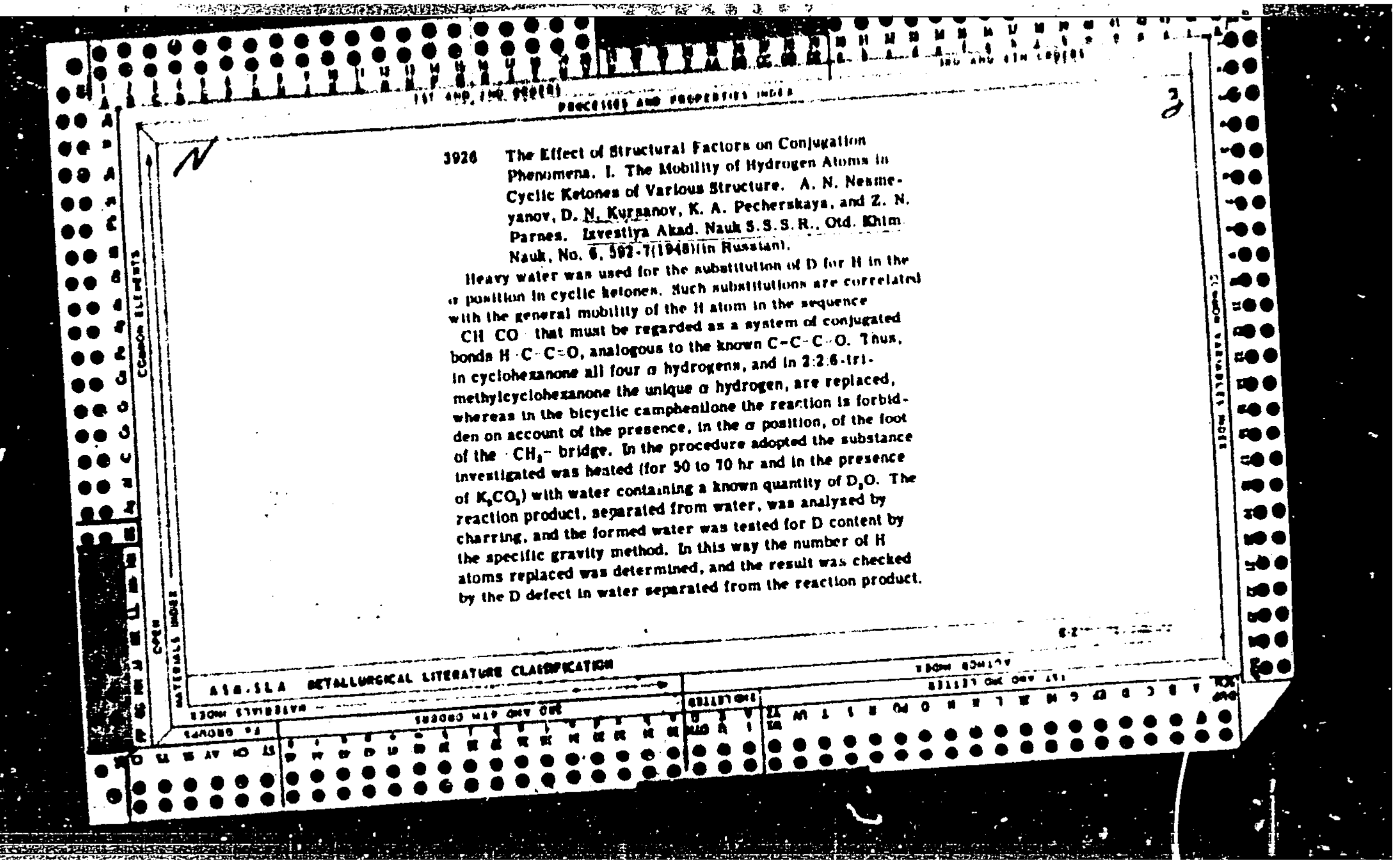

3926 The Effect of Structural Factors on Conjugation
Phenomena. I. The Mobility of Hydrogen Atoms in
Cyclic Ketones of Various Structure. A. N. Nesme-
yanov, D. N. Kursanov, K. A. Pecherskaya, and Z. N.
Parnes. Izvestiya Akad. Nauk S.S.S.R., Otd. Khim.
Nauk, No. 6, 592-7(1948)(in Russian).

Heavy water was used for the substitution of D for H in the α position in cyclic ketones. Such substitutions are correlated with the general mobility of the H atom in the sequence CH CO that must be regarded as a system of conjugated bonds H·C–C=O, analogous to the known C=C–C=O. Thus, in cyclohexanone all four α hydrogens, and in 2:2:6-trimethylcyclohexanone the unique α hydrogen, are replaced, whereas in the bicyclic camphenilone the reaction is forbidden on account of the presence, in the α position, of the foot of the ·CH$_2$– bridge. In the procedure adopted the substance investigated was heated (for 50 to 70 hr and in the presence of K$_2$CO$_3$) with water containing a known quantity of D$_2$O. The reaction product, separated from water, was analyzed by charring, and the formed water was tested for D content by the specific gravity method. In this way the number of H atoms replaced was determined, and the result was checked by the D defect in water separated from the reaction product.

KURSANOV, D. N.

PA 36/49T14

USSR/Chemistry - Alcohols, Reactions of With Allyl Pyridine Chloride Sep 48
Chemistry - Alkoxy Groups

"The Interaction of Allyl Pyridine Chloride and Alcohol," D. N. Kursanov, O. M. Shemyakina, Inst Org Chem, Acad Sci USSR, Moscow Textile Inst, 3 pp

"Dok Ak Nauk SSSR" Vol LXII, No 3

It has been established that an alkoxy-methyl radical changes places easily with hydrogen in the hydroxy group, resulting in transformation of alcohols. Attempts to find if this reaction

[redacted] 36/49T14

USSR/Chemistry - Alcohols, Reactions of With Allyl Pyridine Chloride (Contd) Sep 48

can be extended to quaternary salts of ammonia with other radicals. Finds that allyl radical and alkoxy-methyl radicals of quaternary ammonia salts behave in the same fashion during interaction with alcohols. However, in this case, yield was only a little over 10% of the theoretical. Submitted by Acad B. A. Kazanskiy, 13 Jul 48.

[redacted] 36/49T14

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Exchange reactions and cleavages of the quaternary ammonium salts. II. Reaction of quaternary ammonium salts of the type $ROCH_2N$ X with carboxylic acids and their salts. V. N. Setkina and D. N. Kursanov. *Izvest. Akad. Nauk S.S.S.R., Otdel Khim. Nauk* 1949, 190-7; cf. *C.A.* 42, 4922. Quaternary ammonium salts contg. the $ROCH_2$ radical react with salts of carboxylic acids, yielding alkoxymethyl esters, while the free acids yield esters without the alkoxymethyl group, the CH_2O residue being eliminated as polyoxymethylene. Heating 25.2 g. 1-(butoxymethyl)quinolinium chloride and 8.2 g. dry NaOAc 3 hrs. at 150-70° gave 72% *$BuOCH_2OAc$*, b_{10} 118-19°, b. 167-8°, d_4^{20} 0.9328, n_D^{20} 1.4040, and quinoline. Similarly, 1-(decyloxymethyl)pyridinium chloride at 180-200° gave 60% *decyloxymethyl acetate*, b_{10} 167.5°, d_4^{20} 0.9072, n_D^{20} 1.4301. 1-(Tetradecyloxymethyl)pyridinium chloride similarly (150-60°) gave 70% *tetradecyloxymethyl acetate*, b_{10} 211°, d_4^{20} 0.8960, n_D^{20} 1.4390. Heating 13.8 g. 1-(butoxymethyl)quinolinium chloride with 6.2 g. $PrCO_2Na$ 2 hrs. to 130-50° at a water-pump vacuum gave 75% *$PrCO_2CH_2OBu$*, b_9 81°, d_4^{20} 0.9299, n_D^{20} 1.4147, while $AmCO_2Na$ at 190-200° gave 69% *$AmCO_2CH_2OBu$*, b_{14} 132.5°, d_4^{20} 0.9121, n_D^{20} 1.4210, from 1-(butoxymethyl)pyridinium chloride; the latter and NaOBz at 180-200° at a water-pump vacuum gave *$BzOCH_2OBu$*, b_{11} 158°, d_4^{20} 1.0440, n_D^{20} 1.4930. Substitution of 1-(decyloxymethyl)pyridinium chloride (200-30°) in the above gave 51% *decyloxymethyl benzoate*, b_{0} 223-5°, d_4^{20} 0.9511, n_D^{20} 1.4778. 1-(Butoxymethyl)pyridinium chloride (14.2 g.) and 8.1 g. $PhCH_2CO_2Na$ after 3 hrs. at 130-40° gave 57% *$PhCH_2CO_2CH_2OBu$*, b_{1} 133°, b_{14} 167.5-8.5°, d_4^{20} 1.0509, n_D^{20} 1.4981. Hydrolysis of the products by dil. HCl gave ROH, CH_2O, and the corresponding acids. Heating 22.5 g. 1-(butoxymethyl)quinolinium chloride and 5 g. AcOH to 130-50° 7 hrs. gave 57% BuOAc, while $PrCO_2H$ at 150-60° gave $PrCO_2Bu$. 1-(Decyloxymethyl)pyridinium chloride and $AmCO_2H$ at 150-60° gave 28% *$AmCO_2C_{10}H_{21}$*, b_{10} 183-4°, n_D^{20} 1.4353, d_4^{20} 0.8610, 22% *$C_{10}H_{21}OCH_2O_2CAm$*, b_{10} 213-14°, d_4^{20} 0.8908, n_D^{20} 1.4365, and 2.5 g. *$(C_{10}H_{21}O)_2CH_2$*, b_{1} 202-5°, d_4^{20} 0.8451, n_D^{20} 1.4400 (the previous derivs. gave CH_2O polymers on distn.). 1-(Butoxymethyl)quinolinium chloride and $PhCH_2CO_2H$ in 6 hrs. at 160-80° gave *$PhCH_2CO_2Bu$*, b_{8} 138-40°, d_4^{20} 0.9980, n_D^{20} 1.4908 (65%). Heating 1-(butoxymethyl)quinolinium chloride with AcOH in Ac_2O (to insure anhyd. conditions) 5 hrs. at 150-60° and 8 hrs. at 160-80° gave 61% BuOAc. $BuOCH_2OAc$ (17 g.) and 18 g. AcOH heated 7.5 hrs. at 195-200°, with recovery of the volatiles, gave CH_2O (detected as the dimedon deriv., m. 189°), 30% BuOAc, and 11 g. starting ester. G. M. Kosolapoff

