-Me_2CO it gave 11.5 g. [illegible] II. Passage of dry HCl into 15 g. I in [illegible] followed by 3 days at room temp. gave a viscous [illegible] which was decanted from pptd. H_2O, satd. with HCl, heated 1 hr. at 50-60°, poured into H_2O, and washed with K_2CO_3, yielding 9 g. III, b_4 131-2°, n_D^{20} 1.5255, d_{20} 1.0018; oxidation of this with CrO_3 in AcOH gave cyclohexanone. Passage of dry HCl 1 min. into 20 g. I in 40 ml. Me_2CO, followed by 0.5 hr. on a steam bath and evapn. of the solvent gave 10.5 g. III. When dry HCl was passed 3 min. into 25 g. I in [illegible] ml. Me_2CO and the mixt. was refluxed 6 hrs. there was obtained 8.2 g. III and 13% $(C_6H_{11})_2CHCOCH_2CH_2CO_2H$; a 33.7% yield of this acid was obtained when I was boiled in aq. Me_2CO with concd. HCl 8 hrs.; a small yield of III was also obtained. G. M. Kosolapoff

(II)



(III)

KUCHEROV, V.F.

USSR 4

Stereochemistry of cyclic compounds. III. cis- and trans-4-Cyclohexene-1,2-dicarboxylic acids and their transformations. I. N. Nazarov and V. F. Kucherov. *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.* 1954, 255-73 (Engl. translation) --See C. A. 49, 5429a. H. L. H.

KUCHEROV, V. F.

USSR.

Stereochemistry of cyclic compounds. III. *cis*- and *trans*-3-Cyclohexene-1,2-dicarboxylic acids and their transformations. I. N. Nazarov and V. F. Kucherov (N. D. Zelinskii Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1954, 852-67; cf. *C.A.* 49, 1686g.—Heating 15 g. di-Me fumarate with 30 g. CH_2:$CHCH$:CH_2 in CaH_2 in a steel ampul 3.6 hrs. at 200-5° gave 19.5 g. *di-Me trans-3-cyclohexene-1,2-dicarboxylate*, (I), bp 137°, n_D^{20} 1.4656; d_4 1.1234; with Br in $CHCl_3$ it gave the *dibromide*, m. 85-6° (from petr. ether). Satn. of the ester with H over Pd gave the *satd. analog* of I, bp 135°, n_D^{20} 1.4524, d_4 1.0946. Hydrolysis of I with 20% KOH gave the free *trans-acid* (II), m. 171-2° (from dil. Me_2CO), while the satd. ester gave the corresponding satd. *trans-acid* (IIa), decomp. 218-20°, also obtained by hydrogenation of the unsatd. acid over Pd. Refluxing 7.5 g. II with 50 ml. AcCl 2 hrs. gave 4.8 g. II *anhydride*, m. 188-9° (cf. Alder and Schumacher, *C.A.* 44, 1666g), which hydrogenated over Pd in $CHCl_3$ gave the satd. *anhydride*, m. 145-6°, also obtained by treatment of the unsatd. acid with AcCl as above. II anhydride (3 g.) refluxed 2 hrs. with 50 ml. abs.

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OVER

I. N. NAZAROV

MeOH gave 2.8 g. II *mono-Me ester*, m. 53-4°, which is hydrogenated over Pd gave the *satd. mono-Me ester*, m. 58-9° (cf. Werner, Conrad, *Ber.* 32, 3522 (1899)), which is also formed from the satd. anhydride and MeOH. Refluxing 40 g. *cis-Δ⁴-cyclohexene-1,2-dicarboxylic anhydride* with 350 ml. MeOH 3 hrs. gave 42.7 g. *mono-Me ester*, m. 84-5° (from Et₂O-petr. ether), which on hydrogenation gave the *satd. mono-Me ester*, m. 68-9°, identical with previously reported specimen (cf. Vavon and Peignier, *C.A.* 28, 4206). Treatment of *cis-Δ⁴-cyclohexene-1,2-dicarboxylic acid* with CH_2N_2 gave the *di-Me ester* (III), b. 114-15°, n_D^{20} 1.4728. Similarly was obtained *di-Me cis-cyclohexane-1,2-dicarboxylate* (IV), b. 110-11°, n_D^{20} 1.4590, which also forms on hydrogenation of the unsatd. ester over Pd. Refluxing 2.8 g. III with 7.5 g. Na in 180 ml. MeOH 15 hrs. gave 66.6% II after evapn. and acidification. IV similarly gave 75% IIa. Heating II anhydride 2 hrs. at 200° gave 80% *cis*-isomer, m. 102-3°; similarly IIa anhydride gave after 2 hrs. at 200° followed by refluxing with H_2O, 75% *cis*-IIa. II mono-Me ester (2 g.) in dry CCl_4 treated with 2 ml. $(COCl)_2$ 3 hrs. at room temp. gave 1.9 g. II *mono-Me ester chloride*, b. 112-2.5°, n_D^{20} 1.4970 (hydrolyse with 10% NaOH in 10 min. gave II); treatment in the cold with NH_3 in Et_2O gave II *mono-Me ester monoamide*, m. 120-3° (from dil. MeOH).

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I. M. NAZAROV

Similarly, IIa mono-Me ester gave the corresponding *mono-Me ester chloride*, b. 114.5–6°, n_D^{20} 1.4750, and the *mono-Me ester monoanilide*, m. 156–7.5°. To 1 g. *cis*-IIa mono-Me ester in C_6H_6 was added 1 ml. $(COCl)_2$ and the mixt. kept 2 hrs., evapd., taken up in Et_2O and treated in the cold with $PhNH_2$, yielding almost 75% *cis-cyclohexane-1,3-dicarboxylic-phenylimide*, m. 132–3°. Similarly was obtained from *cis*-II the corresponding *phenylimide*, m. 115–16°. Treatment of *cis*-IIa mono-Me ester with $(COCl)_2$ gave the corresponding *mono-Me ester chloride*, a liquid, which refluxed 5 min. with 5% NaOH gave *cis*-IIa, m. 191–2°; the ester chloride can be distd., b. 113–14°, n_D^{20} 1.4740, but the process is accompanied by isomerization, as on hydrolysis it yields IIa as well as *cis*-IIa. Treatment of the distd. chloride with $PhNH_2$ similarly gave the *trans*-anilide Me ester and *cis*-phenylimide. Similarly *cis*-II *mono-Me ester* gave the *ester chloride* which hydrolyzed directly to *cis*-II; distn. of the chloride, b. 118–19°, n_D^{20} 1.4685, gave a product which on hydrolysis gave mixed *cis-trans* acids, while treatment with $PhNH_2$ gave a mixt. of the *trans*-anilide and the *cis*-phenylimide.

G. M. Kosolapoff

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KUCHEROV, V.F.

NAZAROV, I.N.; KUCHEROV, V.F.

Synthesis of polycyclic compounds related to steroids. Report no.22: Research in the field of stereochemistry of polycyclic compounds. Part 2: Semiesters of cis- and trans-1-methylcyclohexane- (and Δ^4-cyclohexane)-1,2-dicarboxylic acids and their conversions. Izv.AN SSSR. Otd.khim.nauk no.1:63-79 Ja-F '54. (MLRA 7:4)

1. Institut organicheskoy khimii Akademii nauk SSSR. (Esters)

Kucherov, V.F.

USSR/Chemistry - Cyclic compounds

Card 1/2 Pub. 40 - 11/27

Authors : Nazarov, I. N.; Kucherov, V. F.; and Andreyv, V. M.

Title : The stereochemistry of cyclic compounds. Part 4. Condensation of 1-vinyl- ' -cyclohexene with citraconic anhydride

Periodical : Izv. AN SSSR. Otd. khim. nauk 1, 73-88, Jan-Feb 1955

Abstract : A study of the diene condensation of 1-vinyl- ' -cyclohexene with citraconic anhydride showed that the condensation products are normal ortho- and meta-adducts. The products obtained through saponification of cis-anhydrides are listed. Unsaturated cis-anhydrides and their cis-acids were observed to hydrogenate easily over Pt-catalysts into

Institution : Acad. of Sc., USSR, The N. D. Zelinskiy Inst. of Org. Chem.

Submitted : April 6, 1954

Card 2/2 Pub. 40 - 11/27

Periodical : Izv. AN SSSR. Otd. khim. nauk 1, 78-88, Jan-Feb 1955

Abstract : homologous saturated compounds which is connected with the screening effect of the cis-substitutes on the double bond. The results obtained by isomerization of cis-diesters with sodium methylate are described. Eleven references : 8 USSR and 3 USA (1948-1953).

Kucherov, V. F.

USSR/ Chemistry - Cyclic compounds

Card 1/2 Pub. 40 - 12/27

Authors : Nazarov, I. N.; Kucherov, V. F.; and Andreyev, V. M.

Title : The stereochemistry of cyclic compounds. Part 5. Condensation of 1-vinyl-^{1}-cyclohexene with dimethyl ester of mesaconic acid

Periodical : Izv. AN SSSR. Otd. khim. nauk 1, 89-97, Jan-Feb 1955

Abstract : The characteristics of three isomeric trans-methyl - ^{4}-octalin-1,2-dicarboxylic acids obtained from the condensation of 1-vinyl-^{1}-cyclohexene with dimethyl ester of mesaconic acid, are described. It was established that the trans-acids have an ortho-structure and are distinguished from each other only by the orientation of the hydrogen atom.

Institution : Acad. of Sc., USSR, The N. D. Zelinskiy Inst. of Org. Chem.

Submitted : April 6, 1954

Card 2/2 Pub. 40 - 12-27

Periodical . Izv. AN SSSR. Otd. khim. nauk 1, 89-97, Jan-Feb 1955

Abstract : Hydrogenation of the trans-acid and its anhydride with PtO results in the formation of individual compounds the properties of which are listed. Five references: 4 USA and 1 USSR (1943-1955).

KUCHEROV, V. F.

USSR/ Chemistry - Biochemistry

Card 1/1 Pub. 40 - 13/26

Authors : Nazarov, I. N.; Kucherov, V. F.; and Andreyev, V. M.

Title : The stereochemistry of cyclic compounds. Part 6. Lactonization of cis-and trans- Δ^4-octalin-1,2-dicarboxylic acids

Periodical : Izv. AN SSSR. Otd. khim. nauk 2, 289 - 297, Mar-Apr 1955

Abstract : Investigations were conducted to determine the lactonization of cis-methyl-Δ^4-octalin-1,2-dicarboxylic acid and to obtain data regarding the structure of the cis-lacto acids which are formed during the lactonization process. It was found that of all the epimeric trans-acids only a certain group of trans-acids is capable of lactonization. Trans-acids of other groups having double bonds between the cycles are not lactonizable. Experimental facts regarding steric hindrances observed during the lactonization are explained. Seven references: 2 USSR, 1 German, 1 Swiss, 2 USA and 1 French (1932-1955).

Institution : Acad. of Sc., USSR, The N. D. Zelinskiy Inst. of Organ. Chem.

Submitted : April 6, 1954

KUCHEROV, V. F.

USSR/ Chemistry - General chemistry

Card 1/1 Pub. 40 - 14/26

Authors : Nazarov, I. N., and Kucherov, V. F.

Title : The stereochemistry of cyclic compounds. Part 7. Geometrical isomerism of 4-methylcyclchexane-1,2-dicarboxylic acid

Periodical : Izv. AN SSSR. Otd. khim. nauk 2, 298 - 307, Mar-Apr 1955

Abstract : The stereochemistry of tri-substituted cyclohexane derivatives - 4-methyl-cyclohexane-1,2-dicarboxylic acid - was investigated for the purpose of establishing the absolute geometrical configuration of these cyclic compounds. The derivation of all four theoretically possible isomers of 4-methylhexa-hydrophthalic acid through hydrogenation of cis- and trans-4-methyl-Δ^4-cyclo-hexene-1,2-dicarboxylic acid and its anhydrides is discussed. The effect of heating and isomerizing media on the mutual stereochemical conversions of the four isomers is explained. Ten references: 2 USSR, 6 USA, 1 Scandi-navian and 1 German (1929-1954).

Institution : Acad. of Sc., USSR, The N. D. Zelinskiy Inst. of Organ. Chem.

Submitted : April 6, 1954

NAZAROV, I.N.; KUCHEROV, V.F.; KUDATOVA, G.P.

Research in the field of the stereochemistry of cyclic compounds Report no.8. Condensation of cis-1-vinyl-6,9-dimethyl-Δ^{4}-cyclohexanol with citraconic anhydride. Izv.AN SSSR. Otd.khim nauk no.3:487-500 My-Je '55. (MLRA 8:9)

1. Institut organicheskoy khimii im. N.D.Zelinskogo Akademii nauk SSSR.
(Cyclohexanol) (Citraconic anhydride)

Kucherov, V.F.

USSR/Chemistry - Organic chemistry

Card 1/1 Pub. 22 - 26/53

Authors : Nazarov, I. N., Acad.; Kucherov, V. F.; and Andreyev, V. M.

Title : The stereochemistry of diene condensation of 1-vinyl-Δ^1-cyclohexene with maleic anhydride and its geometrical isomerism of Δ^4-octalin-1,2-dicarboxylic acid

Periodical : Dok. AN SSSR 102/4, 751-754, Jun 1, 1955

Abstract : Interesting experimental data are presented regarding the diene condensation of 1-vinyl-Δ^1-cyclohexene with maleic anhydride. It was found that the condensation is followed by the formation of two possible steric isomers the conversion of which makes it possible to obtain all four possible geometrical isomers of Δ^4-octalin-1,2-dicarboxylic acid. A study of the thermal conversions of these acids showed that the isomer with anti-cis-configurations is the most stable and easily forming isomeric acid. Eleven references: 6 USA, 1 German and 4 USSR (1937-1955).

Institution : Acad. of Sc., USSR, The N. D. Zelinskiy Inst. of Org. Chem.

Submitted : March 29, 1955

KOCHEROV, V. F.