METALLURGICAL LITERATURE CLASSIFICATION

Exchange and cleavage reactions of quaternary ammonium salts. III. Reaction of quaternary ammonium salts with esters. D. N. Kursanov and V. N. Setkina. *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* **1949**, 274-8; cf. C.A. **43**, 6618*f*. 1-(Butoxymethyl)quinolinium chloride (10 g.) and 25 g. EtOAc in 5 hrs. at 170-5° gave 10 g. EtOAc and 3.0 g. BuOAc ([illegible]), as well as some quinoline. *1-(Decyloxymethyl)pyridinium chloride* (10 g.) and 120 g. EtOAc in 10 hrs. at 195-205° gave 10 g. EtOAc and 82.5% *decyl acetate*, b_4 118-19°, n_D^{20} 1.4272. EtOBz (32.3 g.) and 28.4 g. 1-benzylpyridinium chloride in 8 hrs. at 195-205° gave 4 g. pyridine, 1.5 g. BzOH, and 60% BzOCH$_2$Ph. The reaction probably proceeds by formation of an oxonium deriv. at the O of the ester after cleavage of the R group from the quaternary compound.

IV. Mechanism of the reactions of quaternary ammonium salts with alcohols. V. N. Setkina and D. N. Kursanov. *Ibid.* 311-16. Pyridine MeI (37 g.) and 21.8 g. decanol in 12 hrs. at 190-220° gave 38% decene, b_{760} 167°, 18% *Me decyl ether*, b_{14} 93.5°, d_4^{20} 0.8022, n_D^{20} 1.4210, and 32% *didecyl ether*, b_6 180-7°, d_4^{20} 0.8188, n_D^{20} 1.4414. Octanol similarly gave in 6 hrs. at 210-30° 1.[illegible]% octene, b. 122°, 10% *Me octyl ether*, b. 170-2°, d_4^{20} 0.[illegible], n_D^{20} 1.4140, and *dioctyl ether*, 51%, b_4 112.5-8.5°, d_4^{20} 0.[illegible], n_D^{20} 1.4427. Heating 62.0 g. 1-(butoxymethyl)pyridinium chloride and 18.4 g. PhCH$_2$OH 4 hrs. at 180-200° gave 30% HCH(OBu)$_2$, 11% BuOCH$_2$Ph, 0.2% *BuO(PhCH$_2$O)CH$_2$*, b_4 118-19°, d_4^{20} 0.9851, n_D^{20} 1.4830, and 4.4 g. (PhCH$_2$)$_2$O; the residue contained benzylpyridinium ion, shown by the *picrate*, m. 117-18°. The results are discussed in terms of formation of the products through oxonium derivs. formed from radical cleavage of the quaternary salts. G. M. K.

Influence of the structural factors on conjugation phenomena. I. Mobility of hydrogen atoms in various cyclic ketones. A. N. Nesmeyanov, D. N. Kursanov, K. A. Pecherskaya, and Z. N. Parnes (Inst. Org. Chem., Moscow). *Izvest. Akad. Nauk S.S.S.R., Otdel Khim. Nauk* **1949**, 592-7.—2,2,6-Trimethylcyclohexanone completely exchanges one H for a D atom after 70 hrs. at 130° in enriched H_2O; cyclohexanone exchanges 4 H atoms for D atoms in 50 hrs. at 100°. Spiro[4.5]decan-6-one exchanges between 1 and 2 H atoms for D in 70 hrs. at 130°. No exchange takes place with camphenilone or camphorquinone; this is explained by nonexistence of conjugation between the CO group and CH, which follows from Bredt's rule. **II. Mobility of hydrogen atoms in acetylacetone and its cobalt and aluminum salts.** A. N. Nesmeyanov, D. N. Kursanov, T. A. Smolina, and Z. N. Parnes. *Ibid.* 598-600.—CH_2Ac_2 kept 70 hrs. at 17° in H_2O enriched with D_2O in the presence of dioxane showed exchange of 2 H (within 15%) for 2 D. The Co salt and the Al salt show no enrichment by D. The result is explained on the basis of impossibility of conjugation of the residual CH bond with CO due to perpendicularity of the axes of the CH link and that of the π-function of the CO group, which as well as to Favorskii's rule (*C.A.* **35**, 2840^8), which forbids allene formation in 6-member rings. G. M. K.

PROCESSES AND PROPERTIES INDEX

CA

10

Reaction of quaternary ammonium salts with ethers. D. N. Kursanov and V. N. Setkina. *Doklady Akad. Nauk S.S.S.R.* **65**, 847-50(1949).—EtOCH$_2$Ph (13.6 g.) and 20.5 g. 1-benzylpyridinium chloride after 6 hrs. at 180-90° gave 8.7 g. unreacted ether and 18.5% (PhCH$_2$)$_2$O, b$_{16}$ 172°, and the acidic ext. gave *4-benzylpyridine*, isolated as the *picrate*, m. 137-8°. Bu$_2$O (15.5 g.) and 1-(decyloxymethyl)pyridinium chloride (16 g.) in 5 hrs. at 180-200° gave 11.8 g. unreacted Bu$_2$O, 11% decyl chloride, b$_{15}$ 105-5.5°, 9.4% *C$_{10}$H$_{21}$O(BuO)CH$_2$*, b$_{12}$ 148-50°, d_4^{20} 0.8472, n_D^{20} 1.4320, and 55.5% *(C$_{10}$H$_{21}$O)$_2$CH$_2$*, b$_3$ 208°, d_4^{20} 0.8451, n_D^{20} 1.4410. Similarly PhCH$_2$NPhMe$_2$Cl and Bu$_2$O gave under the above conditions 11% (PhCH$_2$)$_2$O and 25% *p-benzyl-N,N-dimethylaniline*, b$_5$ 180-1°, d_4^{20} 1.0120, n_D^{20} 1.6001. PhOMe and 1-benzylpyridinium chloride in 8 hrs. at 180-200° gave 1.4% PhOCH$_2$Ph, b$_{10}$ 167°, and 8% of mixed *4-hydroxydiphenylmethane*, m. 82-2.5°, and *4-methoxydiphenylmethane*, m. 81°; the acid ext. contained 4-benzylpyridine, identified as the picrate, m. 138°. The use of PhOEt in the above gave 8.2% PhOCH$_2$Ph, and 10% mixed 4-hydroxydiphenylmethane and the 4-EtO deriv., as well as a little PhOH. G. M. Kosolapoff

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

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Exchange reactions and cleavages in the quaternary ammonium salt group. VI. Reaction of salts of alkoxymethylpyridinium with phenols. V. N. Setkina and D. N. Kursanov. *Izvest. Akad. Nauk S.S.S.R., Otdel Khim. Nauk,* 1950, 380-93; cf. C.A. 42, 4023; 44, 9337e.—*Phenols* and *(alkoxymethyl)pyridinium salts* yield, as primary products, phenyl alkyl formals; secondary reactions yield dialkyl formals, phenolformaldehyde resins, and aliphatic alcs. The dialkyl formals react with ArOH, yielding ROH and the resins. $(PhO)_2CH_2$ appears to react with pyridine-HCl via an ion-chain reaction mechanism, yielding protonated adducts which cleave into PhOH and $PhOCH_2$ ions, the latter carrying the chain reaction that yields the resin by successive addn. of H ion. Heating 43.2 g. 1-(butoxymethyl)pyridinium chloride and 25.2 g. PhOH 70 min. to 150-60° gave 9.4 g. (50%) $(BuO)_2CH_2$, 14.6% *$BuOCH_2OPh$*, b_{10} 127-8°, d_4^{20} 0.9752, n_D^{20} 1.4880, 70% resin, and an unstated amt. of pyridine-HCl; 6 hrs. at 180-5° gave 15% BuOH, 57% $(BuO)_2CH_2$, some pyridine, and 80.7% resin. 1-(decyloxymethyl)pyridinium chloride yielded, similarly, in 1 hr. at 130-50° 5% PhOH, 5% decyl chloride, 4.8% decyl alc., 30% *decyl Ph formal*, $b_{0.11}$ 187.5-8.0°, n_D^{20} 1.4780, d_4^{20} 0.9266, 57.5% *didecyl formal*, b_6 208-10°, n_D^{20} 1.4418, d_4^{20} 0.8468, and 62% resin. 1-(Tetradecyloxymethyl) analog gave 92% *ditetradecyl formal*, m. 42-2.5°, and 80% resin. 2-Naphthol (8 g.) and 10.2 g. 1-(tetradecoxymethyl)pyridinium chloride in 10 hrs. at 150-60° gave 98% ditetradecyl formal, pyridine-HCl, and an unstated yield of resin; 1-naphthol gave 90% of the above formal and an alkali-sol. resin. Heating 4.5 g. PhOH and 20 g. $(BuO)_2CH_2$ 3.5 hrs. at 160-90° gave 68% BuOH and 4 g. phenolformaldehyde resin; 2-naphthol reacted similarly. Heating 3.9 g. PhOH and 10 g. didecyl formal 6 hrs. at 180-200° gave 8 g. *decyl alc.* (83%), b_{14} 146°, n_D^{20} 1.4378, d_4^{20} 0.8336, and 2.6 g. NaOH-insol. resin. The absence of $(PhO)_2CH_2$ in the products is explained by the following fact: heating this formal (10 g.) with 2.5 g. pyridine-HCl 10 hrs. at 195-202° gave 1.5 g. NaOH-sol. resin, 36% PhOH, and 4.7 g. resinous residue after distn. of the PhOH.