Geometric isomers of decahydronaphthalene-1,2-dicarboxylic acid and their transformations. I. N. Nazarov, V. F. Kucherov, and V. M. Andreev (N. D. Zelinskii Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Doklady Akad. Nauk S.S.S.R.* 102, 1127-30(1955); cf. preceding abstr.—Condensation of 1-vinylcyclohexene with maleic anhydride gave 2 isomers of *octahydronaphthalene-1,2-dicarboxylic anhydrides* (I), m. 54° and a liquid, which hydrogenated and hydrolyzed, resp., to the *decahydro acids*, m. 212°, and m. 153°, which are the *cis-syn-cis* and *trans-anti-cis* structures. *Mono-Me esters* of I were subjected to isomerization by heating with MeONa. Thus the *syn-cis* isomer gave *syn-cis ester* esterified at the 2-carboxyl, while saponification of the *syn-cis di-Me ester* with KOH gave mainly the *syn-cis mono-Me ester* esterified at 1-carboxyl; the former ester, m. 139°, the latter, m. 126°. Hydrogenation gave the *decahydro analogs*, m. 144°, and 121°, resp. Treatment with MeONa isomerized the satd. ester (m. 144°) yielding *cis-syn-trans-decahydronaphthalene-1,2-dicarboxylic acid*, m. 218° (*anhydride*, m. 76°); *di-Me ester*, m. 60°. The other mono-Me ester isomer isomerized with MeONa and hydrolyzed gave *cis-anti-trans-decahydronaphthalene-1,2-dicarboxylic acid*, m. 203° (*anhydride*, m. 138°; *di-Me ester*, m. 44°). Similarly were treated the mono-esters of *anti-cis* configuration. The liquid isomer of I (*anti-cis*) with MeOH gave the *mono-Me ester*, m. 137° (esterified mainly at *2-position*), which hydrogenated to the *trans-anti-cis-decahydronaphthalene-1,2-dicarboxylic acid mono-Me ester*, m. 85°, isomerized with MeONa to the *trans-anti-trans isomer* of the *free acid*, m. 200° (*di-Me ester*, m. 55°; *anhydride*, m. 115°). Hydrolysis of di-Me ester from the liquid anhydride I with 1 mole KOH gave a *mono-Me ester*, a liquid; hydrogenation of this gave the corresponding *trans-anti-cis isomer* of the *decahydro analog*, which failed to isomerize with MeONa and yielded the initial *trans-anti-cis dicarboxylic acid*, m. 153° (*anhydride*, m. 128°; *di-Me ester*, a liquid). This fact is peculiar to the *trans*-decahydronaphthalene configuration at the 1 and 9 carbons. Heating *cis-syn-cis* anhydride of the decahydro acid, m. 76°, to 250° gave a new *anhydride*, m. 60°, which probably has the *cis-anti-cis* configuration; its hydrolysis gave the corresponding *dicarboxylic acid*, m. 198°, which with CH_2N_2 gave *di-Me ester*, liquid. The anhydride with MeOH gave the *mono-Me ester* with cis-anti-cis configuration esterified at 2-carboxyl and m. 93°, which with MeONa gave the *free acid*, m. 263°, while conventional increase of chain length at the 1-carboxyl gave the corresponding *2-carboxydecahydronaphthalene-1-acetic acid*, m. 182°, which dehydrogenated and decarboxylated to 1-$MeC_{11}H_7$. Isomerization of the mono-Me ester (m. 93°) with MeONa gave the previously described cis-anti-trans dicarboxylic acid, m. 203°. Hydrolysis of the di-Me ester with 1 mole KOH gave the *mono-Me ester* at the 1-carboxyl (m. 95°) and the mixed *isomerization product*, m. 168°. The former, isomerized with MeONa, gave the known *cis-syn-trans dicarboxylic acid*, m. 218°, while the isomeric mono-Me ester gave (after treatment with CH_2N_2) *cis-anti-trans di-Me ester*, m. 44°. Arndt-Eistert method for chain increase gave, from this mono-ester, *1-carboxydecahydronaphthalene-2-acetic acid*, m. 199°, which dehydrogenated and decarboxylated to 2-$MeC_{11}H_7$. Thus of 8 possible isomers of decahydronaphthalene-1,2-dicarboxylic acid, 6 were isolated and identified; 4 are of the cis series and 2 of trans series. Three of the cis isomers heated to 250° are nearly quantitatively converted in 1 hr. to *cis-anti-cis* series; the *trans-anti* acid yields *trans-anti-cis* acid (as anhydride). Thus the most stable is the anti configuration at C atoms 1 and 9 with cis configuration of the anhydride ring (5 atomic). The unknown isomers of the trans series (*trans-syn-trans* and *trans-syn-cis*) are apparently rather unstable (cf. Robins and Walker, *C.A.* 49, 15836h). G. M. K.

(2)

Kucherov, V.F.

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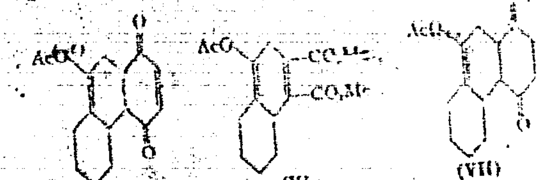
1-Acetoxyvinyl-1-cyclohexene [illegible] New path of synthesis of polycyclic [illegible] condensation. [illegible] the α-decalone nucleus. I. N. Nazarov, V. F. Kucherov, V. M. Andreev, and G. M. Segal' (N. D. Zelinskii Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). Doklady Akad. Nauk S.S.S.R. 104, 729-32(1955).—To a warm mixt. of 0.02 g. HgO, 1 ml. Ac_2O, and 0.6 ml. $BF_3 \cdot Et_2O$ was added [illegible] 6 ml. AcOH, 1 ml. Ac_2O and the mixt. [illegible] 0.5 hr. with 16.? g. 1-ethynyl-1-cyclohexene [illegible] and 1 ml. Ac_2O, after 30 min. diluted with [illegible] poured into cold 10% Na_2CO_3 yielded [illegible] 37% 1-acetoxyvinyl-1-cyclohexene [illegible] n_D^{20} 1.4972, d_{20} 1.0072. Hydrolysis with [illegible] (semicarbazone [illegible]) 1-acetyl-1-cyclohexene, b. 70-80°, n_D^{20} 1.4902 (semicarbazone, m. 220-1°). Refluxing 8 g. I with 4 g. $CH_2:CHCO_2Me$ in [illegible] PhMe with a little pyrogallol 15 hrs. gave [illegible] Δ⁸-octahydronaphthalene-1-carboxylate (II), [illegible] 1.4910, d_{20} 1.1030. Similarly, I and maleic anhydride in refluxing C_6H_6 gave 81% anti-cis-[illegible]-acetoxy-Δ⁸-octahydronaphthalene-1,2-dicarboxylic anhydride (III), m. 200-1°. I and benzoquinone similarly gave 67% IV, m. 121°, while I [illegible]



(IV) (V) (VII)

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Nazarov, I. N. ...

and $(:CCO_2Me)_2$ in boiling MePh apparently gave 81% V, m. 121-4°. II consists of 2 epimers with respect to the H atom at C_4; hydrolysis with KOH gave pure *trans-anti-4-oxo-decahydronaphthalene-1-carboxylic acid*, m. 159° (Me ester, m. 68°), which on Clemmensen reduction gave *trans-anti-decahydronaphthalene-1-carboxylic acid*, m. 88° [illegible] m. 223°). The other epimeric acid was [illegible] m. 92° of *trans-syn-4-oxo-decahydronaphthalene* [illegible] *acid*. Clemmensen reduction of which [illegible] the resulting acid gave *trans-syn-decahydro* [illegible] *amide*, m. 112° (cf. Hückel, C.A. 32, [illegible]). III [illegible] the corresponding *anhydro dicarboxylic acid* [illegible] ester, m. 62°); the free acid with [illegible] *decahydronaphthalene-1,2-dicarboxylic acid* (VI) [illegible] Clemmensen reduction gave *trans-anti-trans-decahydronaphthalene-1,2-dicarboxylic acid*, m. 173° (cf. C.A. 50 [illegible]). The *anti*-cis-di-Me ester, m. 62°, [illegible] a di-Me ester, m. 101°, corresponding to that of VI [illegible] isomer); however, reqm. with 0.5% MeOH [illegible] *trans-anti-trans-4-oxo-decahydronaphthalene* [illegible] m. 92° (2,4-dinitrophenylhydrazone [illegible]) reduction of which gave *trans-anti-trans-decahydronaphthalene-1,2-dicarboxylic acid*, m. 188° (cf. loc. cit.). Hydrogenation of IV gave VII, which with 2% HCl gave *trans-anti-1,4-dimethylperhydrophenanthrene*, m. 138°. G. M. K.

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Name: KUCHEROV, Viktor Fedorovich

Dissertation: Research in the field of stereochemistry of alicyclic carboxylic acids

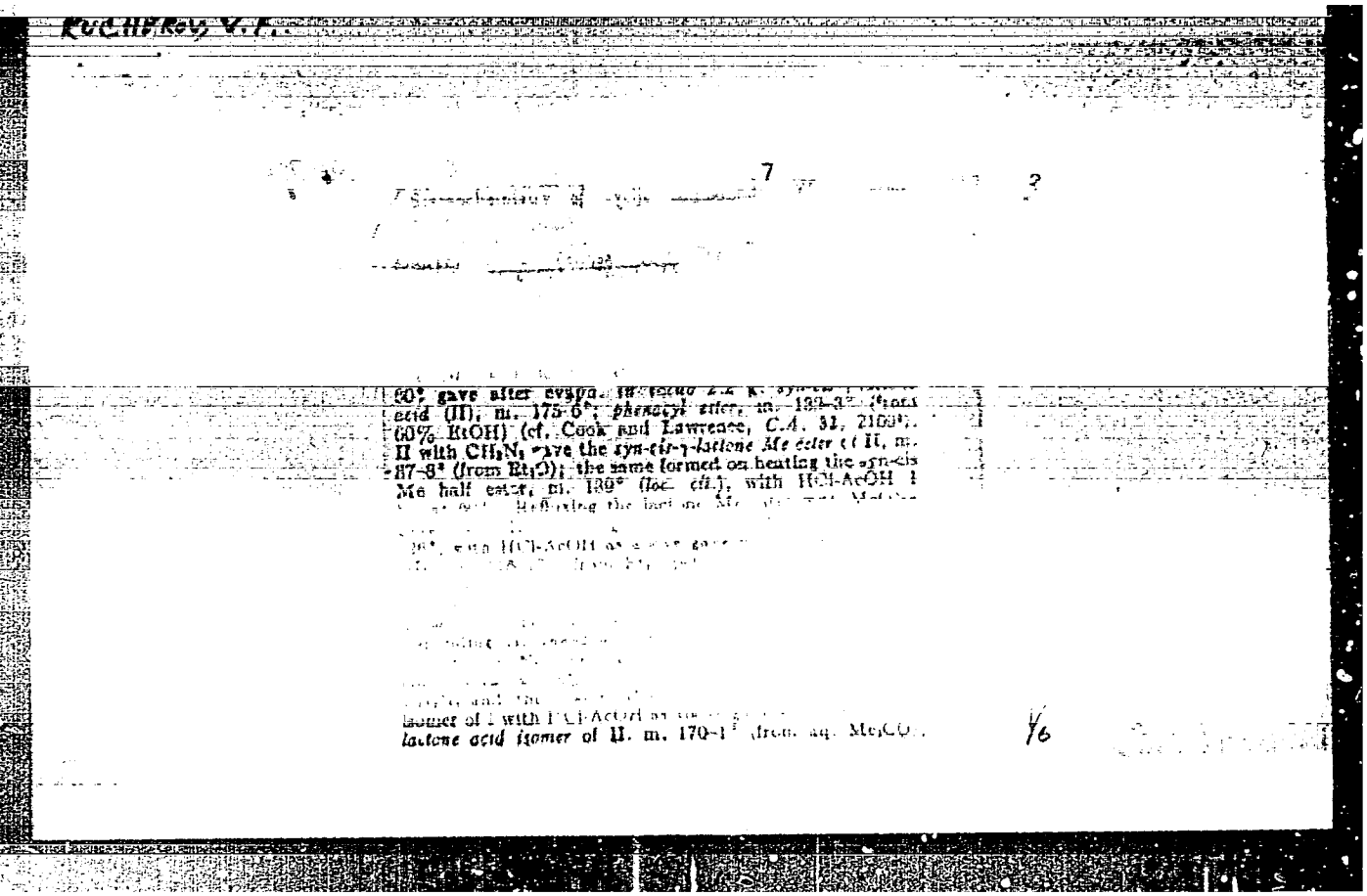
Degree: Doc Chem Sci

Affiliation: [not indicated]

Defense Date, Place: 29 Mar 56, Council of Inst of Organic Chemistry imeni Zelinskiy, Acad Sci USSR

Certification Date: 26 May 56

Source: BMVO 4/57



60°, gave after evapn. in vacuo [illegible] acid (II), m. 175-6°; *phenacyl ester*, m. 132-3° (from 60% EtOH) (cf. Cook and Lawrence, *C.A.* 31, 2109⁹). II with CH_2N_2 gave the *syn-cis-γ-lactone Me ester* (III, m. 87-8° (from Et_2O)); the same formed on heating the *syn-cis* Me half ester, m. 130° (*loc. cit.*), with HCl-AcOH [illegible] lactone of I with HCl-AcOH [illegible] *lactone acid isomer* of II, m. 170-1° (from aq. Me_2CO).

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phenacyl ester, m. 127-8° the acid with CH_2N_2 gave the *syn-trans-lactone Me ester*, m. 98-9° which refluxed 15 hrs with MeONa-MeOH gave on acidification [illegible] *lactone acid*, m. 173-4° identical [illegible] anti-cis isomer of II with [illegible] *trans-cis-δ-lactone acid* IV, m. [illegible] tion occurs at the [illegible] carboxyl, [illegible] Evapn. of the Et_2O mother liquor from the [illegible] gave 40% [illegible] dicarboxylic [illegible] V [illegible] compn. (from Et_2O-petr. ether), [illegible] NaOH 10 min. gave on acidification 60% cis-dicarboxylic acid, m. 194-5°, identical with the [illegible] above. Refluxing V with H_2O 2.5 hr. gave [illegible] lactone acid, m. 193-5°, identical with IV [illegible] gave an *anti-cis-δ-lactone Me ester*, [illegible] refluxing with MeONa-MeOH and [illegible] the initial IV. Heating anti-cis Me [illegible] ester (loc. cit.) with AcOH-HCl 2 hrs. at 60° gave 80% anti-cis-δ-lactone acid, identical with IV. The liquid isomer of the 1-anti-cis mono-Me ester heated similarly with AcOH-HCl gave an uncrystallizable Cl-contg. product; refluxing the material with 20% NaOH and acidifying gave a low yield of the *cis dicarboxylic acid*, m. 19[illegible], identified as the Δ^1 isomer described above. Heating the anti-trans dicarboxylic acid (*loc. cit.*) with AcOH-HCl as above gave mainly unchanged starting material. Thus, II forms from syn-cis I in such a manner that only the polar CO_2H in 1-position [illegible]

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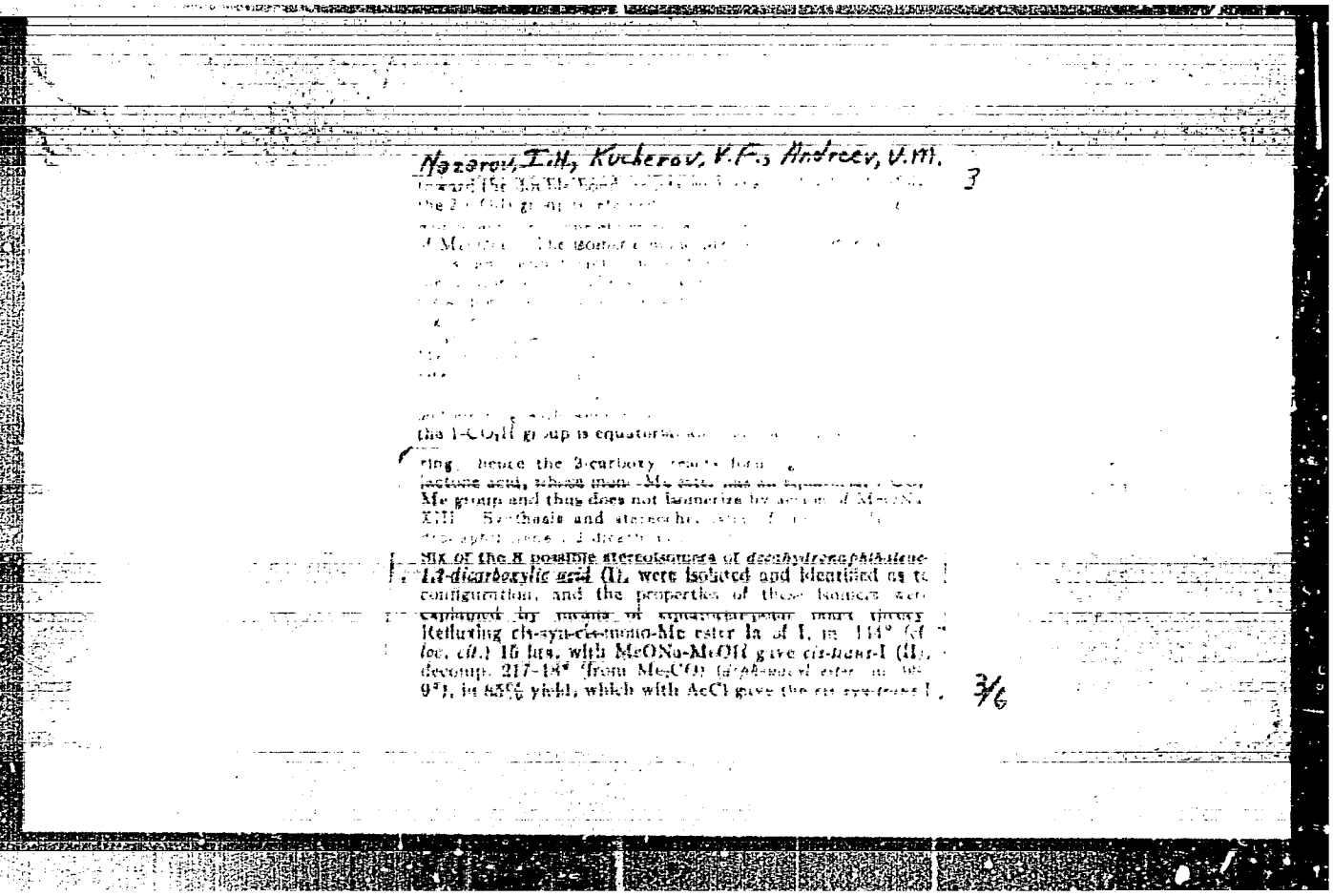

Nazarov, I.N., Kucherov, V.F., Andreev, V.M.

3

the 1-CO_2H group is equatorial

ring, hence the 3-carboxy

lactone acid, whose meth-Me ester

Me group and thus does not isomerize by

XIII. Synthesis and stereochem

Mix of the 8 possible stereoisomers of *decahydronaphthalene-1,3-dicarboxylic acid* (I), were isolated and identified as to configuration, and the properties of these isomers were explained by means of conformational principles. Refluxing cis-syn-cis-trans-Me ester Ia of I, m. 114° (cf. *loc. cit.*) 16 hrs. with MeONa-MeOH gave *cis-trans*-I (II), decomp. 217-18° (from Me_2CO) (diMe ester, m. 98-9°), in 85% yield, which with AcCl gave the cis-syn-trans I

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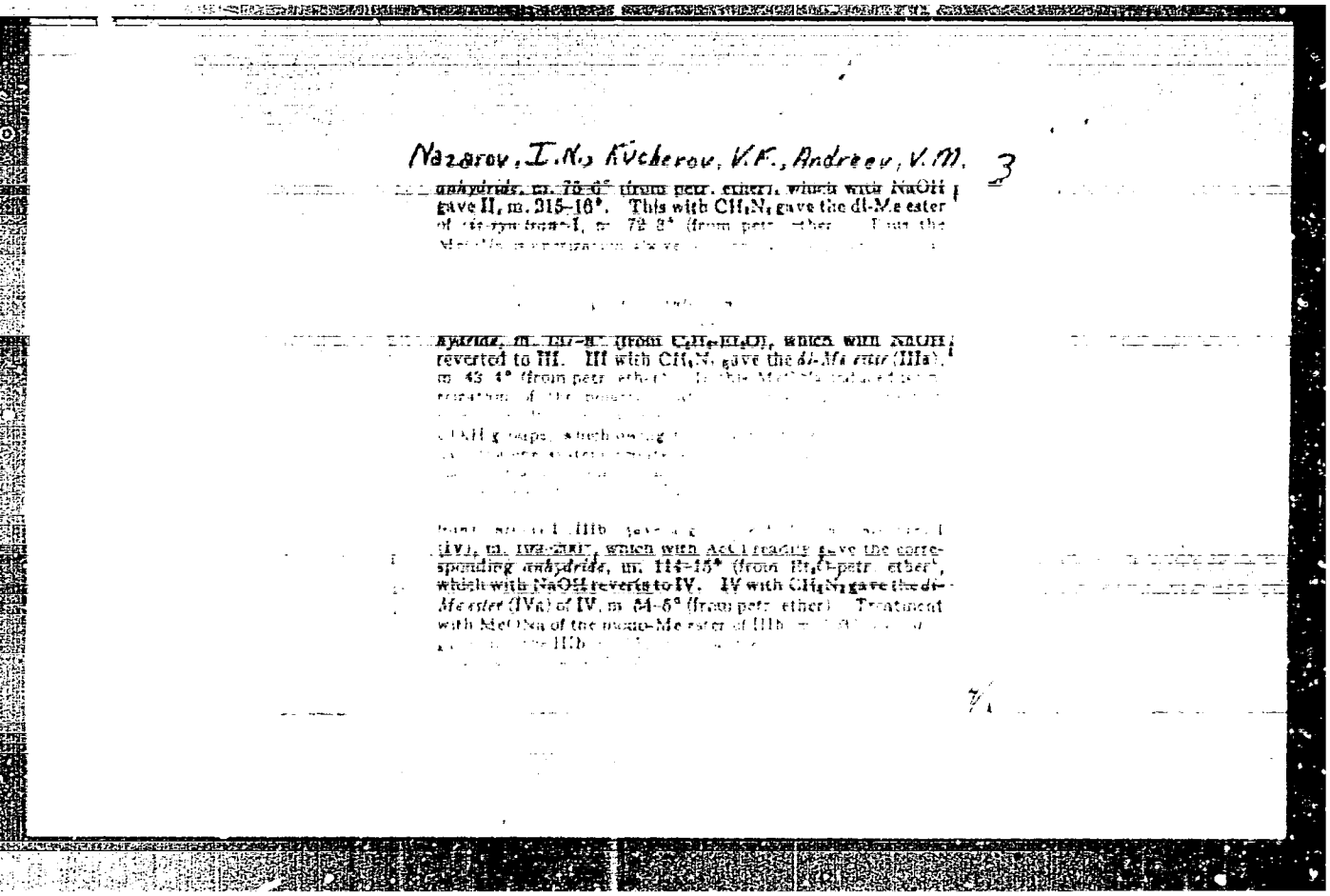

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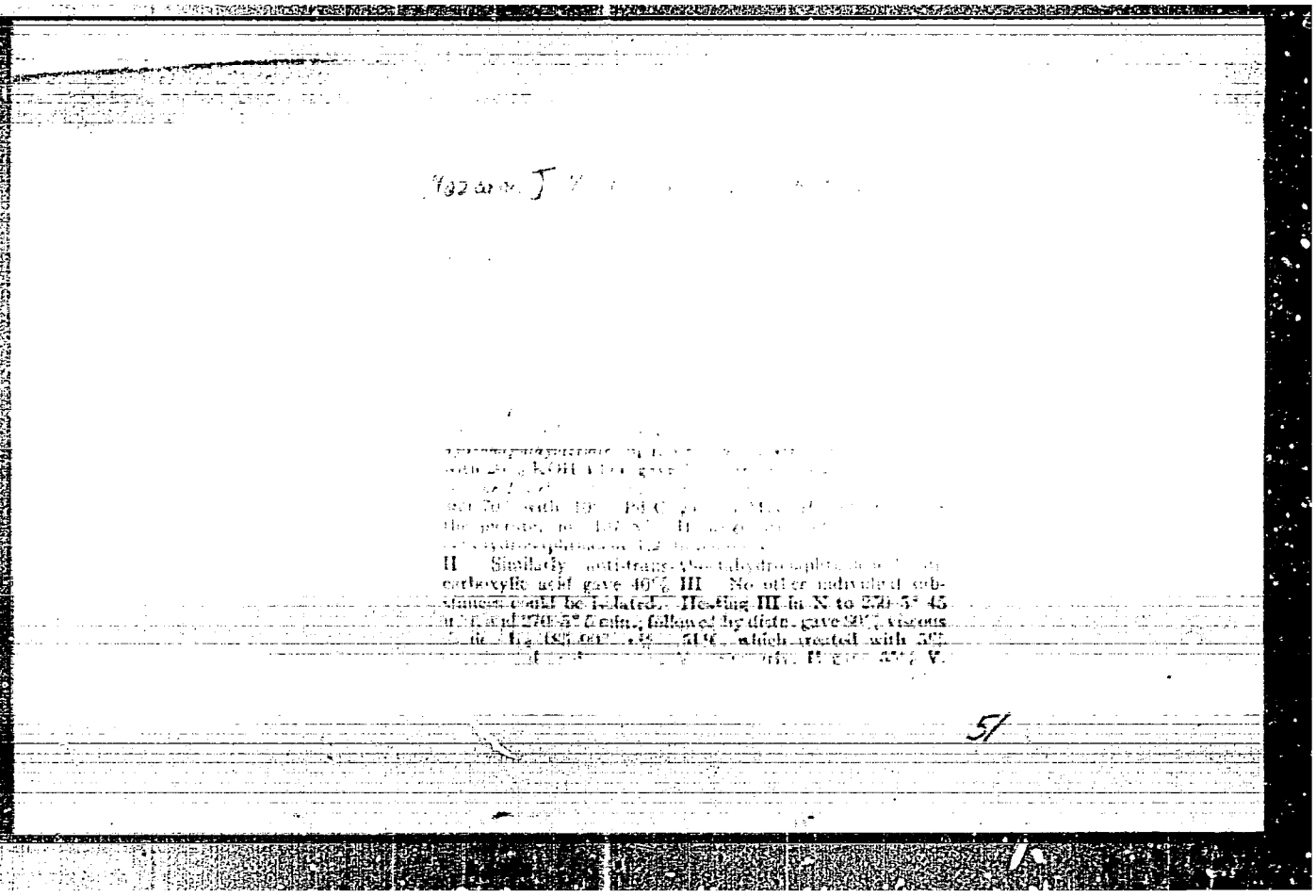
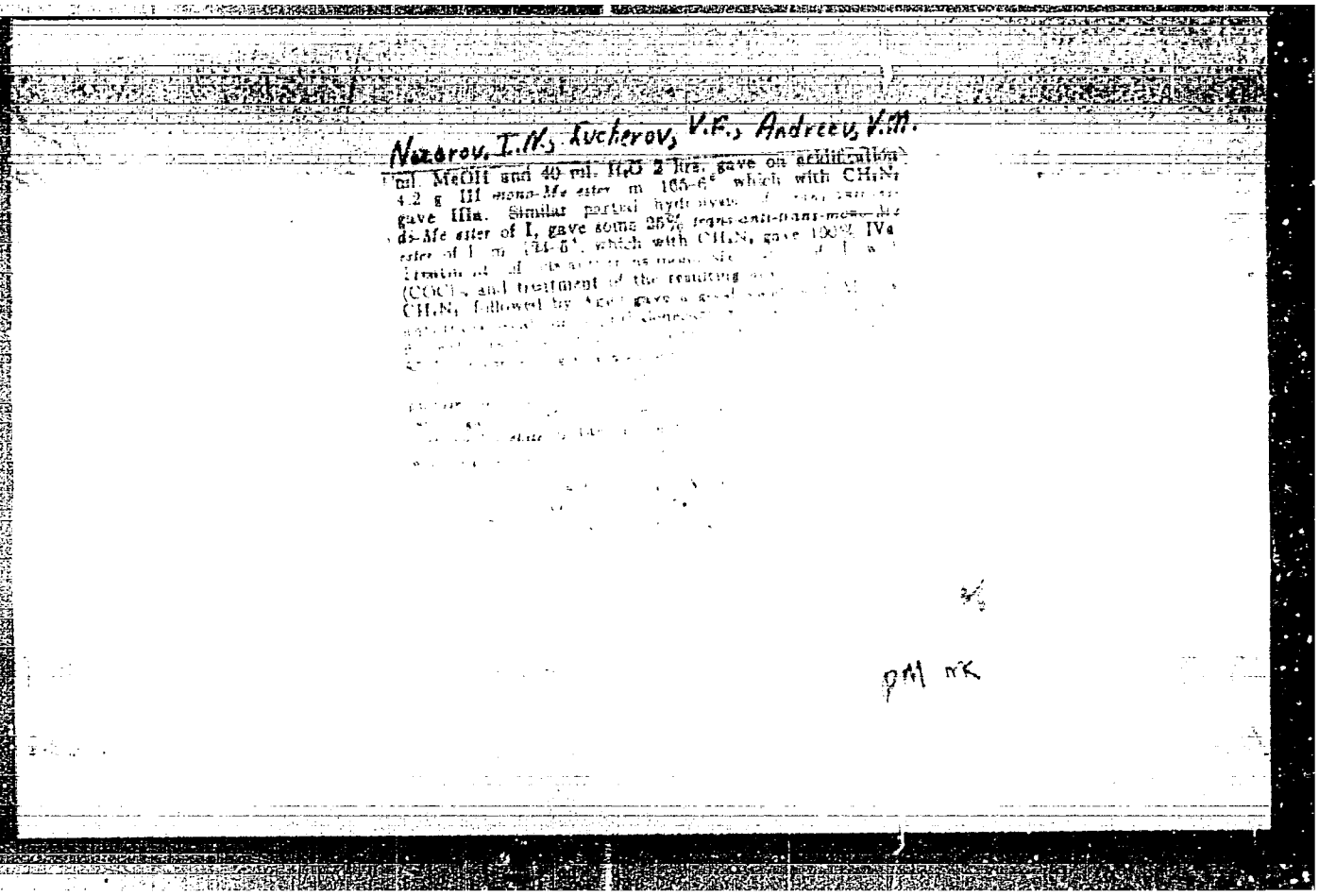
anhydride, m. 78-9° (from petr. ether), which with NaOH gave II, m. 315-16°. This with CH_2N_2 gave the di-Me ester of cis-syn-trans-I, m. 72.2° (from petr. ether). From the