G. M. K.

CA

10

Effect of structural factors on conjugation phenomena. III. Mobility of hydrogen atoms in the dibenzoylmethane molecule. D. N. Kursanov, Z. N. Parnes, and I. A. Smolina. *Izvest. Akad. Nauk S.S.S.R., Otdel Khim. Nauk* **1950**, 512-17; cf. *C.A.* **44**, 3917*d*.—Heating Bz_2CH_2 with H_2O enriched with D_2O 26 hrs. at 19° gave no D-H exchange, but in dioxane-D_2O an exchange of 1 H readily took place after 20 hrs. at 0°; at 17° or 40° somewhat over 1 H is exchanged, and at 150° almost 2 H exchange occurs. Ph_2NH gives similar results. Stearic acid, myristyl alc., and fumaric acid give only fractional exchange with D_2O alone, but on addn. of dioxane the exchange is nearly complete. The results are interpreted as being the consequence of essential insoly. of the given compounds in H_2O alone. G. M. K.

KURSANOV, D. N.

Exchange and cleavage reactions of the quaternary salts of ammonia. VII. Reaction of salts of (alkoxymethyl)pyridinium with alkyl ethers of phenols. D. N. Kursanov and V. N. Setkina. *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1950, 651-8; cf. *C.A.* 45, 6201g.—Heating 28.3 g. 1-(decyloxymethyl)pyridinium chloride with 38.8 g. EtOPh 8 hrs. to 180-95° (sealed tube) gave 29 g. EtOPh, 1 g. decyl chloride, 4.6 g. decyl alc., b_{12} 125°, n_D^{20} 1.4378, d_4^{20} 0.8340, 2 g. $PhOCH_2OC_{10}H_{21}$, b_3 200-5°, n_D^{20} 1.4768, d_4^{20} 0.9210, and 7 g. $(C_{10}H_{21}O)_2CH_2$, b_3 232-4°, n_D^{20} 1.4420, d_4^{20} 0.8462; some 5.2 g. (38%) *phenol-formaldehyde resin* was secured from the residues. (Butoxymethyl)pyridinium chloride (20.1 g.) with 19.8 g. MeOPh 6 hrs. at 190-5° gave 1.4 g. BuOH, 1.1 g. $(BuO)_2CH_2$, b_{760} 178-82°, b_7 62°, n_D^{20} 1.4076, d_4^{20} 0.8580, 1.1 g. *unknown substance*, b_{10} 45-75°, and 7.7 g. (40%) phenol-formaldehyde resin. Heating 10 g. $(C_{10}H_{21}O)_2O$ with 3.9 g. PhOH 6 hrs. to 180-200° gave 8 g. decyl alc. and 2.6 g. solid which was elastic at first, then hardened on attempted distn., i.e. a form of phenol-formaldehyde resin. Hence, the pyridinium salts undergo transetherification with the phenol ethers, yielding formals which symmetrize and then react with the formation of the polymeric resins. The reaction of phenols and of their ethers with salts of (alkoxymethyl)pyridinium ion are analogous.

G. M. Kosolapoff

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KURSANOV, D.N., KABACHNIK, M.I., KAVERZNEVA, Ye.D., PRILEZHAYEVA, Ye. N., SOKOLOV,N.D. and FREYDLINA, R. Kh.

"The Current State of the Theory of Chemical Structure," Usp. Khim., 19, No.5, pp 529-544, 1950

Translation W-16104, 30 Dec 50

APPROVED FOR RELEASE: 03/13/2001 CIA-RDP86-00513R000927810003-1"

KURSANOV, D. N.

N. N. Mel'nikov, A. S. Zabrodina, D. N. Kursanov, and A. K. Ruzhentseva

"S. S. Nametkin's Work in the Field of Petroleum Chemistry," Uspkhi Khimii, Vol. XIX, No. 6, 1950, pp. 657-672

KURSANOV, D.N.

[redacted]

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✓Influence of the structural factors on conjugation phenomena. I. Mobility of hydrogen atoms in cyclic ketones of different structures. A. N. Nesmeyanov, D. N. Kursanov, K. A. Pecherskaya, and Z. N. Parnes. *Uchenye Zapiski Moskov. Gosudarst. Univ. im. M. V. Lomonosov* No. 132, *Org. Khim.* 7, 56-61(1950).—See *C.A.* 44, 3917*a*. II. Mobility of hydrogen atoms in acetylacetone and cobalt and aluminum acetylacetonates. A. N. Nesmeyanov, D. N. Kursanov, T. A. Smolina, and Z. N. Parnes. *Ibid.* 62-5.—See *C.A.* 44, 3917*f*. IV. Reactivity of α-CH link of ketones of different configurations. A. N. Nesmeyanov, K. A. Pecherskaya, and T. P. Tolstaya. *Ibid.* 66-72; cf. *C.A.* 45, 5606*a*.—To 54 g. spiro[4.5]decan-6-one in 150 ml. Et_2O was slowly added 14.7 g. powd. $NaNH_2$; after heating to expel all NH_3, the soln. was treated with 58 g. MeI, dild. with H_2O, and the org. layer sepd. and washed; distn. gave 87% *7-methylspiro[4.5]decan-6-one* (II), b_{11} 101-2°, n_D^{20} 1.4830, d_{20} 0.9813. This (5 g.) in Et_2O was treated with 7.44 g. dioxane-Br in Et_2O and after 2-3 min. the colorless soln. was washed with Na_2CO_3 and distd. yielding 0.8 g. unreacted material and 60% *7-bromo deriv.* (I), b_1 100-1°, n_D^{20} 1.5210, d_{20} 1.3270. Similar reaction of 7 g. spiro[4.5]decan-6-one with 11.3 g. dioxane-Br gave 72% *7-bromospiro[4.5]decan-6-one*, m. 47-8°, which decomps. on exposure to air yielding HBr. *2,2,6-Trimethyl-1-cyclohexanone*, b. 178.5-9.5°, n_D^{20} 1.4493, with 6.5 g. dioxane-Br similarly gave 80% *6-bromo deriv.*, m. 37-8°. Camphenylone failed to react with dioxane-Br after 2 hrs. refluxing in Et_2O. I (3.30 g.) and 0.34 g. Mg in Et_2O yielded a Grignard reagent which treated with CO_2 gave 61% methylspirodecanone, b_6 85°, n_D^{20} 1.4830. Addn. of 0.38 g. $CS(NH_2)_2$ to 1.15 g. 7-bromospiro[4.5]decan-6-one followed by warming led to a vigorous reaction which was accompanied by gas evolution; treatment of the cooled [illegible]

m. 129-30° (from EtOH). II (1 g.) shaken with 1.47 g. dioxane-SO_3 in $(CH_2Cl)_2$ and left overnight, then treated with aq. $BaCO_3$, boiled to expel the org. solvent, filtered and evapd. gave 88% *Ba 1-sulfonate dihydrate*, sol. in H_2O and warm PhMe. Similarly was obtained 90% *2,2,6-trimethyl-1-cyclohexanonesulfonic acid*, isolated as *Ba salt, dihydrate*, sol. in H_2O and warm PhMe. Camphenylone failed to react with dioxane-SO_3. II (2 g.) in 1 ml. concd. HCl was treated with ice cooling with a slow stream of MeONO over 6 hrs.; a green color developed along with sepn. of 0.3 g. colorless *7-nitroso-II*, m. 111-12° (from $CHCl_3$-petr. ether). Similar reaction of *2,2,6-trimethyl-1-cyclohexanone* run at 45-7° gave 35% *6-nitroso deriv.*, decomp. 113-13.5°. Camphenylone failed to react with MeONO. The lack of reactivity of this substance is ascribed to impossibility of conjugation between the CO and the adjacent CH link.