Anhydride, m. 117-8° (from C_6H_6-Et_2O), which with NaOH reverted to III. III with CH_2N_2 gave the *di-Me ester* (IIIa), m. 45.4° (from petr. ether).

(IV), m. 192-3°, which with AcCl readily gave the corresponding *anhydride*, m. 114-15° (from Et_2O-petr. ether), which with NaOH reverts to IV. IV with CH_2N_2 gave the *di-Me ester* (IVa) of IV, m. 54-5° (from petr. ether). Treatment with MeONa of the mono-Me ester of IIIb



orthoxylic acid gave 46%. III. No other individual substances could be isolated. Heating III in N to 270–5° 45 min., followed by distn. gave 2% viscous



Nazarov, I.N., Zucherov, V.F., Andreev, V.M.

ml. MeOH and 40 ml. H_2O 2 hrs. gave on acidification
4.2 g III *mono-Me ester* m 165-6° which with CH_2N_2
gave IIIa. Similar partial hydr[illegible] gave some above *trans-anti-trans-mono-Me di-Me ester* of I, gave some above *trans-anti-trans-mono-Me ester* of I m 244-6°, which with CH_2N_2 gave 100% IVa
[illegible] ($COCl_2$ and treatment of the resulting [illegible] CH_2N_2 followed by [illegible] gave a good [illegible]

pm nk

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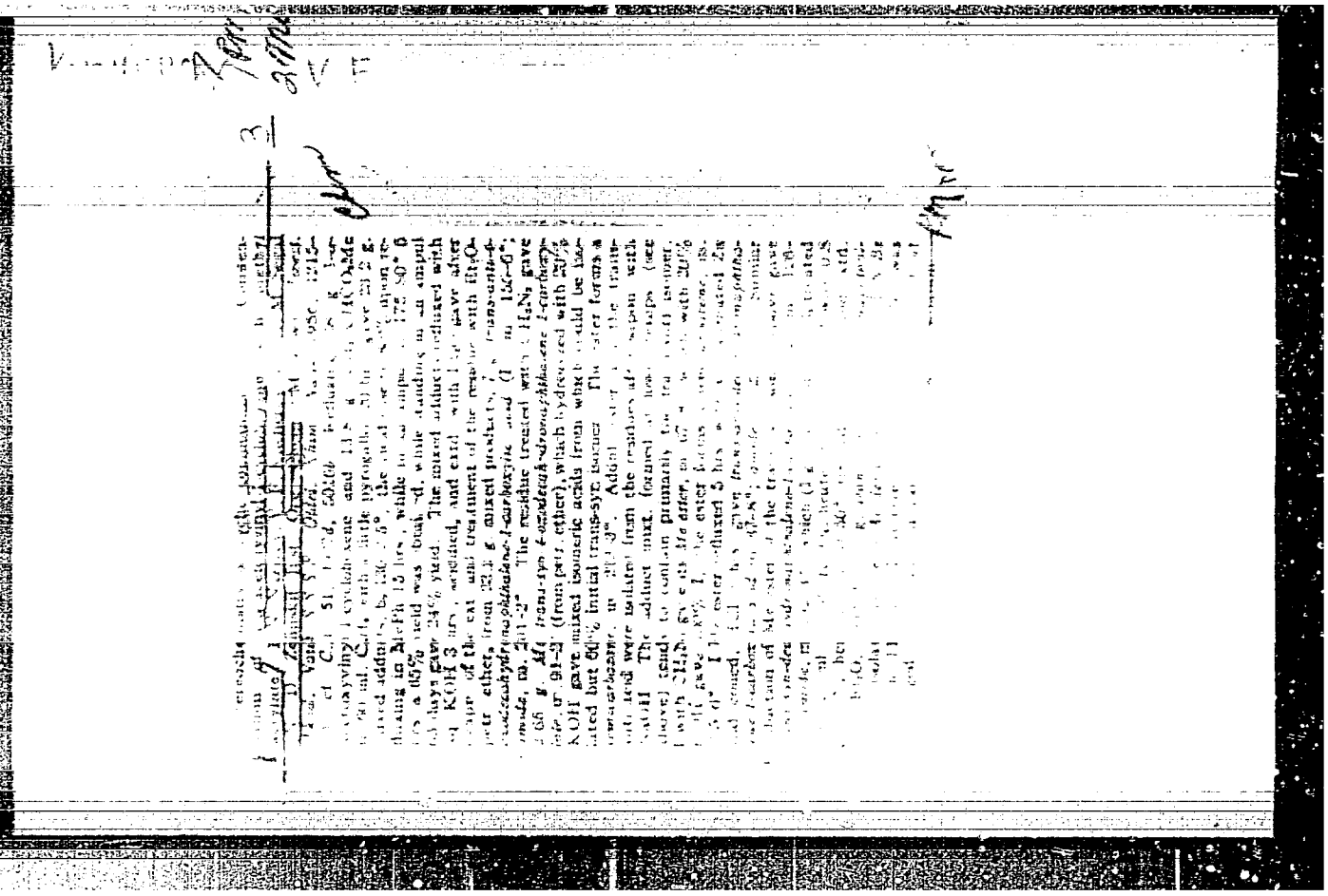
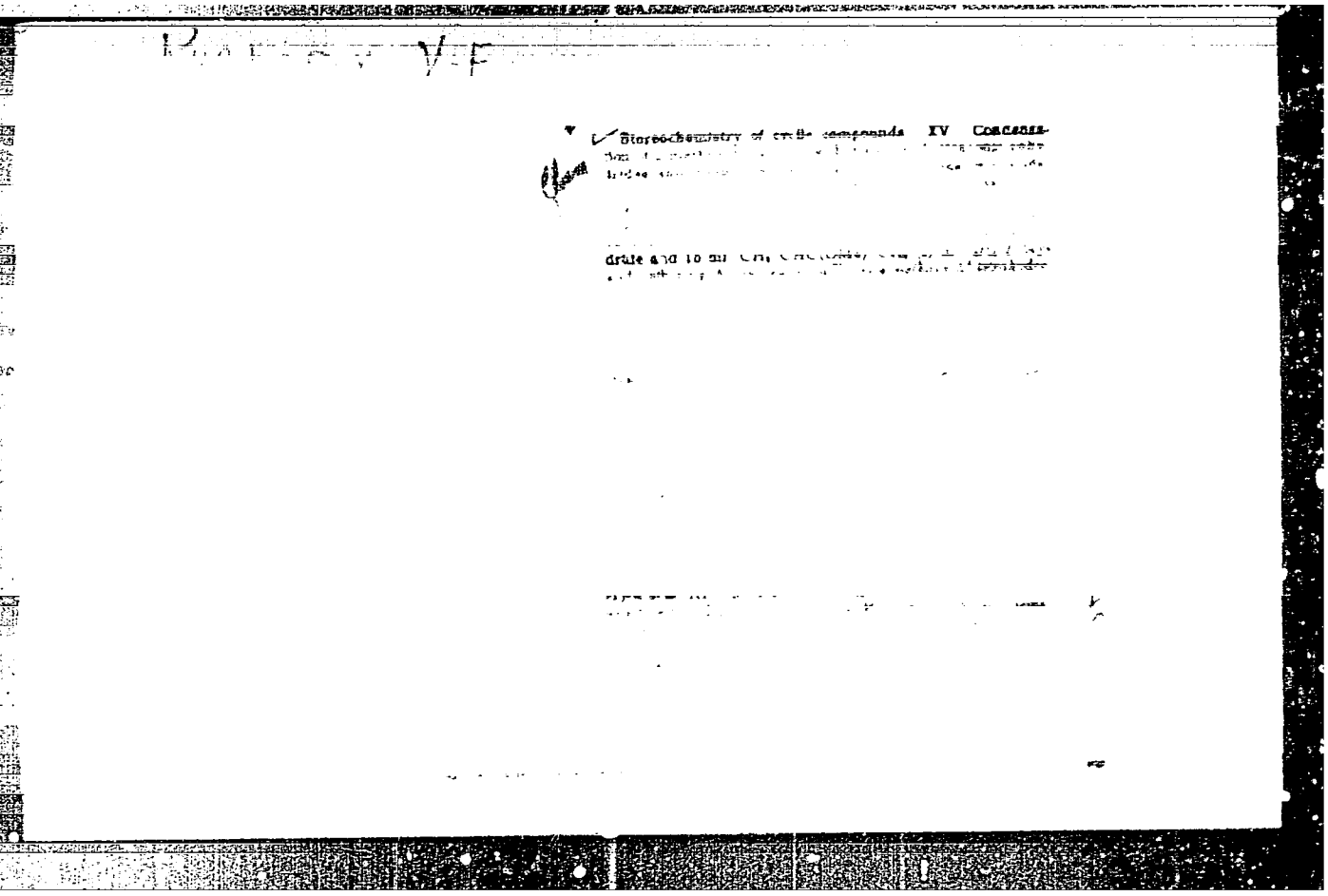
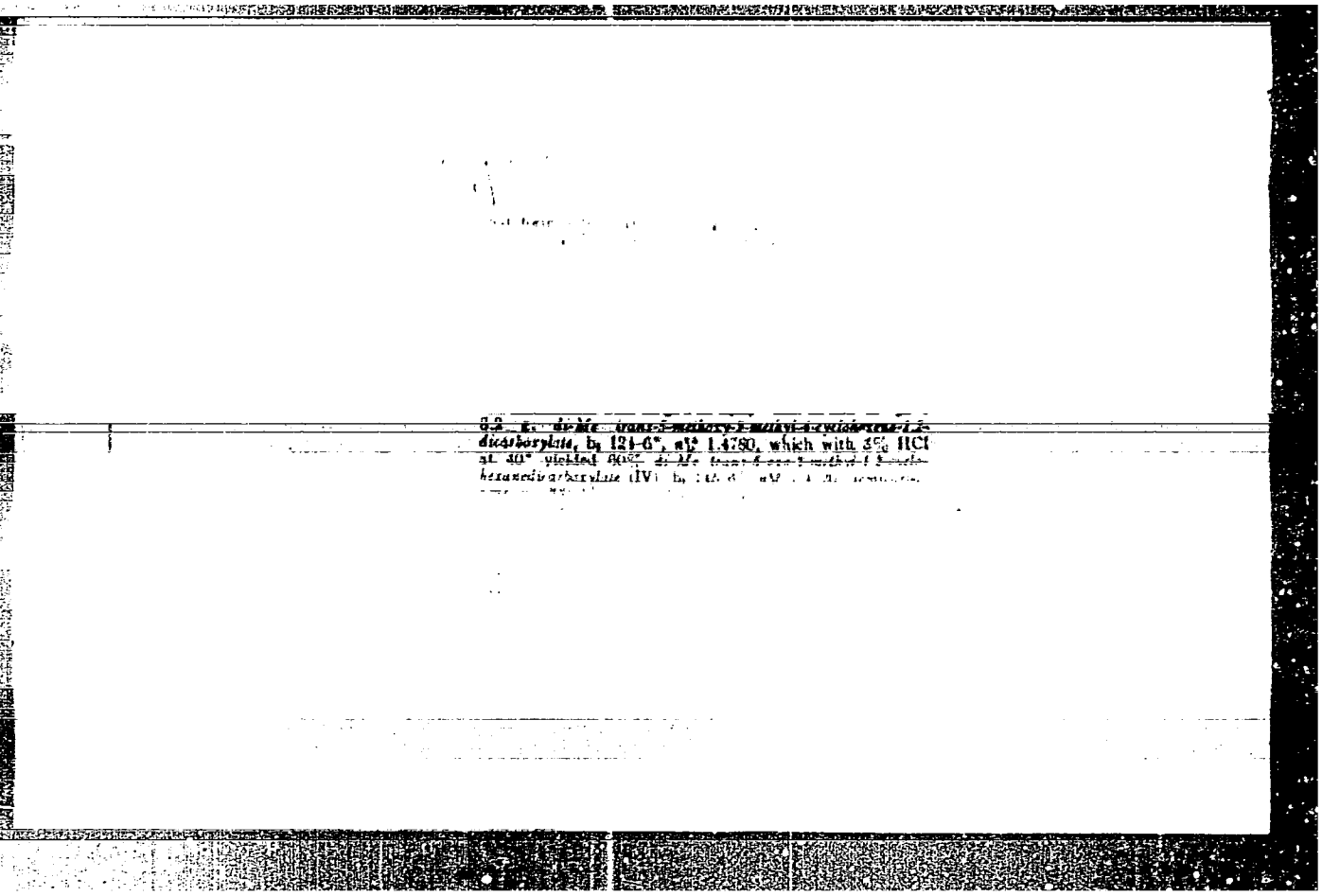






NAZAROV, I.N.; KUCHEROV, V.F.; SEGAL', G.M.

Research in the stereoc hemistry of cyclic compounds. Part 9. Condensation of 1-vinyl-Δ^{1}-cyclohexene with methyl acrylate. Izv.AN SSSR.Otd.khim. nauk no.5:559-568 My '56. (MLRA 9:9)

1.Institut organicheskoy khimii imeni N.D.Zelinskogo Akademii nauk SSSR.
(Cyclohexene) (Acrylic acid)

NAZAROV, I.N.; KUCHEROV, V.F.; ANDRIYEV, V.M.

Research in the field of stereochemistry of cyclic compounds. Part 10 Stereochemistry of the diene condensation of 1-vinyl- Δ^1-cyclohexene with maleic anhydride. Izv.AN SSSR Otd.khim.nauk no.6:715-722 Je '56. (MLRA 9:9)

1.Institut organicheskoy khimii imeni N.D.Zelinskogo Akademii nauk SSSR.
(Cyclohexene) (Maleic anhydride) (Stereochemistry)

NAZAROV, I.N.; KUCHEROV, V.F.; ANDREYEV, V.M.

Research in the stereochemistry of cyclic compounds. Part 11. Stereochemistry of $\Delta^{1'}$-octalin-1,2-dicarboxylic acids. Izv. AN SSSR Otd.khim.nauk no.7:817-826 Jl '56. (MLRA 9:10)

1.Institut organicheskoy khimii imeni N.D.Zelinskogo Akademii nauk SSSR.
(Acids, Fatty) (Stereochemistry)

NAZAROV, I.N.;KUCHEROV, V.F.;ANDREYEV, V.M.

Research in the stereochemistry of cyclic compounds. Part 13. Synthesis and stereochemistry of isomeric decalin-1.2-dicarboxylic acids. Izv. AN SSSR. Otd.khim.nauk no.9:1091-1101 S '56. (MLRA 9:11)

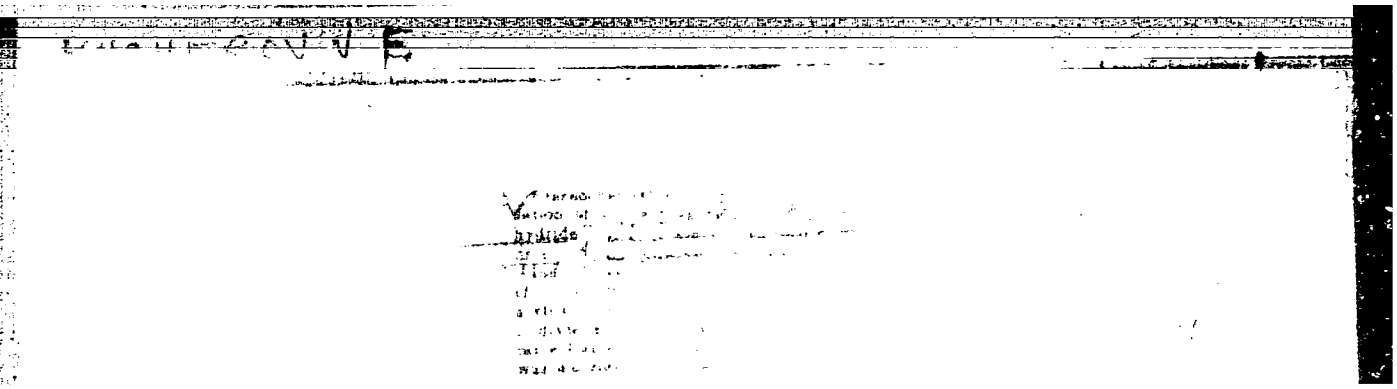
1. Institut organicheskoy khimii imeni N.D.Zelinskogo Akademii nauk SSSR.

(Naphthalenedicarboxylic acid)

KUCHEROV, V.F., and NAZAROV, I.N.

AS USSR

"Orientation sterique et structurale dans les condensations dieniques de vinylcyclenes et stereochimie des produits de ces reactions," paper submitted at 16th International Congress of Pure and Applied Chemistry, Paris, 18-24 July 1957



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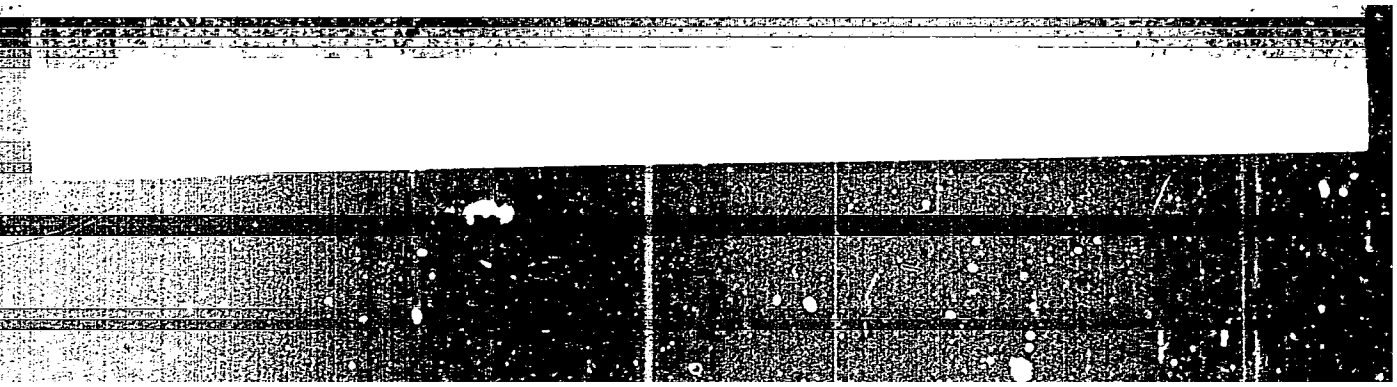

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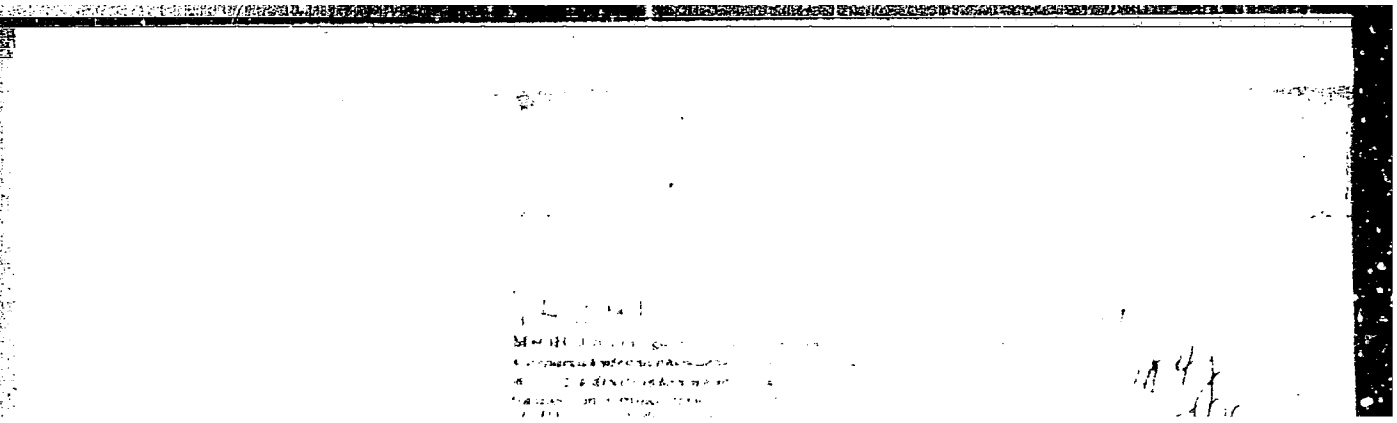

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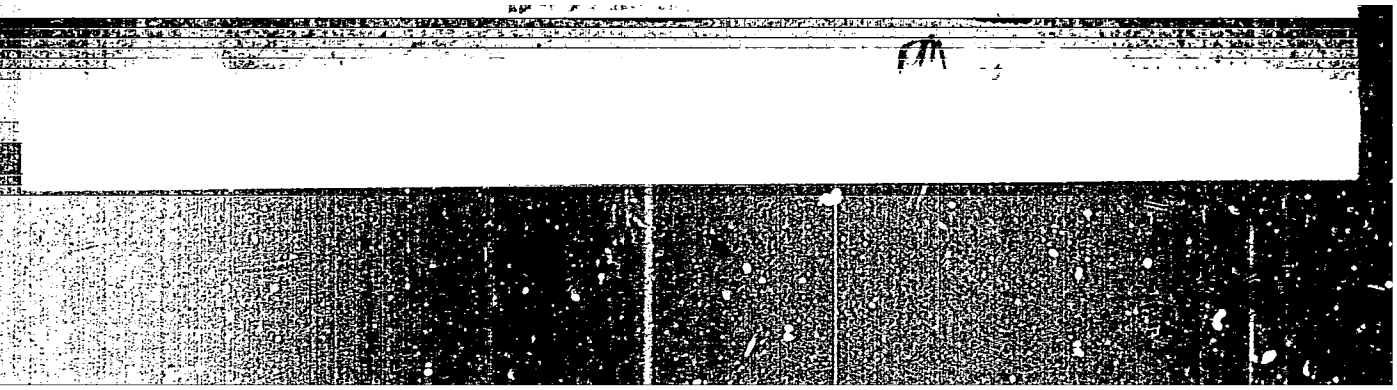

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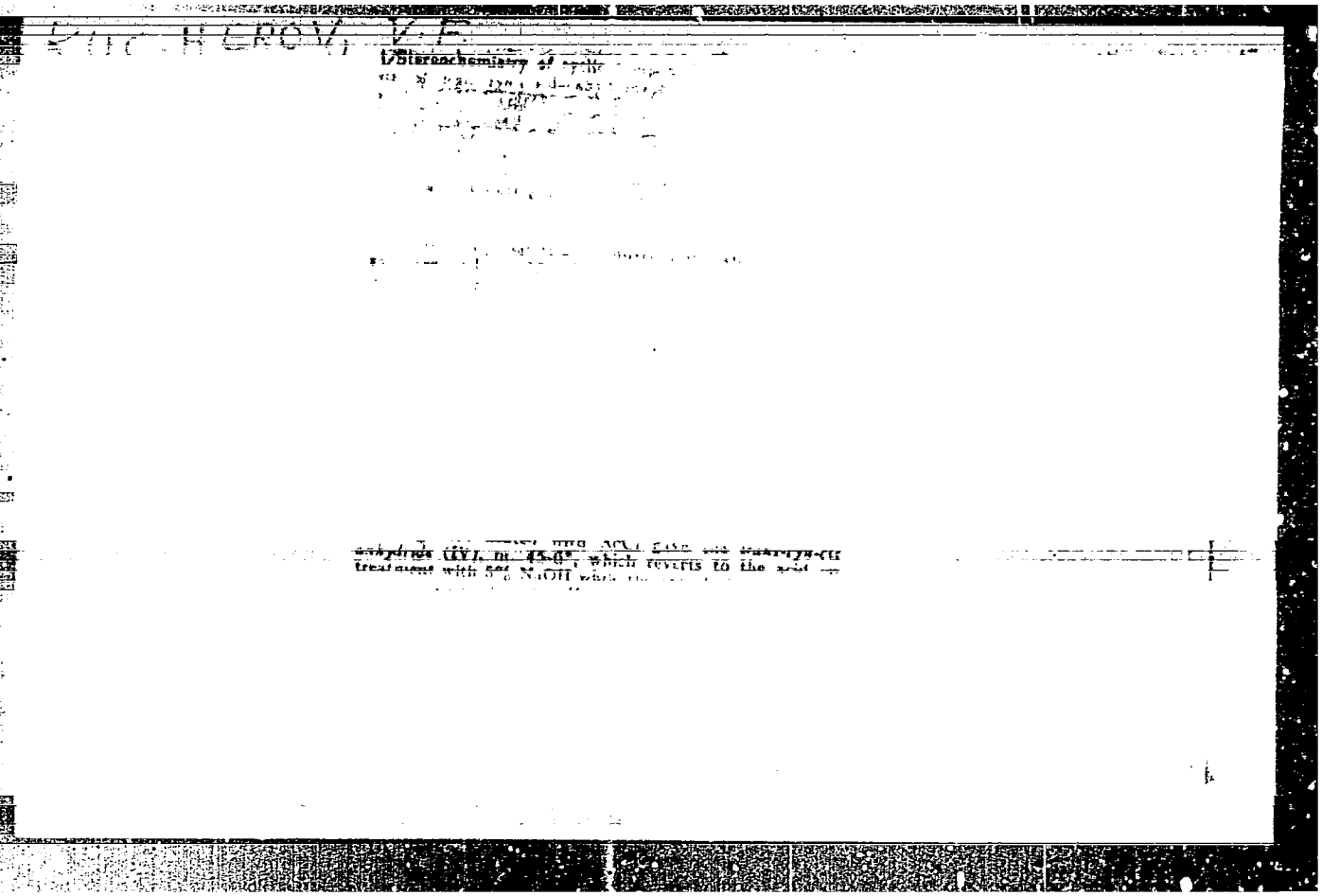

KUCHEROV, V.F

62-1-13/21

AUTHORS: Nazarov, I. N.; Kucherov, V. F.; Bukharov, V. G.