G. M. Kosolapoff

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Exchange and cleavage reactions of quaternary ammonium salts. VIII. Reaction with alcohols and phenols of substituted ammonium salts with a benzyl radical. V. N. Setkina and D. N. Kursanov. *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1951, 81-5; cf. C.A. 45, 6201g, 8528h.—Quaternary ammonium salts contg. benzyl radicals form with alcs. or phenols benzyl ethers of the corresponding alcs. or products of exchange of the mobile H of the phenols for the $PhCH_2$ group both in the OH group as well as in the ortho and para positions; with naphthols the reaction is predominantly nuclear substitution in the ortho and para positions with respect to OH. Heating 15 g. $PhCH_2NMe_2PhCl$ and 9 g. AmOH 5 hrs. at 140-55° gave 6.4 g. *$PhCH_2OAm$*, b_{12} 116-17°, d_4^{20} 0.9142, n_D^{20} 1.4851. Similarly, 13.4 g. 1-benzylpyridinium chloride (I) and 16 g. $C_{10}H_{21}OH$ 8 hrs. at 160-80° gave 7 g. *$PhCH_2OC_{10}H_{21}$*, b. 177-8°, d_4^{20} 0.8884, n_D^{20} 1.4770. 2-$C_{10}H_7OH$ (24.4 g.) and 41.2 g. I in 6 hrs. at 180° gave a wide series of fractions: 12% unreacted naphthol, 60% *1-benzyl-2-hydroxynaphthalene*, m. 111-11.5° (from 80% HCO_2H), b_{10-11} 225-42° (crude), and 1.2 g. *$C_{24}H_{20}O$*, m. 189.5-90.0°, whose structure is unknown. Similarly, 28.8 g. 1-$C_{10}H_7OH$ and 41.2 g. I in 6 hrs. at 180-200° gave 29.5% unreacted naphthol, 31% *1-hydroxy-4-benzylnaphthalene*, b_{10} 237°, m. 125.5°, and 9.5 g. viscous oil, b_4 240-310°, composed of several products from which an extn. with ligroine gave 1 g. $C_{24}H_{20}O$, m. 72°, identified as *1-hydroxy-2,4-dibenzylnaphthalene*. Heating 18.8 g. PhOH with 41 g. I 6 hrs. at 180-200° gave 25% PhOH, 18% *$PhOCH_2Ph$*, m. 39°, b_6 143-6°, 18% mixed isomeric *benzyl ethers of benzylphenols*, b_6 250-65°, 20% almost pure *p-benzylphenol*, m. 84°, and 17% mixed *dibenzylphenols*, b_6 245-52°. G. M. Kosolapoff

1ST AND 2ND ORDERS

PROCESSES AND PROPERTIES INDEX

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2

MAGYAR KIMIAI FOLYOIRAT
HUNGARIAN JOURNAL OF CHEMISTRY
VOL57, --1951
No. 2, Feb.

D. M. Kursanov
and associates:
On the question of the present state of the theory of chemical structure (From the Russian) 51--61

METALLURGICAL LITERATURE CLASSIFICATION

KURSANOV, D.N.

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RmL

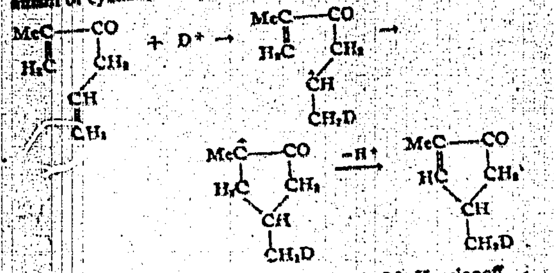
Reaction mechanism of the cyclization by means of deuterium. I. Cyclization of isopropenyl allyl ketone. D. N. Kursanov, Z. N. Parnes, I. I. Zaretskaya, and I. N. Nazarov. *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.* 1953, 103-7(Engl. translation).—See *C.A.* 48, 3271b.
H. L. H.

3-1-55
RmL

KURSANOV, D.N.

6

Reaction mechanism of the cyclization by means of deuterium. I. Cyclization of isopropenyl allyl ketone. D. N. Kursanov, Z. N. Parnes, T. I. Zaretskaya, and I. N. Nazarov. *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1953, 114-20.—Cyclization of $CH_2:CHCH_2CO$-$CMe:CH_2$ (I) was studied in the presence of H_3PO_4 enriched with D (d. 1.79). I and 1 part catalyst were kept 2-24 hrs. at 10-24°; the exchange of D between the catalyst and the I cyclization product is very extensive, being somewhat over that required for exchange of 1 H by 1 D in 20 hrs. at 19°. Fractionation of the product gave *dimethylcyclopentenone*, b_{10} 77-7.7°, n_D^{20} 1.4670, d_{20} 0.9387. The results clearly show that the cyclization is accompanied by introduction of 1 D atom, confirming the Nazarov mechanism of cyclization represented below:



G. M. Kosolapoff

KURSANOV, D.N.

Chemical Abst.
Vol. 48
Apr. 10, 1954
Organic Chemistry

High-molecular compounds. LI. Exchange reaction in polyesters studied by means of the heavy isotope of hydrogen. D. N. Kursanov, V. V. Korshak, and S. V. Vinogradova. *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1953, 140-4; cf. *C.A.* 46, 1446i, 7527d; 48, 2622. In polyesterification reactions it was shown that ester interchange reactions take place. Hydrogenation of di-Et maleate with D-enriched H over Pd gave di Et $(EtO_2CCHD)_2$ contg. some 21% of the theoretical content of D. This was heated with polyhexamethylene adipate in the molten state 10 hrs. at 250° and the polymer was isolated and examd. for D content by the usual combustion method. Some 30% exchange took place under the above conditions, with an original ratio in the mixt. of 1 mole deutero ester/chain unit $[-O(CH_2)_6OCO(CH_2)_4CO-]$ of the polyester chain.

G. M. Kosolapoff

KURSANOV, D. N.

(1)

The mechanism of the cyclization reaction by means of deuterium. II. I. N. Nazarov, I. I. Zaretskaya, Z. N. Parnes, and D. N. Kursanov. *Izvest. Akad. Nauk S.S.S.R. Otdel. Khim. Nauk* **1953**, 519-23; cf. *C.A.* 48, 3271*c*.—It was previously shown that cyclization of 2-methyl-1,5-hexadien-3-one in D-enriched H_3PO_4 results in the entry of D into the cyclopentenone deriv., indicating the correctness of the ionic nature of the reaction as proposed by Nazarov (*C.A.* 48, 611*d*), in which in the initial step D^+ adds to the terminal C of the allyl group. The location of the D in the product was now investigated. The deutero-2,4-dimethyl-2-cyclopenten-1-one, obtained as described above, was ozonized, yielding $HO_2CCHMeCH_2CO_2H$, which contained substantially all the D that was present in the cyclopentenone. Thus the presence of D on the 1-, 2-, 3-, or 6-positions is excluded. Oxidation of the cyclopentenone with SeO_2 gave D-free 2,4-dimethyl-2-cyclopentene-1,5-dione, m. 64-5°. Hence D must be present in the 5-position, i.e. the methylene group adjacent to the carbonyl. This shows that the cyclization is entered not by $CH_2:CHCH_2COCMe:CH_2$, but by its isomer, $MeCH:CHCOCMe:CH_2$. No exchange of D occurs between the cyclopentenone deriv. and AcOH-AcOD. G. M. K.

KURSANOV, D.N.

USSR.

✓Hydrogen exchanges of saturated hydrocarbons in reaction with sulfuric acid. D. N. Kursanov, V. N. Setkina, and O. D. Sterligov. Bull. [redacted] S.R., Div. Chem. Sci. 1953, 921-6 (Engl. translation).—See C.A. 49, 2296h.
H. L. H.

KURSANOV, D. N.

USSR/Chemistry - Isotopes; Hydrocarbons Nov/Dec 53

"Hydrogen Exchange of Saturated Hydrocarbons in the Interaction With Sulfuric Acid," D.N. Kursanov, V.N. Setkina, O. D. Sterligov, Inst Org Chem, Acad Sci USSR

Iz Ak Nauk SSSR, OKhN, No 6, pp 1035-1042

Investigated the exchange capacity of H atoms of n-heptane, n-dodecane, 2-methylpentane, 3-methylhexane, 2,2-dimethylhexane, 2,2,3-trimethylbutane, and 2,2,4-trimethylpentane in the interaction with deuterosulphuric acid (I).

273T12

Found that only hydrocarbons that have a tertiary C atom are capable of this exchange, and that equil is established within several hours at 20-25°. Also established that the highly mobile H atoms of alicyclic hydrocarbons with tert-C atoms are exchanged for deuterium on contact with I. State that the results check with data subsequently published by USA investigators.