TITLE: Investigation into the Field of Stereochemistry of Cyclic Compounds. Part 16. Stereochemistry of Diene Condensation of Cyclopentadiene with Citraconic Anhydride and Steric Conversions of Endo- and Exo-additives (Issledovaniye v oblasti stereokhimii tsiklicheskikh soyedineniy. Soobshcheniye 16. Stereokhimiya diyenovoy kondensatsii tsiklopentadiyena s tsitrakonovym angidridom i prostranstvennyye prevrashcheniya endo- i ekzoadduktov)

PERIODICAL: Izvestiya Akademii Nauk SSSR, Otdeleniye Khimicheskikh Nauk, 1957, No. 1, pp. 91-99 (U.S.S.R.)

ABSTRACT: In order to study the stereochemistry of the diene synthesis, the authors investigaged the condensation of cyclopentadiene with citraconic anhydride at a temperature of 190 - 195°. It was found that the condensation goes in both possible steric directions and leads to the formation of a mixture of stereoisomeric endo- and exo-anhydrides, from which a 30% yield of exo-acid was separated after saponification. It was also established that the condensation at increased temperatures violates the principle of "accumulation of

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Inst. Organic Chemistry im N D Zelinskiy, Acad. Sci USSR

62-1-13/21

Investigation into the Field of Stereochemistry of Cyclic Compounds. Part 16

Nonsaturizability" with the formation of an exo-additive. The configuration of the stereoisomeric anhydrides was confirmed by studying the lactonization and mutual steric conversions of the homologous acids. Experiments showed that the lactonization of the endo-acid, regardless of the endo-position of both carboxyl groups, follows only the tertiary carboxyl and that the gamma-lacto acid with trans-orientation of the methyl and carboxyl groups is more stable. Saturated exo-cis-anhydride obtained through hydrogenation of another exo-cis-anhydride (II) after saponification gives a saturated exo-cis-acid which together with diazomethane, forms exo-cis-diester.

There are 12 references, of which 2 are Slavic.

Card 2/3

62-1-13/21

Investigation into the Field of Stereochemistry of Cyclic Compounds. Part 16

ASSOCIATION: Academy of Sciences of the USSR, Institute of Organic Chemistry imeni N. D. Zelinskiy

PRESENTED BY:

SUBMITTED: December 2, 1955

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Card 3/3

NAZAROV, I.N.

YUGOSLAVIA/Organic Chemistry. Synthetic Organic Chemistry. G

Abs Jour: Ref Zhur-Khimiya, No 22, 73969.

Author : I.N. Nazarov, V.F. Kucherov, V.M. Andreyev, G.M. Segal'.

Inst :

Title : Upon the Spatial Directivity of Diene Condensations and Stereochemistry of Cyclic Carboxylic Acids.

Orig Pub: Croat. chem. acta, 1957, 29, No 3-4, 369-392.

Abstract: Trans-1,2-dimethylbutadiene-1,3 (I) was prepared by the dehydration of methylethylvinylcarbinol at 300 to 310° on $MgSO_4$, yield - 50 to 60%, boil. p. - 76.5 to 78°, $n^{20}D$ - 1.4515. Boiling (4 hours) 51.5 g of I with 56 g of malein anhydride in C_6H_6 resulted in anhydride (III) of cis-cis-3,4-dimethyl-Δ^4-cyclohexenedicarboxylic-1,2 acid (IV), yield - 56.5 g,

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YUGOSLAVIA/Organic Chemistry. synthetic Organic Chemistry. G

Abs Jour: Ref Zhur-Khimiya, No 22, 73969.

melt. p. - 67 to 68° (from ether - petroleum ether). 17.3 g of IV, melt. p. 172 to 173° (dissociates, from water) was obtained from the mother liquor by saponification after separation of III. The boil. p. of dimethyl ester of IV (V) is 122 to 123°/5 mm, $n^{20}D$ = = 1.4750, d_4^{20} = 1.0987. The thermal isomerization of III (210 to 215°, 4 hours, N_2 flow) in the presence of diethylaniline led to a mixture of substances, boil. p. - 186 to 188°/35 mm, $n^{20}D$ = 1.4950, from which cis-trans-3,4-dimethyl-Δ^4-cyclohexanedicarboxylic-1,2 acid (VI) was separated after saponification, yield - 60%, melt. p. - 160 to 161° (from water); anhydride of VI (VII), melt. p. - 46 to 47 (from petroleum ether); dimethyl ester of VI (VIII), boil. p. 116 to 117°/5 mm, $n^{20}D$ = 1.4730, d_4^{20} = 1.0921.

Card : 2/14

YUGOSLAVIA/Organic Chemistry. Synthetic Organic Chemistry. G

Abs Jour: Ref Zhur-Khimiya, No 22, 73969.

2-monomethyl ester of IV (IX), yield 3.1 g, melt. p. 114 to 115° (from ether + petroleum ether, 1 : 1) and 2-monomethyl ester of VI (X), yield 1.05 g, melt. p. 112 to 113° (from 50%-ual CH_3OH) were produced by partial saponification of 4.4 g of V and 1.9 g of VIII correspondingly with 1 mole KOH solution. Trans-trans-3,4-dimethyl- Δ^4 -cyclohexene-dicarboxylic -1,2 acid (XI), yield 0.9 g, melt. p. 149 to 150°, and its trans-cis-isomer (XII), yield 0.4 g, melt. p. 184 to 185° (from water) were synthetized by the isomerization of 1.2 g of IX and 0.6 g of X correspondingly by boiling with CH_3ONa and absolute CH_3OH and following saponification. The melting points of XI and XII anhydrides were 100 to 101° (from ether + petroleum ether) and 100 to 101° (from ligroin)

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correspondingly. Cis-cis-1,4-lacto-3,4-dimethyl-cyclohexanecarboxylic-2 acid (XIII) was obtained by heating 5 g of IV (1 hour, 60°) in glacial CH_3-COOH saturated with HCl (gas), yield 3.4 g, melt. p. 186 to 187° (water), the melt. p. of the methyl ester thereof was 109 to 110° (from 70%-ual CH_3OH). Under these conditions, XII (0.9 g) undergoes a preliminary cycle conversion producing trans-cis-1,4-lacto-3,4-dimethylcyclohexane-carboxylic-2 acid (XIV) in the result of a following lactonization, yield 0.55 g, melt. p. 154 to 155° (from 20%-ual aqueous acetone). Methyl ester of XIV, melt. p. 57 to 58° (from petroleum ether + ether) produced XIII by isomerization with CH_3ONa and following saponification. Similarly,

YUGOSLAVIA/Organic Chemistry. Synthetic Organic Chemistry.

Abs Jour: Ref Zhur-Khimiya, No 22, 73969.

2.5 g of VI are lactonized into a mixture, from which 1.1 g of cis-trans-2,4-lacto-3,4-dimethylcyclohexanecarboxylic-1 acid (XV), melt. p. 199 to 201° (from 15%-ual aqueous acetone) was separated. After the separation of XV, the mother liquor was treated with CH_2N_2 and 0.75 g of ester, melting p. 63 to 65°, was obtained; that ester, after saponification, produced cis-trans-1,4-lacto-3,4-dimethylcyclohexanecarboxylic-2 acid, yield 0.6 g, melt. p. 161 to 162° (from water). Under the same conditions, XI (2.2 g) produced only 0.7 g trans-3,4-dimethyl-Δ^5-cyclohexenedicarboxylic-1,2 acid of melt. p. 161 to 162° (from water). It was established that the catalytic hydrogenation of 2.15 g of IV on Pt in CH_3OH proceeds spatially

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YUGOSLAVIA/Organic Chemistry. Synthetic Organic Chemistry.

Abs Jour: Ref Zhur-Khimiya, No 22, 73969.

selectively from the side opposite to COOH groups and led to cis-cis-cis-3,4-dimethylcyclohexanedicarboxylic-1,2 acid (XVI), yield 2 g, melt. p. 187 to 188° (dissociates, from 50%-ual acetone). 10 g of III was converted into 9.6 g of anhydride of XVI (XVII), boil. p. 145 to 146° /5 mm, n_D^{20} = 1.4835, d_4^{20} = 1.1435 in a similar way (but in C_6H_6). Boiling of 5.9 g of XVII in absolute CH_3OH led to 1-monomethyl ester of XVI, yield 4.25 g, melt. p. 110 to 111° (from 60%-ual CH_3OH), 1.5 g of which yielded 1.2 g of trans-cis-cis-3,4-dimethylcyclohexanedicarboxylic-1,2 acid (XVIII), melt. p. 183 to 184° (from water) by isomerization with CH_3ONa and following saponification; anhydride of XVIII, melting

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YUGOSLAVIA/Organic Chemistry. Synthetic Organic Chemistry. G

Abs Jour: Ref Zhur-Khimiya, No 22, 73969.

acid (XXXIV), melt. p. 183° (from acetone) was precipitated by the dissolution of 3.5 g of XXXII in aqueous NaOH and following acidification with HCl (acid), while 1.5 g of XXXIII produced chlorohydrin under these conditions; chlorohydrin converts at 130° into 1.1 g of cis-cis-trans-cis-2,4-lacto-3,4-dimethyl-5-chloro-cyclohexanedicarboxylic acid, melt. p. 173 to 174° (from 20%-ual acetone). The corresponding 5-keto acid (XXXV), yield 1.2 g., melt. p. 189 to 190° (from ethylacetate) was synthetized by the oxidation of 2.8 g of XXXIV with CrO_3 in CH_3COOH; methyl ester of XXXV, melt. p. 92 to 93°. The reduction of 2 g of XXXV according to Klemmensen produced a mixture, from which 0.25 g of

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YUGOSLAVIA/Organic Chemistry. Synthetic Organic Chemistry. G

Abs Jour: Ref Zhur-Khimiya, No 22, 73969

cis-cis-trans-3,4-dimethyl-cyclohexanedicarboxylic 1,2 acid, melt. p. 166 to 167° (from 20%-ual acetone) was precipitated; dimethyl ester (XXXVI), boil. p. 119 to 120°/6 mm, n_D^{20} = 1.4580. XXXVI produced XXII by isomerization with CH_3ONa and following saponification. The oxidation of anhydride of syn-cis-Δ^4-octalindicarboxylic-1,2 acid (12 g) with 90%-ual CH_3COOH in $CHCl_3$ at 0° also resulted in a mixture of oxides, from which 6.6 g of β-oxide, melt. p. 161 to 162° (from benzene), and 3.7 g of α-oxide, melting p. 82 to 83° (from ether + benzene) were separated. A review of works of Nazaroff and coworkers concerning the study of diene condensation of vinylcyclenes published earlier is presented.

Cardq : 14/14

AUTHORS: Kucherov, V. F., Berezin, I. V., Nazarov, I. N. 62-2-9/28

TITLE: Investigations in the Field of the Stereochemistry of Cyclic Compounds (Issledovaniye v oblasti stereokhimii tsiklicheskikh soyedineniy). Report 19: Infrared Spectra of Cyclic Lactones (Soobshcheniye 19. Infrakrasnyye spektry tsiklicheskikh laktonov).

PERIODICAL: Izvestiya AN SSSR Otdeleniye Khimicheskikh Nauk, 1958, Nr 2, pp. 186-191 (USSR).

ABSTRACT: As was already shown in a paper published earlier the method of infrared spectroscopy can successfully be employed for proving the structure of lactones. For the purpose of the systematic investigation of the dependence of the infrared spectra on the structure of diverse polycyclic lactones the authors examined the spectra of the carboxyl-frequencies. They determined some structural regularities of the carboxyl-frequencies of this type of compounds. On the basis of the analysis of the infrared spectra of lactones-1 and 2-methyldecaline-1, 2-dicarboxylic acids their configuration was determined and from it the conclusions on the stereochemistry of the diene condensation of 1-vinyl-Δ-cyclohexane with citracon anhydride

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Investigations in the Field of the Stereochemistry of Cyclic Compounds. 62-2-9/28

were drawn.
There are 4 tables and 10 references, 6 of which are Slavic.

ASSOCIATION: State University imeni M.V. Lomonosov, Moscow (Moskovskiy gosudarstvennyy universitet imeni M.V. Lomonosova) and Institute for Organic Chemistry AN USSR imeni N.D. Zelinskogo (Institut organicheskoy khimii imeni N.D. Zelinskogo Akademii nauk SSSR).

SUBMITTED: September 7, 1956

AVAILABLE: Library of Congress

1. Stereochemistry-Cyclic compounds 2. Lactones-Structural analysis 3. Cyclic compounds-Structural analysis

Card 2/2

Kucherov, V. F.

AUTHORS: Nazarov, I. N., Kucherov, V. F., Bakhirov, V. G. 62-2-10/25

TITLE: Investigations in the Field of the Stereochemistry of Cyclic Compounds (Issledovaniye v oblasti stereokhimii tsiklicheskikh soyedineniy). Report 20: The Stereochemistry of the Oxidation by Peracetic Acid of Isomeric 1,4-Endomethylene-Δ-Cyclohexene-2,3-Dicarboxylic Acids and Their Derivatives (Soobshcheniye 20. Stereokhimiya okisleniya peruksusnoy kislotoy izomernykh 1,4-endometilen-Δ-tsiklogeksen-2,3-dikarbonovykh kislot i ikh proizvodnykh).

PERIODICAL: Izvestiya AN SSSR Otdeleniye Khimicheskikh Nauk, 1958, Nr 2, pp. 192-199 (USSR).

ABSTRACT: As was already shown earlier the reactions of the addition compound of the double bond in the systems of bicyclo-(1,2,2)-heptane are strictly stereospecific. They can only be realized from the side of the endomethylene-bridge. For the authors it was of interest to investigate the stereochemistry of the oxidation of the isomeric 1,4-endomethylene-Δ-cyclohexene-2,3-dicarboxylic acids and their derivatives by peracetic acid. Especially because in this part the configuration of the oxidation cycle can be proved with the aid of stereospecific

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52-2-10/28

Investigations in the Field of the Stereochemistry of Cyclic Compounds. Report 20: The Stereochemistry of the Oxidation by Peracetic Acid of Isomeric 1,4-Endomethylene-Δ^5-Cyclohexene--2,3-Dicarboxylic Acids and Their Derivatives.

reactions of lactonization and hydrogenation. Therefore the above-mentioned oxidation as well as the conversions of the oxides forming were carried out in the present paper. It was shown that the oxidation of the endo- and transdicarboxylic acids (references 6 and 7) due to the presence of free endo--carboxyl-groups takes place simultaneously with the formation of oxy-γ-lacto-acids (references 5 and 9). By means of hydrogenation of the oxides (references 13 and 20) under pressure the hydroxyesters corresponding to them (references 21, 22) were produced with a high yield. On oxidation of them by chromium anhydride the corresponding keto-esters form (references 23 and 24). By means of hydrogenation and other conversions it was proved that the oxidation of the isomeric 1,4-endomethylene-Δ^5-cyclohexane-2,3-dicarboxylic acids and their derivatives takes place from outside and leads to oxides with an external position of the oxide-cycle. There are 11 references, 1 of which is Slavic.

ASSOCIATION: Institute for Organic Chemistry AN USSR imeni N.D. Zelinskiy

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62-2-10/28

Investigations in the Field of the Stereochemistry of Cyclic Compounds. Report 20: The Stereochemistry of the Oxidation by Peracetic Acid of Isomeric 1,4-Endomethylene-Δ^5-Cyclohexene--2,3-Dicarboxylic Acids and Their Derivatives.

(Institut organicheskoy khimii imeni N.D. Zelinskogo Akademii nauk SSSR).

SUBMITTED: September 7, 1956

AVAILABLE: Library of Congress

1. Stereochemistry-Cyclic compounds 2. Cyclic compounds-Structural analysis

Card 3/3

62-58-3-12/30

AUTHORS: Nazarov, I. N., Kucherov, V. F., Bukharov, V. G.

TITLE: Investigation in the Field of the Stereochemistry of Cyclic Compounds (Issledovaniye v oblasti stereokhimii tsiklicheskikh soyedineniy) Communication 21. Oxides of the Isomeric 1,4-Endomethylene-2-Methyl- Δ^5-Cyclohexene-2,3-Dicarboxylic Acids and Their Reactions (Soobshcheniye 21. Okisi izomernykh 1,4-endometilen-2-metil- Δ^5-tsiklogeksen-2,3-dikarbonovykh kislot i ikh prevrashcheniya)

PERIODICAL: Izvestiya Akademii Nauk SSSR, Otdeleniye Khimicheskikh Nauk, 1958, Nr 3, pp. 328 - 334 (USSR)

ABSTRACT: As it was shown in previous reports, the oxidation of the isomeric dicarboxylic acids of the bicyclo-(1,2,2)-heptane series leads through peracids to relaxing oxidations and to the oxo-configuration of the oxidation cycle. For the purpose of a further investigation of the stereochemistry and the direction of the above-mentioned reactions the authors investigated the conversions of the oxides in the example of the isomeric 1,4-endomethylene-2-methyl- Δ^5-

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62-58-3-12/30

Investigation in the Field of the Stereochemistry of Cyclic Compounds. Communication 21. Oxides of the Isomeric 1,4-Endomethylene-2-Methyl-Δ^5-Cyclohexene-2,3-Dicarboxylic Acids and Their Reactions

-dicarboxylic acids and their derivatives. It was shown that in the oxidation of the endo-anhydride by acetic peracid in chloroform only an exo-oxide can be obtained with good yields. The authors proved the structure of the isomeric oxy-γ-lactic acids. They further showed that the inner-molecular lactonization over the oxide ring mainly takes place over the tertiary carboxyl-group. There are 5 references, 3 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR
(Institute for Organic Chemistry imeni N. D. Zelinskiy, AS USSR)

SUBMITTED: September 7, 1956

Card 2/2

62-58-3-22/30

AUTHORS: Kucherov, V. F., Segal', G. M., Nazarov, I. N.

TITLE: The Stereochemistry of the Oxidation of the Δ^4-Octaline-Carboxylic Acids (Stereokhimiya okisleniya Δ^4-oktalinkarbonovykh kislot)

PERIODICAL: Izvestiya Akademii Nauk SSSR, Otdeleniye Khimicheskikh Nauk, 1958, Nr 3, pp. 367-369 (USSR)

ABSTRACT: It was of interest to the authors to investigate the stereochemistry of the oxidation of the above mentioned (and of similar) acids by means of acetic acid and osmium anhydride. The investigations carried out showed that sin- and anti-Δ^1-octaline-1-carboxylic acids produce individual α-oxides with good yields in the oxidation with peracetic acid. Their configurations correspond to the disposition of the oxycycle which is opposite to that of carboxylic acid groups. Such a configuration of the α-oxides was proved by a number of stereospecific reactions. They made at the same time possible the synthesis of stereo-isomeric 4-ketodekaline-carboxylic acids. See formulae 1-10.

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The Stereochemistry of the Oxidation of the Δ^4-Octaline-Carboxylic Acids 62-58-3-22/30

Different from this the oxidation of the sin-cis-Δ^4-octaline-1,2-dicarboxylic acid takes place in both possible stereo directions with simultaneous formation of isomeric α- and β-oxides (see formulae 14-18, 19-25 and 26-30).
There are 5 references, 4 of which are Slavic.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute for Organic Chemistry imeni N. D. Zelinskiy, AS USSR)

SUBMITTED: October 16, 1957

Card 2/2

AUTHORS: Shidlovskaya, A. N., Syrkin, Ya. K., Corresponding Member of the AS USSR, Nazarov, I. N., Member of the AS USSR, (Deceased), Kucherov, V. F. 20-118-5-33/59

TITLE: Dipole Moments of Ethers of the Isomeric Cyclohexane-1,2-Dicarboxylic Acids (Dipol'nyye momenty efirov izomernykh tsiklogeksan-1,2-dikarbonovykh kislot)

PERIODICAL: Doklady Akademii Nauk SSSR, 1958, Vol. 118, Nr 5, pp. 967-969 (USSR)

ABSTRACT: Usually it is proceeded from the fact that the fauteuil-like configuration with a maximum number of equatorial substituents is the most stable. This assumption was chiefly confirmed by the investigation of different cyclic compounds which have methyl and hydroxyl groups as substituents. In this context the investigation of such compounds is interesting which have more strongly polar substituents (references 1,2). In the series of the 1,2-substituted cyclohexanes 3 isomers are possible: a cis-isomer with an equatorial-axial position of the substituents (e - a), or a trans-isomer in a diequatorial form (e - e) or in a diaxial form (a - a). Dipole moments of

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Dipole Moments of Ethers of the Isomeric Cyclohexane-1,2-Di- 20-118-5-33/59
carboxylic Acids

10 substances, derivates of cyclohexane and cyclohexene, were measured. The tables 1 and 2 show: structural formulae, temperature constants, complexe poarizations P_{∞}, electronic polarizations P_{El}, orientation polarizations P_{Or}, and dipole moments. The comparison of the latter of the isomers of the cyclohexane and cyclohexene derivates showed that the double linkage causes only slight changes of the moment for the cis--form as well as for the trans-form. The dipole moments of the isomers of the monomethylether of the cyclohexane-1,2--dicabonic acid are decreased as compared to dimethylether. Perhaps this can be explained by the formation of an intramolecular hydrogen linkage between the oxygen of the carbonyl group and the hydrogen of the O-H group. It is interesting to compare the dipole moments of the isomers of the methylethers of the cyclohexanedicarbonic acid with those of the ethers of unsaturated dicarbonic acids (for example the diethyl ether of maleic and fumaric acid). The difference in the radicals of the ether group is said to have no noticeable influence on the value of the moments. As is shown in publications (reference 3) the dipole moment of the ether of

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maleic acid is greater than of that of fumaric acid. This is moreover confirmed by the cis-configuration of the compound number 3 (table 1). Table 2 shows moments of molecules which differ from those treated above by having an additional methyl group at C_4. As could be expected for the isomers 1 and 2 equal values of the moments were obtained, as the moment of the CH_3-group is equal to that of the C-H group.

The isomers 3 and 4 have somewhat greater moments. Isomer 4 is also the most stable. All other isomers are finally trans- formed into isomer 4. Contradictory to the formula (references 4-6) the authors maintain that for substituents of the type of ethers of the cyclohexane-1,2-dicarbonic acids which con- tain irregular groups the moment of the diaxial isomer (a-a) may not be set equal to zero. In order to determine the con- figuration of the isomers of the dimethylethers of cyclo- hexane-1,2-dicarbonic acid the dipole moments were computed by assuming a free rotation of the $COOCH_3$ groups, taking into consideration their direction as irregular groups in relation to the cyclohexane nucleus. The moment of the isomer a-a was determined as 2,3o D. The experimental value of the moment

Dipole Moments of Ethers of the Isomeric Cyclohexane-1,2-Dicarboxylic Acids

of the cis-isomer lies between the computed values 2,51 - 2,30 D. The experimental moment of the trans-isomer (=2,14) does not correspond to the computed value of the moment of the isomer d-d if a free rotation is assumed. There are 2 tables and 9 references, 2 of which are Soviet.

ASSOCIATION: Moskovskiy institut tonkoy khimicheskoy tekhnologii im. M. V. Lomonosova (Moscow Institute for Refined Chemical Technology imeni M. V. Lomonosov)

SUBMITTED: October 1, 1957

AUTHOR: Nazarov, I. N., Member, Academy of Sciences, USSR (Deceased), Kucherov, V. F., Andreyev, V. M., Segal', G. M.

TITLE: The Stereochemistry of the Diene-Condensation of 1-α-Acetoxyvinyl- Δ^1-Cyclohexene With Maleic Aldehyde (Stereokhimiya diyenovoy kondensatsii 1-α-atsetoksivinil-Δ^1-tsiklogeksena s maleinovym angidridom)

PERIODICAL: Doklady Akademii Nauk, 1958, Vol. 119, Nr 5, pp. 943-946 (USSR)

ABSTRACT: The reaction mentioned in the title in boiling benzene (ref 1) yields a liquid adduct I, whose saponification by means of an 8% yield of individual anti-cis-4-acetoxy-Δ^4-octaline-1,2-dicarboxylic acid II, its configuration was proved. On the basis of the data obtained the conclusion was drawn that the above-mentioned liquid adduct I possesses an anti-cis-configuration and that the diene-configuration is under these conditions on the whole formed in contrast to the rule of the accumulation of unsaturatedness. It was then proved that the adduct is not individual and that it contains a small quantity of

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The Stereochemistry of the Diene-Condensation of [illegible] 20-[illegible]
-o-Acetoxyvinyl-Δ^1-Cyclohexene With Maleic Aldehyde

isomeric syn-cis-4-acetoxy-anhydride V (ref 2). It became evident that in an acid saponification of the crystalline mixture remaining after the liberation of anti-syn-cis-4-acetoxy acid II (yield 8 %) it is possible to obtain the isomeric trans-syn-cis-4-keto acid VI (melting point 177-178°C). The latter is characterized as a crystalline diether VII. The same trans-syn-cis-4-ketoacid VI can also be isolated with a 10-15 % yield from the products of the acid saponification of the individual anti-cis-4-acetoxyacid II. This was surprising enough and indicated that either the initial acid was not quite individual or that the saponification of the epoxyacetate group is not stereospecific. The latter would be more probable (ref 4). The trans-syn-cis-4-keto acid VI as well as its diether VII according to their constants proved to be different from those found by English authors (ref 2). This made the proof of their configuration necessary. For this purpose syn-cis-anhydride XI was obtained by chromium anhydride after the decomposition of the complex and after the treatment of the hydroxyacid

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The Stereochemistry of the Diene-Condensation of 1,4-Acetoxyvinyl-Δ^1-Cyclohexene With Maleic Aldehyde

product with diazomethane, cis-glycol-XI-ether was isolated. The configuration of the latter corresponds to the addition of osmium anhydride from the side opposite to the carboxyl groups (ref 5). Thanks to the axial position of the tertiary hydroxyl group this glycol proved to be easily capable of dehydration on heating with p-toluene sulfo acid and yielded the above-described trans-syn-heterodiether XII. As far as such a conversion does not immediately touch the centers of asymmetry in C_1, C_2 and C_4 and leads to a trans-

addition of the cycles it must be stated that the keto ether produced on that conversion as the main reaction product really possesses a trans-syn-cis-configuration. The latter is a sufficiently unique confirmation of the configuration of 4-ketone VI and the diether VII produced in a stereosynthesis. An experimental part with the usual data follows. There are 9 references, 5 of which are Soviet.

Card 3/4

The Stereochemistry of the Diene-Condensation of
-α-Acetoxyvinyl-Δ^1-cyclohexene With Maleic Aldehyde

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute for Organic Chemistry imeni N. D. Zelinskiy AS USSR)

SUBMITTED: December 21, 1957

Card 4/4

1959-1961

KUCHEROV, V. F.

G. M. Segal' and V. F. Kucherov, "Stereochemistry of the Oxidation of Δ^4-Octaline Carboxylic Acids."

report presented at the Symposium on Concepts of Conformation in Organic Chemistry which took place in Moscow at the IOKh AN SSSR (Institute of Organic Chemistry, AS USSR) from September 30 to October 2, 1958.