Reactions of hydrogen exchange of α,β-unsaturated ketones. D. N. Kursanov and Z. N. Parnes (Acad. Sci. U.S.S.R., Moscow). Doklady Akad. Nauk S.S.S.R. 91, 1125-8(1953).—When various satd. ketones are heated with H_2O enriched with D_2O in dioxane in the presence of a small amt. of base (1,2-dihydro-1-methyl-2-methylimino-pyridine) exchange of D for all H atoms on α-C atoms takes place readily. However, $(PhCH:CH)_2CO$, $PhCH:CHCOCMe_3$ and PhCH:CHBz do not react or show at most a very minute D-H exchange. If the unsatd. links in these ketones are satd. by hydrogenation, the D-H exchange takes place readily. Thus, H atoms on α-C atoms in α,β-unsatd. ketones do not exchange H for D, as a result of suppression of carbonyl-double bond conjugation. When $Me_2C:CHCOCH:CMe_2$ or $H_2C:CHCOCH:CMe_2$ are subjected to D-H exchange, the exchange takes place readily but only at the Me groups, to which the proton mobility is transferred. CH_2Ac_2 readily exchanges 2 H atoms for 2 D atoms, but $AcCH:CMeOC_2OEt$ does not exchange H for D at all. The latter substance was prepd. from EtO_2CCl with $NaCHAc_2$; b_8 118-9°, d_{20} 1.0791, n_D^{20} 1.4485.

O. M. Kosolapoff

KURSANOV, D. N.

USSR.

Hydrogen exchange of cyclic saturated hydrocarbons in reaction with sulfuric acid. V. N. Setkina, D. N. Kursanov, and A. L. Liberman. Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci. 1954, 499(Engl. translation). C.A. 49, 6111.

H. L. H.

KURSANOV, D. N.

USSR.

C-Hydrogen exchange of cyclic saturated hydrocarbons in reaction with sulfuric acid. V. N. Setkina, D. N. Kursanov, and A. L. Liberman (Inst. Org. Chem. [redacted] [redacted]R., Moscow). *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1954, 103-16; cf. *C.A.* 49, [illegible].—D-H exchange of cyclic hydrocarbons in the presence of D-enriched H_2SO_4 was examd. The D-H exchange is entered into by monocyclic hydrocarbons which contain tertiary C atoms (methyl-, 1,4-dimethyl-, and 1-methyl-4-ethylcyclohexane, methylcyclopentane), and the equil. is established at room temp. in a few hrs. No exchange takes place with cis and trans forms of decahydronaphthalene. In mixts. of hydrocarbons which contain secondary and tertiary C atoms, only the latter react. Substantially no exchange occurs with cyclohexane. 1,1-Dimethylcyclohexane also does not react, neither does cyclopentane. When the exchange takes place, all H atoms are capable of exchange. Isomerization of substituted cyclohexanes is taken into account.

G. M. Kosolapoff

KURSANOV, D. N.

Reaction mechanism of the cyclization by means of deuterium. III. D. N. Kursanov, Z. N. Parnes, I. I. Zaretskaya, and I. N. Nazarov (N. D. Zelinskii Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1954, 858-64; cf. *C.A.* 48, 9930b. —Heating $Me_2C:C(CHMe_2)COCH_2CH(OMe)Me$ with *p*-$MeC_6H_4SO_3H$ yielded *$Me_2C:C(CHMe_2)COCH:CHMe$*, b_{11} 93-3.5°, n_D^{20} 1.4735, d_{20} 0.8799. This on cyclization with H_3PO_4 (cf. *C.A.* 44, 8307i) gave *2-isopropyl-3,3,4-trimethyl-2-cyclopentenone* (I), b_{17} 112-12.5°, n_D^{20} 1.4779, d_{20} 0.9245, which was then used for the study of D-H exchange by 2 hrs. contact with H_3PO_4 (98%) enriched with D; almost no D-H exchange was observed with this cyclic ketone and a similar result was obtained in a similar treatment of the initial dienone. The latter (14.4 g.) was then treated with D_3PO_4, prepd. from 9.6 g. P_2O_5 and 4.4 g. D_2O, 8 hrs. at 20-1°, yielding I contg. 1 D atom per mol. This was ozonized yielding HCO_2H and higher org. acids, the latter yielding cryst. *α-deutero-α-isopropyl-β,β-dimethyllevulinic acid*, m. 48°. Oxidation of this with $Br-H_2O$ gave *α-deutero-α-isopropyl-β,β-dimethylsuccinic acid*, m. 134-5°, which retained the same amt. of D as the cyclic ketone. A mechanism for the cyclization is presented which is consistent with the exptl. results. G. M. Kosolapoff

62

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KURSANOV, D N

AID P - 1118

Subject : USSR/Chemistry

Card 1/1 Pub. 119 - 1/5

Authors : Kursanov, D. N. and Voyevodskiy, V. V. (Moscow)

Title : Some new data on hydrogen exchange between organic radicals and ions

Periodical : Usp. khim., 23, no. 6, 641-653, 1954

Abstract : Hydrogen exchange of free organic radicals and of organic cations is reviewed. Experimental data on the hydrogen exchange of carbonyl compounds with D_2SO_4 are compiled in a table. One table, 38 references (19 Russian: 1934-54).

Institution : None

Submitted : No date

KURSANOV, D. N.

M Reactions of hydrogen exchange of saturated ketones with acids. D. N. Kursanov and V. N. Setkina (N. D. Zelinskii Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Doklady Akad. Nauk S.S.S.R.* 94, 69-72(1954).—D-H exchange was studied in the series of satd. aliphatic ketones in media containing H_2SO_4 and H_3PO_4 enriched with D. The following extents of exchange, reported as percentages of exchange of all α-H atoms in the ketones, were found: in D_2SO_4, MeCOBu 99.5, cyclopentanone 102.9, cyclohexanone 82.6; in D_3PO_4, MeCOBu 100.3, cyclopentanone 104.9, cyclohexanone 100.0. The proof that the exchanged D atoms were located in α-positions was had by treatment of the D-exchanged ketones with BzH yielding the dibenzal derivs., which were devoid of D content. The reactions in D_2SO_4 were run 1 hr. at room temp., those in D_3PO_4 for 48 hrs. at room temp. Cf. *C.A.* 47, 851*f*. G. M. Kosolapoff

KURSANOV, D. N.

USSR/Chemistry

Card : 1/1

Authors : Lavrushin, V. F., Kursanov, D. N., Memb. Corres. of Acad. of Sc. USSR.; and Setkina, V. N.

Title : Reaction of saturated hydrocarbons with sulfuric acid

Periodical : Dokl. AN SSSR, 97, Ed. 2, 265 - 266, July 1954

Abstract : Experiments showed that saturated hydrocarbons absorb light in the range of very short waves thus indicating that the curves of their sulfuric acid solutions owe their origin to hydrocarbon-sulfuric acid reaction products. Since the absorption curves of hydrocarbons are analogous to each other and with the absorption curves of trimethylcarbinol it becomes evident that the nature of their reaction with sulfuric is also identical. It was also proven that the particles, forming during the reaction of hydrocarbons with sulfuric acid, are identical. Six references. Graph

Institution : Acad. of Sc. USSR, Inst. of Element. - Organic Compounds and the A. M. Gorkiy State University, Kharkov

Submitted : March 24, 1954

KuRSANOV, D.N.
USSR/Chemistry - Physical chemistry

Card 1/1 : Pub. 22 - 21/48

Authors : Kurasnov, D. N., Memb. Corresp. of Acad. of Sc. USSR.; Setkina, V. N.; and Bykova, E. V.

Title : About the intra-molecular effect of positive-charged centers on the proton mobility of H-atoms

Periodical : Dok. AN SSSR 97/5, 835-838, August 11, 1954

Abstract : The effect of positive-charged centers on the proton mobility of hydrogen atoms, is explained. The difficulties involved in studying the effect of a tri-covalent positive charged (oxonium) O-atom on the proton activity of H-atoms, are discussed. The results of the hydrogen interchange reactions are shown in tables. Four references: 3-USSR and 1-German (1933-1954).

Institution : ...

Submitted : April 8, 1954

Kursanov, D. N.

USSR/Chemistry - Elementorganic compounds

Card 1/1 Pub. 22 - 21/40

Authors : Parnes, Z. N., and Kursanov, D. N., Memb. Corresp. of Acad. of Sc. USSR

Title : Effect of substitutes on the mobility of hydrogen atoms of unsaturated and aromatic ketones

Periodical : Dok. AN SSSR 99/2, 265-268, Nov 11, 1954

Abstract : Experiments were conducted to determine whether the nature of the R radical in ketones has any effect on the mobility of hydrogens of the methyl group oriented opposite the carbonyl group and whether the conjugations of the R radical and methyl group with the carbonyl group are independent from each other. It was found that the nature of the radical in ketones has a definite and essential effect on the mobility of the hydrogen atoms in the methyl group. The rate of the hydrogen exchange increases with the increase in the electron-acceptor characteristics of the R radical. The effect of the ethylene (or aromatic) bond in alpha, beta position, relative to the carbonyl group on the hydrogen atom mobility in the case of an alpha-carbon atom oriented on the other side of the carbonyl group, is elucidated. Two USSR references (1949 & 1953). Tables

Institution : Acad. of Sc. USSR, Institute of Elementoorganic Compounds

Submitted : June 18, 1954

Kursanov, D. N

USSR/ Chemistry - Analytical chemistry

Card 1/1 Pub. 22 - 32/63

Authors : Setkina, V. N.; Plate, A. F.; Sterligov, O. D.; and Kursanov, D. N., Memb. Corres. of Acad. of Sc. USSR

Title : Possibility of adapting the hydrogen exchange reaction for the analysis of saturated hydrocarbon mixtures

Periodical : Dok. AN SSSR 99/6, 1007-1010, Dec 21, 1954

Abstract : The characteristics of hydrogen exchange reaction and the possibility of applying this reaction for analytical purposes were investigated. A compulsory condition for the adaption of the hydrogen exchange reaction for the analysis of saturated hydrocarbon mixtures was found to be the attainment of reaction equilibrium. It was established that the hydrogen exchange reaction of aliphatic and alicyclic hydrocarbon mixtures containing from 5 to 7 carbon atoms in the molecule begins within a period of 10 - 20 hrs. The results, obtained during the reaction of two-component saturated hydrocarbon mixtures, are tabulated. Nine USSR references (1935-1954). Tables.

Institution: ....

Submitted: June 18, 1954

Kursanov, D.N.

11

Exchange reactions and cleavage in the group of quaternary ammonium salts. IX. Reaction of quaternary ammonium salts with secondary and tertiary alcohols. V. N. Setkina, N. K. Baranetskaya, and D. N. Kursanov (Inst. Hetero-org. Compounds, Acad. Sci. U.S.S.R., Moscow). *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1955, 750-6; *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.* 1955, 667-72 (Engl. translation); cf. *C.A.* 46, 4584.—Quaternary ammonium salts contg. the $ROCH_2$ group react with secondary and tertiary alcs. with formation of formals. Thus, cyclohexyloxymethylpyridinium chloride (I) (30.64 g.) and 13.47 g. cyclohexanol after 6 hrs. at 100° gave 18 g. $(C_6H_{11}O)_2CH_2$ (II), b_{760} 279-80°, d_4^{24} 0.9716, n_D 1.470. *sec*-Octyloxymethylpyridinium chloride (IIa) and *sec*-octyl alc. gave 46% $(C_6H_{13}CHMeO)_2CH_2$ (III), b_3 152.5-3°, d_{20} 0.8419, n_D^{20} 1.4322. I and MeEtCHOH gave 24.9% $(MeEtCHO)_2CH_2$, b_{17} 60.5-60.8°, d_{20} 0.8472, n_D^{20} 1.4124, 52.9% $MeEtCHOCH_2OC_6H_{11}$, b_{18} 99.5-101°, d_{20} 0.9076, n_D^{20} 1.4402, and 22.2% II. I and iso-PrOH gave 18.4% $(iso\text{-}PrO)_2CH_2$, 52.2% $iso\text{-}PrOCH_2OC_6H_{11}$, b_{18} 70-70.5°, d_{20} 0.9089, n_D^{20} 1.4370, and 29.4% II. Isopropoxymethylpyridinium chloride and Me_3COH gave 38.4% $iso\text{-}PrOCH_2OCMe_3$, b_{760} 71.1-1.5°, d_{20} 0.8223, n_D^{20} 1.3930, 40.6% $(iso\text{-}PrO)_2CH_2$, and 21% $(Me_3CO)_2CH_2$, b_{760} 77-9.5°, d_{20} 0.8300, n_D^{20} 1.3982. IIa and Me_3COH in 17 hrs. at 120° gave 8.9% $(Me_3CO)_2CH_2$, 48% $Me_3COCH_2OCHMeC_6H_{13}$, b_{20} 128-9°, d_{20} 0.8351, n_D^{20} 1.4204, and 43.1% III. I and *tert*-AmOH in 16 hrs. at 110-15° gave II and $C_6H_{11}OCH_2OCMe_2Et$, b_{14} 119.5-20.5°, d_{20} 0.9103, n_D^{20} 1.4453, in combined yield of 26%. $C_6H_{13}CHMeOCH_2Cl$ b_{15} 88-9°, d_{20} 0.9240, n_D^{20} 1.4357.

G. M. Kosolapoff

(1)

Application of the Ball reaction on aromatic alcohols. I. Shigehiko Sugasawa and Kitaro Mizukami (Univ. Tokyo). *Pharm. Bull.* (Japan) 2, 341-2 (1954).—Ball's method (S. *et al.*, *C.A.* 42, 8916f) for oxidizing polyene alcs. in Et_2O with activated MnO_2 to unsatd. aldehydes was applied to aromatic alcs. with the following results (alc., reaction temp., reaction time in hrs., and % yield and m.p. of the semicarbazone of the corresponding aldehyde given): $PhCH_2OH$, 22-35°, 2, 70, 215-16°, $3,4\text{-}CH_2O_2C_6H_3CH_2OH$, 35°, 1, 65, 177°, $2\text{-}HOC_6H_4CH_2OH$, 20°, 3, 60, 224°, furfuryl, 19-20°, 3.5, 40, 190-2°, 3-pyridyl, 21°, 1.5, 50, 213-14°, and 4-pyridyl, 35°, 3, 60, 213-15°.

W. T. S.

Kursanov, D.N.

48

Reaction of 1-apocamphanecarboxylic acid with hydrazoic acid. D. N. Kursanov and S. V. Vitt. *Zhur. Obshchei Khim.* 25, [illegible](1955). Refluxing 6.2 g. ketonic acid with 10 ml. triethylene glycol, 6 g. $N_2H_4.H_2O$ and 7 g. powd. KOH, with gradual distn. of H_2O and excess N_2H_4, maintaining the distn. temp. at 195° and finally at 202° 3.5 hrs. yielded after cooling and acidification with H_2SO_4 85% *1-apocamphanecarboxylic acid*, m. [illegible]. This ([illegible] g.) in 25 ml. C_6H_6 and 15 ml. concd. H_2SO_4 was treated with 2.28 g. NaN_3 over 0.5 hr. at 35-40°; after 1 hr. at 50° the mixt. was treated with ice and extd. with C_6H_6 and the aq. layer steam distd. after addn. of NaOH, yielding [illegible]% *1-apocamphylamine*, m. 173-7° (sealed tube). N-Acetyl deriv., m. 131-2° (cf. Bartlett and Knox, *C.A.* 34, [illegible]). No by-products were formed in the Schmidt reaction. G. M. K.

Kursanov, D.N.

Reactions of hydrogen exchange of aldehydes. D. N. Kursanov and Z. N. Parnes. *Doklady Akad. Nauk S.S.S.R.* 105, 817-0(1955). D-H exchange was studied in several aldehydes in dry dioxane treated with D_2O in the presence of *N,N'*-dimethylpyridonimine catalyst at 100° in sealed ampuls. The % exchange found in 50 hrs. was enanthaldehyde 90, cyclamenal 92, BzH 1, PhCH:CHCHO 2, citralal 70, Me_3CCHO 0.5, and jasminealdehyde 5. The exchange takes place with the H atoms of the Me and methylene groups at the γ-C atom in unsatd., and at the α-C atom in satd. compds. (Cf. *C.A.* 48, 10540c). G. M. K.

Chem

2

KURSANOV, D.N.

7

Reaction of hydrogen exchange in saturated carboxylic acids with sulfuric acid-d_2. V. N. Setkina, E. V. Bykova, and D. N. Kursanov (Inst. Heteroorg. Compds., Acad. Sci. U.S.S.R., Moscow). *Doklady Akad. Nauk S.S.S.R.* 104, 869-71(1955).—The following percentages of H-D exchange took place between carboxylic acids and D_2SO_4 in the indicated number of hrs. (in parentheses): iso-$PrCO_2H$ (110) 82%, (185) 98%, (260) 91%; Et_2CHCO_2H (120) 102%, (310) 89%; iso-$PrCH_2CO_2H$ (120) 100%, (310) 91%; iso-$AmCO_2H$ (189) 94%, (214) 87%; iso-$AmCH_2CO_2H$ (240) 42%, (2520) 89%; Me_3CCO_2H 0%. The exchange takes place only with H atoms on the α-C atom and the extent of exchange is equal to the total no. of α-H atoms available. No exchange took place with acids contg. Br atoms in the α-position. The mechanism of exchange is discussed briefly. G. M. Kosolapoff

KURSANOV, D.N.

8

3

Reaction of hydrogen exchange of saturated hydrocarbons with one and several tertiary carbon atoms and sulfuric acid. D. N. Kursanov, V. N. Setkina, and A. P. Meshcheryakov (Inst. Heteroorg. Compds., Acad. Sci. U.S.S.R., Moscow). *Doklady Akad. Nauk S.S.S.R.* 105, 279-81 (1955); cf. *C.A.* 47, 851*f*.—H-D exchange of several branched hydrocarbons with D_2SO_4 was studied in exposures up to 10.5 hrs. *n*-Octane gave 1.8-2% exchange; 3-methylheptane 100.1%; 2,3,4-trimethylpentane 98-9% exchange. Exchange of 3-methyl-3-D-heptane with H_2SO_4 resulted in considerable enrichment of the acid with D and a corresponding loss of D by the hydrocarbon. The labeled hydrocarbon was prepd. by dehydration of 3-hydroxymethylheptane over Al_2O_3 at 400°, yielding mixed octenes which with HCl gave 3-chloro-3-methylheptane, b_4 46.5-6.8°, d_{20} 0.8773, n_D^{20} 1.4322, which was converted to RMgCl and this decompd. with D_2O; 3-methyl-3-D-heptane was distd. and purified by chromatography on SiO_2; the product used had n_D^{20} 1.3982. The exchange reactions were run in a shaker at room temp. G. M. Kosolapoff

Chem

KUDRYAVTSEV, R.V.; OTTESEN, B.V.; KURSANOV, D.N.

Determination of oxygen isotope content in organic compounds.
Kudriavtsev, Zhur.ob.khim. 26 no.4:1035-1039 Ap '56. (MLRA 9:8)
(Oxygen--Isotopes)

KURSANOV, D.N.