Izvestiya Akademii nauk SSSR, Otdeleniye khimicheskikh, 1959, No. 3, 561-564.

KUCHEROV, V. F.

V. M. Andreyev and V. F. Kucherov, "Synthesis and Configuration of All Possible Isomers of 3,4-Dimethyl-Δ^4-Octaline Carboxylic Acids."

report presented at the Symposium on Concepts of Conformation in Organic Chemistry which took place in Moscow at the IOKh AN SSSR (Institute of Organic Chemistry, AS USSR) from September 30 to October 2, 1958.

Izvestiya Akademii nauk SSSR, Otdeleniye khimicheskikh nauk, 1959, No. 3, 561-564.

KUCHEROV, V. F. (IOKh AS USSR, Moscow)

V. F. Kucherov and N. Ya. Grigor'yeva, " Application of the Principles of Conformational Analysis for Proving the Configuration of Isomers of 3-Acetoxy Cyclohexane-1,2,-dicarboxylic Acids."

report presented at the Symposium on Concepts of Conformation in Organic Chemistry which took place in Moscow at the IOKh AN SSSR (Institute of Organic Chemistry, AS USSR) from September 30 to October 2, 1958.

Izvestiya Akademii nauk SSSR, Otdeleniye khimicheskikh nauk, 1959, No. 3, 561-564.

5(3) SOV/62-59-4-17/42

AUTHORS: Kucherov, V. F., Segal', G. M., Nazarov, I. N.

TITLE: Investigation in the Field of Stereochemistry of the Cyclic Compounds (Issledovaniye v oblasti stereokhimii tsiklicheskikh soyedineniy). Communication 22. Stereochemistry of the Oxidation of Syn-Δ^4-Octaleno-1-Carboxylic Acid and the Configuration of the Products Thus Obtained (Soobshcheniye 22. Stereokhimiya okisleniya sin-Δ^4-oktalin-1-karbonovoy kisloty i konfiguratsiya poluchennykh pri etom produktov)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 4, pp 673-681 (USSR)

ABSTRACT: In the present work the previously described (Ref 1) syn-Δ^4-octaleno-1-carboxylic acid (I) was investigated. It was found that the oxidation of this acid as well as its catalyzed hydrogenation are sterically selective and that only a single crystalline oxide (II) is quantitatively formed by the action of peracetic acid in chloroform. This oxide gives with diisomethane a liquid ester (III). The α-oxide shows a strong tendency to lactonize. When subjected to the action of

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Investigation in the Field of Stereochemistry of the 307/62-32-4-17/42
Cyclic Compounds. Communication 22. Stereochemistry of the Oxidation of
Syn-Δ^4-Octaleno-1-Carboxylic Acid and the Configuration of the Products
Thus Obtained

hydrogen chloride in ether or when boiled in methanol it gives the hydroxy-γ-lactone (IV) in a high yield. The latter is also formed when the oxydole ester (III) is boiled in liquid dioxane in the presence of sulphuric acid. The consideration of a model of epimeric hydroxy-γ-lactones shows that the axial hydroxyl group in hydroxy-γ-lactone (IV) is less shielded than the equatorial group in hydroxy-γ-lactone (IX), in which the lactone nucleus can exercise its steric action. As is apparent from the configuration of syn-Δ^4-octaleno-1-carboxylic acid (I), its oxidation with osmic acid anhydride and with peracetic acid can take place only from the side opposite to the shielded axial carboxyl group. Owing to the cis-hydroxylation, cis-glycol of the cis-decalin series (XIV) is formed in this case and the ester (XV) of this compound is formed in a similar manner by the oxidation of the syn-ester (XVI). The dehydration of the cis-glycol (XIV) with p-toluenesulphonic acid gives syn-cis-4-ketodecalin-1-carboxylic acid (XVII), the ester of

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Investigation in the Field of Stereochemistry of the Cyclic Compounds. Communication 22. Stereochemistry of the Oxidation of Syn-Δ^4-Octaleno-1-Carboxylic Acid and the Configuration of the Products Thus Obtained SOV/62-59-4-17/42

which is also formed by the dehydration of cis-glycol ester (XV). The stereochemistry of the oxidation of syn-Δ^4-octaleno-1-carboxylic acid (I) with peracetic acid and osmic acid anhydride can be demonstrated by molecular models (Page 676). The configuration and conformation of the α-oxide (II) of the cis-glycol (XIV) and all their conversion products have been confirmed by infrared spectra, stereospecific reactions and molecular models. There are 11 references, 5 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR)

SUBMITTED: July 10, 1957

Card 3/3

5(3) SOV/62-59-4-18/42

AUTHORS: Kucherov, V. F., Segal', G. M., Nazarov, I. N.

TITLE: Investigation in the Field of the Stereochemistry of the Cyclic Compounds (Issledovaniye v oblasti stereokhimii tsiklicheskikh soyedineniy). Communication 23. Stereochemistry of the Oxidation of Anti-Δ^4-Octaleno-1-Carboxylic Acid (Soobshcheniye 23. Stereokhimiya okisleniya anti-Δ^4-oktalin-1-karbonovoy kisloty)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 4, pp 682-689 (USSR)

ABSTRACT: In the present work the oxidation of anti-Δ^4-octaleno-1-carboxylic acid (IV), in which the shielding action of the equatorial carboxyl leads only to the trans-decalin system, was investigated. In spite of a more widely opened double bond in (IV) its oxidation is also sterically selective and forms a single, individual α-oxide (V) in a yield of 80 %. When treated with diazomethane this oxide gives a liquid oxide ester (VI). Owing to the presence of the equatorial carboxyl the α-oxide cannot form lactones and when boiled in aqueous dioxane in the presence of sulphuric acid gives the trans-glycol (VII).

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Investigation in the Field of the Stereochemistry of the Cyclic Compounds. Communication 23. Stereochemistry of the Oxidation of Anti- Δ^4-Octaleno-1-Carboxylic Acid

The reaction has a similar course in the case of the oxide ester (VI), under formation of trans-glycol ester (VIII). This is also obtained by treating (VII) with a diazomethane ester solution. To prove the configuration of (VII) the dehydration of its ester (VIII) with p-toluene sulphonic acid was investigated. It was found that this does not cause lactonization whereas the previously described (Ref 4) ester of trans-anti-4-ketodecalin-1-carboxylic acid (IX) is formed in a good yield. This fact proves that the transglycol (VII) contains a trans-decalin system with a diaxial distribution of the hydroxyl groups at C_4 and C_{10} and the carboxyl at C_1 in an equatorial position. This configuration confirms also the α-configuration of the oxide cycle in the initial oxide (V). This configuration results from the addition of the oxygen from the direction opposite to the equatorial carboxyl group. From the same direction the hydroxylation of (IV) with osmic acid anhydride is effected. The resulting cis-glycol (XII) was found unable to lactonize. Its ester, also formed when the

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ester of anti-Δ^4-octaleno-1-carboxylic acid (XIV) is reacted with osmic acid anhydride, formed upon dehydration the ester of trans-anti-ketonic acid (IX). The cis-adduct (XXI) was obtained by condensing trans-1,2-dimethylbutadiene with methacrylate at room temperature. According to the general steric laws applicable to diene synthesis, (XXI) must contain the carboxyl group in axial position. For this reason the cis-2,3-dimethyl-Δ^3-cyclohexane-1-carboxylic acid (XXII) formed by the saponification of (XXI) forms easily the γ-lactone. A similar course has the oxidation of (XXII) with peracetic acid. The fact that the resulting α-oxide (XXIV) can easily form the hydroxy-γ-lactone (XXV) proves clearly the cis-configuration of the initial acid (XXII) having the carboxyl at C_1 in axial position and the α-configuration of the oxide (XXIV). There are 8 references, 6 of which are Soviet.

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SOV/62-59-4-18/42

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR)

SUBMITTED: July 10, 1957

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5 (3)
AUTHORS: Kucherov, V. F., Grigor'yeva, N. Ya., SOV/62-59-5-14/40
Nazarov, I. N.

TITLE: Investigations in the Field of the Stereochemistry of Cyclic Compounds (Issledovaniye v oblasti stereokhimii tsiklicheskikh soyedineniy). Communication 24. Diene Condensations of 1-Acetoxybutadiene With Maleic Anhydride and Dimethyl Fumarate and Configuration of the Products Obtained (Soobshcheniye 24. Divenovyye kondensatsii 1-atsetoksibutadiyena s maleinovym angidridom i dimetilfumaratom i konfiguratsiya polychennykh adduktov)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 5, pp 849-860 (USSR)

ABSTRACT: In this work the diene condensation of 1-acetoxybutadiene with maleic anhydride and dimethyl fumarate and the configuration and spatial transformation of the products formed were given a thorough investigation. 1-Acetylbutadiene was synthesized according to the Flaig method. The condensation with maleic anhydride showed spatial selectivity with formation of the cis-cis-product (II). The configuration was proved by hydrogenation and lactonization. With condensation of

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Investigations in the Field of the Stereochemistry of Cyclic Compounds. Communication 24. Diene Condensations of 1-Acetoxybutadiene With Maleic Anhydride and Dimethyl Fumarate and Configuration of the Products Obtained SOV/62-59-5-14/40

1-acetoxybutadiene with dimethyl fumarate both isomers possible were obtained: trans-trans and trans-cis (XIV and XV), the configuration of which was proved by their catalytic hydrogenation, saponification, and by the observation of molecular models. The derivatives of the cis-cis order and trans-cis order with an axial arrangement of the acetoxy group have a low stability. They separate acetic acid with catalytic hydrogenation, alkaline saponification, and heating while various cyclohexane-1,2-dicarboxylic acids are formed. The isomeric compounds of the trans-trans order with the equatorially arranged acetoxyl group are sufficiently stable so that some of their derivatives could be obtained. Three (out of four theoretically possible) isomers could be synthesized by means of diene synthesis, catalytic hydrogenation and a thorough investigation of the chemical transformations: 3-acetoxy-, cis-, trans-1,2-dicarboxylic acid and two isomeric trans-3-oxycyclohexane-1,2-dicarboxylic acids. There are 9 references, 2 of which are Soviet.

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Investigations in the Field of the Stereochemistry [illegible] 107/62-32-5-14/40
of Cyclic Compounds. Communication 24. Diene Condensations of 1-Acetoxy-
butadiene With Maleic Anhydride and Dimethyl Maleate and Configuration of
the Products Obtained

ASSOCIATION : Institut organicheskoy khimii im. N. D. Zelinskogo Akademii
nauk SSSR (Institute of Organic Chemistry imeni N. D.
Zelinskiy of the Academy of Sciences, USSR)

SUBMITTED: July 10, 1959

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5 (3)

AUTHORS: Kucherov, V. F., Andreyev, V. M., Nazarov, I. N. SOV/62-59-6-17/36

TITLE: Investigations in the Field of Stereochemistry of Cyclic Compounds (Issledovaniye v oblasti stereokhimii tsiklicheskikh soyedineniy). Communication 25. The Condensation of Trans-1,2-dimethylbutadiene With Maleic Anhydride. Synthesis and Configuration of Four Isomers of the 3,4-dimethyl-Δ^4-cyclohexane-1,2-dicarboxylic Acid (Soobshcheniye 25. Kondensatsiya trans-1,2-dimetilbutadiyena s maleinovym angidridom. Sintez i konfiguratsiya chetyrekh izomerov 3,4-dimetil-Δ^4-tsiklogeksen-1,2-dikarbonovoy kisloty)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 6, pp 1058 - 1067 (USSR)

ABSTRACT: The synthesis of the diene condensation (see title) which with stereochemical selection forms the cis-cis-configuration (IV) was investigated. Up to now only the cis-cis-configuration could be obtained. By further heating and in the presence of diethylaniline (IV) may be transformed into the isomeric cis--trans-anhydride (VII). By means of saponification (VII) may

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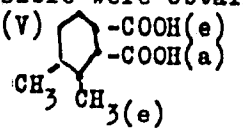
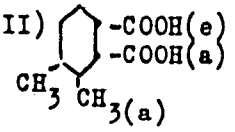
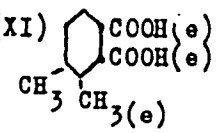
be transformed into the diaxially arranged carboxylic acid (VIII). The epimeric acid (V) corresponds to (VIII); the two latter ones form the corresponding diesters (VI and IX). In aqueous methanol (VI) could be transformed into a cis-cis-diester which by the action of sodium methylate isomerizes to the trans-trans-3,4-dimethyl-Δ^4-cyclohexane-1,2-dicarboxylic acid (XI). The last possible spatial isomer, the trans-cis-3,4-dimethyl-Δ^4-cyclohexane-1,2-dicarboxylic acid (XIV), is formed in an analogous way. Thus, all four spatial isomers which are possible were obtained:

(V) 

(VIII) 

(XI) 

melting point 173° melting point 161° melting point 150°

Investigations in the Field of Stereochemistry of Cyclic Compounds. Communication 25. The Condensation of Trans-1,2-dimethylbutadiene With Maleic Anhydride. Synthesis and Configuration of Four Isomers of the 3,4-dimethyl-Δ^4-cyclohexane-1,2-dicarboxylic Acid

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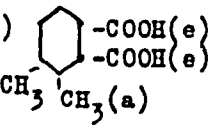
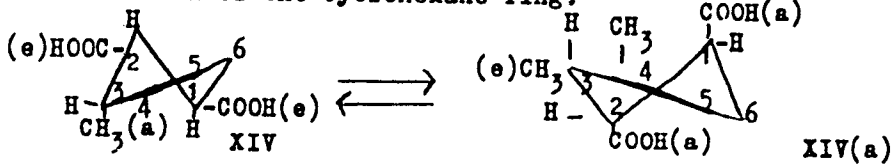
(XIV) 

melting point 185°

The existing configuration was determined by means of lactonization of the different compounds. When studying the spatial orientation of the lactonization it could be observed that with the isomeric cis-trans- and trans-cis-acids (VII) and (XIV) also conversion forms take part, which are caused by repeated isomerization of the cyclohexane ring.



XIV XIV(a)

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