Hydrogen exchange of carbonium ions with acids and hydrogen exchange of carbonyl compounds with deuterium oxide in an alkaline medium. Ukr.khim.zhur. 22 no.1:34-37 '56. (MLRA 9:6)
(Hydrogen) (Carbon compounds)

"APPROVED FOR RELEASE: 03/13/2001 CIA-RDP86-00513R000927810003-1

KURSANOV, D. N.

USSR/ Physical Chemistry - General Problems on Isotope Chemistry B-7

Abs Jour : Referat Zhur - Khimiya, No 3, 1957, 7414

Author : Kudriyavtsev, R.V., Ottesen, B.V., and Kursanov, D.N.

Title : Determination of the Isotope Composition of Oxygen in Organic Compounds

Orig Pub : Zh. obshch. khimii, 1956, Vol 26, No 4, 1035-1039

Abstract : A method is described for the destructive hydrogenation of organic substances for the purpose of determining the isotope composition of the oxygen in these substances; the hydrogenation is carried out at 300° in an H_2 atmosphere and over a Ni catalyst. At 300-400° there is no exchange between the walls of the tube, made of Mo-glass, and H_2O^{18}. The catalyst contains oxygen which can be exchanged with the water vapor. In order to establish the equilibrium for this exchange four passes of vapor over the catalyst at 300° are sufficient. The error in the determination is 3-4 percent.

Card 1/2

APPROVED FOR RELEASE: 03/13/2001 CIA-RDP86-00513R000927810003-1

USSR/ Physical Chemistry - General Problems on Isotope Chemistry B-7

Abs Jour : Referat Zhur - Khimiya, No 3, 1957, 7414

The method cannot be used with substances which contain S, P, halogens, and other elements which will poison the catalyst, nor with substances which boil above 200°.

Card 2/2

KURSANOV, D.N.; KUDRYAVTSEV, R.V.

Study of the hydrolysis mechanism with the aid of a heavy oxygen isotope. Part 1. Hydrolysis of ethyl propionate in an alkaline medium. Zhur.ob.khim. 26 no.4:1040-1041 Ap '56. (MLRA 9:8)
(Hydrolysis) (Oxygen--Isotopes) (Propionic acid)

KURSANOV, D.N.

5

Synthesis of ethyl alcohol containing [illegible] oxygen. V. V. [illegible] *Obshchei Khim.* 25, 2054-6 (1955) [illegible] AcH vapor passed through an [illegible] tionating column contg [illegible] gave AcH contg. 1.06-1.1% O^{18} [illegible] of O^{18}) which passed over Raney Ni [illegible] $EtO^{18}H$, b. 78-8.1°, [illegible] 1.3020 [illegible]

[illegible]

RM ug

KURSANOV, D.N.

4/ 7

Study of the mechanism of hydrolysis by means of heavy oxygen isotope. II. Hydrolysis of dimethyl sulfate in acid and alkaline media. D. N. Kursanov and R. V. Kudryavtsev. *Zhur. Obshchei Khim.* 26, 2057-9(1956); cf. C.A. 50, 10638f; Lauder and Green, C.A. 43, 8776c.—Heating Me_2SO_4 with aq. NaOH in H_2O^{18} contg. 1.2% O^{18}, with continuous distn. of MeOH, gave MeOH contg. 0.82% O^{18}, when a small amt. of aq. soln. was used, whereas with large excess of aq. soln. the MeOH obtained had 1.10% O^{18}. Heating Me_2SO_4 with H_2O^{18} contg. a trace of H_2SO_4 gave MeO^{18} contg. 1.08% O^{18} and some MeOH contg. 1.01% O^{18}. The results indicate that hydrolysis of Me_2SO_4 does not involve the S-O bond, but is directed only at the C-O link, in both acid and alk. solns. However, the content of O^{18} in the resulting MeOH is below that in starting H_2O^{18} caused by exchange of O in the SO_2 group. This was confirmed by the higher content of O^{18} in the product obtained with large excess of H_2O^{18}. G. M. K.

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KURSANOV, D. N.

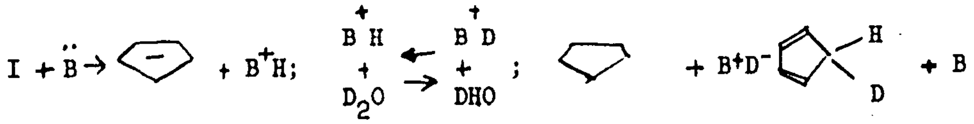
USSR/ Organic Chemistry - Theoretical and general questions of organic chemistry E-1

Abs Jour : Referat Zhur - Khimiya, No 4, 1957, 11570

Author : Kursanov D.N., Parnes Z.N
Inst : Academy of Sciences USSR
Title : On Hydrogen Exchange Reaction of Cyclopentadiene

Orig Pub : Dokl. AN SSSR, 1956, 109. No 2, 315-318

Abstract : All 6 atoms of H of cyclopentadiene (I), under mild conditions (20 hours, 20°, solvent: dioxane), in the presence of N, N'-dimethyl-alpha-pyridomimine, take part in the hydrogen exchange reaction (HER) with D_2O. Under these conditions sylvane and cycloheptatriene do not undergo HER. Pyrrole exchange only the H atom linked to N.



Ready occurence of HER in the case of I is due to the stability of the cyclopentadienyl anion, having an aromatic nature, and the delocaliza-

Card 1/2

USSR/ Organic Chemistry - Theoretical and general questions
of organic chemistry E-1

Abs Jour : Referat Zhur - Khimiya, No 4, 1957, 11570

tion of the negative charge in the anion. The many times repeated establishment of acid-base equilibrium of delocalization of the negative charge results in complete exchange of H atoms (see scheme). In neutral and acid medium the HER of I does not occur. Ferrocene does not undergo HER with D_2O, which shows that the bond between Fe and cyclopentadienyl residue must be regarded as covalent .

Card 2/2

KURSANOV, D N

USSR/ Organic Chemistry - Theoretical and general questions
on organic chemistry

E-1

Abs Jour : Referat Zhur - Khimiya, No 4, 1957, 11574

Author : Setkina V.N., Kursanov D.N.
Inst : Academy of Sciences USSR
Title : On Hydrogen Reactions of 1-Methylcyclohexanol-1 with Phosphoric Acid

Orig Pub : Dokl AN SSSR, 1956, 109, No 3, 552-554

Abstract : A study was made of hydrogen exchange reaction (HER) of 1-methylcyclohexanol-1(I) with D_3PO_4 I undergoes HER at -5 -0°. Content of D in I after the experiment was determined on the basis of excess density of water of I combustion and that of the combustion of methylcyclohexenes produced by dehydration of I with iodine. On HER of 1-methylcyclohexene-1 (II) under the same conditions, II is not hydrated to I and exchange of II is considerably lower than that of I, therefore HER of I does not take place with intermediate formation of cyclo-olefin. On the basis of these data, and also the data of cryoscopic and

Card 1/2

USSR/ Organic Chemistry - Theoretical and general questions on organic chemistry E-1

Abs Jour : Refeat Zhur - Khimiya, No 4, 1957, 11574

spectral investigation of solutions of tertiary alcohols in H_2SO_4 the conclusion is arrived at, that I forms with D_3PO_4 a carbonium ion which undergoes HER.

Card 2/2

Kursanov, D.N.

Effect of nucleophilicity of an anion on the character of the bond in tropylium compounds. M. E. Vol'pin, I. S. Akhrem, and D. N. Kursanov. *Khim. Nauka i Prom.* 2, 356-7(1957).—The character of the bond between $C_7H_7^+$ and [illegible]pends on the nucleophilicity of the X^- ion, an inde[illegible]h may be the dissocn. const., K, of the respective acid HX. Thus the transitions between ionic and covalent salts of $C_7H_7^+$, at present, are $K = 1.2 \times 10^{-4}$ (HNCO) and 7.2×10^{-10}(HCN). To reduce the range, compds. were synthesized with AcOH and EtOH. Both were covalent liquids (b. 55-6° and 78-82°, resp.), sol. in nonpolar solvents. The covalency was also established by the ultraviolet absorption spectra and by the ease of hydrolysis in H_2O and NaOH to give oxides and the ease of bromination. Hydrolysis of C_7H_7CN in concd. HCl resulted in partial isomerism to form phenylacetic acid. Thus acids

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bromination. Hydrolysis of C_6H_5CN in concd. HCl resulted in partial isomerism to form phenylacetic acid. Thus acids with $K = 1.2 \times 10^{-4}$ give ionic salts and those with $K = (0.3\text{-}1.75) \times 10^{-4}$ (BzOH and AcOH) give covalent derivs. This agrees with the results of Doering, *et al.* (*C.A.* 49, 8832h).

I. Bencowitz

KURSANOV, D.N.; VITT, S.V.

On the mechanism of the alkylation of alcohols by N-trimethyl-
α-phenethylammonium iodide. Dokl. AN SSSR 113 no.3:607-609
Mr '57. (MIRA 10:6)

1. Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR.
2. Chlen-korrespondent Akademii nauk SSSR (for Kursanov).
(Alkylation) (Phenethylamine) (Ammonium compounds, Substituted)

KURSANOV, D.N.; BARANETSKAYA, N.K.; SETKINA, V.N.

Interaction on benzylpyridinium chloride with lithium cyclopentadienyl. Dokl. AN SSSR 113 no.1:116-119 Mr-Ap '57. (MIRA 10:6)

1. Chlen-korrespondent Akademii nauk SSSR (for Kursanov).
2. Institut elementoorganicheskikh soyedineniy Akademii naul SSSR.
(Pyridinium compounds) (Cyclopentadienyl)

"APPROVED FOR RELEASE: 03/13/2001 CIA-RDP86-00513R000927810003-1

[illegible]

[illegible] [illegible]EV, A.V.; [illegible], D.N.

Using the heavy isotope of oxygen for studying the mechanism of alkali re-etherification of complex ethers. Zhur.ob.khim. 27 no.6:1686-1687 Je '57. (MIRA 10:[illegible])

1. Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR. (Oxygen--Isotopes) (Ethers)

APPROVED FOR RELEASE: 03/13/2001 CIA-RDP86-00513R000927810003-1"

"APPROVED FOR RELEASE: 03/13/2001 CIA-RDP86-00513R000927810003-1

KURSANOV, D.N.; VITT, S.V.

Study of the mechanism of alkylation of phenols by N-trimethyl-α-phenylethylammonium iodide. Dokl. AN SSSR 113 no.5:1066-1069 Ap '57. (MIRA 10:7)

1. Chlen-korrespondent Akademii nauk SSSR (for Kursanov).
2. Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR.

(Alkylation) (Ammonium compounds, Substituted) (Phenols)

APPROVED FOR RELEASE: 03/13/2001 CIA-RDP86-00513R000927810003-1"

Kursanov D. N.

7 5

4E4j

New method of preparation of tropylium and methyltropylium compounds. D. N. Kursanov and M. E. Vol'pin (Inst. Hetero-Org. Compds., Acad. Sci., Moscow). *Doklady Akad. Nauk S.S.S.R.* 113, 339-42(1957); cf. Doering and Knox, *C.A.* 49, 88[illegible]h.—Photochem. reaction of C_6H_6 with CH_2N_2 (D. and K., *C.A.* 48, 6166) yielded *cycloheptatriene* (I) (contg. 5% MePh after fractional distn.), b_{11} 116.3-7°, n_D^{20} 1.5228. This (0.08 g.) added with cooling to 3 ml. conc[illegible] H_2SO_4, kept 10 days, then dild. with 1 vol. H_2O, and treated with chloroplatinic acid, gave 18% *tropylium chloroplatinate*. While nonoxidizing acids did not effect this transformation, CrO_3, HNO_3, S_2O_3, SO_2Cl_2, and BF_4 also gave tropylium salts. Addn. of 0.91 g. I to 4.1 g. PCl_5 in 40 ml. CCl_4 resulted in a colorless ppt.; after stirring 1 hr. and refluxing 15 min. this was sepd., washed with CCl_4 and treated with cooling with 4 ml. H_2O. The flask was rinsed down with EtOH and the aq. EtOH layer treated with a slight excess of 30% $HClO_4$ yielding [illegible] tropylium *perchlorate*. Addn. of chloroplatinic acid to the filtrate gave 10% tropylium chloroplatinate. When the reaction was run overnight without heating the total [illegible] reached [illegible]%. *Tropylium chloride*, m. 97° (from M[illegible]), its aq. solns. gave the tests for Cl ion and tropylium ion. Photochem. reaction of MePh with CH_2N_2 gave a fraction, b_{11} [illegible], n_D^{20} 1.5114, contg. some 70% methylcycloheptatriene. This treated with PCl_5 as above gave a salt of methyltropylium, which was isolated as a yellow *chloroplatinate*, darkened at 140°; the yield was about 50%. G. M. K.

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"APPROVED FOR RELEASE: 03/13/2001 CIA-RDP86-00513R000927810003-1

KURSANOV, D. N.

7

21 5

4E4j

Mechanism of pinacolone rearrangement by deuterium-exchange study. D. N. Kursanov and Z. N. Parnes (Inst. Heteroorg. Compds., Acad. Sci. U.S.S.R., Moscow). *Zhur. Obshchei Khim.* 27, 668-71(1957).—Adding 100% D_2SO_4 with ice cooling to $(Me_2COH)_2$, keeping 1 hr in the cold, treating with $NaHCO_3$, and extg. with Et_2O, showed on isotopic analysis of the resulting product, b. 102-6°, either by conversion to semicarbazone or oxidation to Me_3CCO_2H (making an allowance for leaching of D from Me groups during neutralization), that the resulting compound was Me_3CCOCD_3; thus Me_3CCO_2H was free of D. Thus, during the

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traction is practically irreversible. G. M. Kosolapoff

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Kursanov, D.N.

Distr: 4E4j/4E3d/4E2c(j)

Reaction of bromotropilidene with phosphorus pentachloride. M. E. Vol'pin, I. S. Akhrem, and D. N. Kursanov (Inst. Heteroorg. Compds., Moscow). *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1957, 760-1.—Ultraviolet illumination of 0.11 mole CH_2N_2 in 4 l. PhBr until N evolution ceased gave a product, b_{10} 48-51°, contg. 69.4% *bromotropilidene*, as detd. by hydrogenation over Pt. This product (0.53 g.) and 1.32 g. PCl_5 stirred in CCl_4 5 hrs., filtered, and the solid taken up in H_2O, neutralized with Na_2CO_3, and extd. with Et_2O gave 0.21 g. *tropone*, b_4 105°, n_D^{18} 1.6095 (cf. Dauben and Ringold, *C.A.* 45, 6675i). This in C_6H_6 satd. with HBr yielded colorless nonhygroscopic *hydroxytropilium bromide*, decomp. 250°, λ (H_2O) 312 mμ, insol. in Et_2O, sol. in EtOH and H_2O. Heating 0.15 g. bromotropilidene with 0.76 g. PCl_5 in heptane 0.5 hr. and taking up the isolated ppt. in $MeNO_2$ gave with H_2PtCl_6 an orange *hydroxytropilium hexachloroplatinate*, $C_{14}H_{14}O_2PtCl_6$, also formed on similar treatment of tropone with H_2PtCl_6.

G. M. Kosolapoff

Kursanov D. N.

SETKINA, V.N.; KURSANOV, D.N.; BYKOVA, Ye.V.

Carbonium ions in the hydrogen exchange reaction. Probl. kin. i kat. 9:234-241 '57. (MIRA 11:3)
(Carbonium compounds) (Hydrogen--Isotopes)

Most of the papers in this collection were presented at the Conf. on Isotopes in Catalysis which took place in Moscow, Mar 31-Apr 5, 1956.

KURSANOV, D.N.; SETKINA, V.N.; VITT, S.V.; PARNES, Z.N.

Study of reaction mechanism by the hydrogen exchange method. Probl. kin. i kat. 9:242-244 '57. (MIRA 11:3)

(Chemical reaction--Conditions and laws)
(Hydrogen--Isotopes)

Kursanov, D. N.

62-11-12/29

AUTHORS: Kursanov, D.N., Vol'pin, M. Ye., Akhrem, I. S., Kachkurova, I. Ya.

TITLE: Curtius' (Kurtsius) Rearrangement in the Series of Isomeric Cycloheptatrienecarbonic and Norcaradienecarbonic Acids (Peregruppirovka Kurtsiusa v ryadu izomernykh tsiklogeptatriyenkarbonovykh i norkaradiyenkarbonovoy kislot).

PERIODICAL: Izvestiya AN SSSR, Otdelenie Khimicheskikh Nauk, 1957, Nr 11, pp. 1371-1378 (USSR)

ABSTRACT: Here Curtius' rearrangement in the series of isomeric α-cycloheptatrienecarbonic-(I), (R - COOH), β-cycloheptatrienecarbonic-(II) (R - COOH), γ-cycloheptatrienecarbonic -(III) (R - COOH) acids are systematically investigated. It is shown that the rearrangement takes place under the conditions here existing without an isomerization of the migrating hydrocarbon radical.
For the first time here 1,3,5-, 1,3,6- and 2,4,6- cycloheptatrienylisocyanate, norcaradienylisocyanate, 1,3,5,-1,3,6, and 2,4,6-cycloheptatrienylurea, norcaradienylurea, N-phenyl-N'-1,3,5-, 1,3,6- and 2,4,6-cycloheptatrienylurea

Card 1/2

"APPROVED FOR RELEASE: 03/13/2001 CIA-RDP86-00513R000927810003-1

Curtius' (Kurtsius) Rearrangement in the Series of Isomeric Cycloheptatrienecarbonic and Norcaradienecarbonic Acids. 62-11-12/29

as well as N-phenyl-N'-norcaradienylurea were produced synthetically. The absorption-spectra in the near ultra-violet area (25000 - 50000 cm^{-1}) of 22 derivatives of the cycloheptatriene and norcaradiene were investigated. It is shown that in the series of norcaradiene-derivatives (IVR = COOH, COOCl, $CONH_2$, NCO) the three-termed cycle transfers the linking similar to a double bond. There are 5 figures, 1 table, and 14 references, none of which is Slavic.

ASSOCIATION: Institute for Element-Organic compounds of the AN USSR (Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR).

SUBMITTED: July 2, 1956.

AVAILABLE: Library of Congress

Card 2/2

APPROVED FOR RELEASE: 03/13/2001 CIA-RDP86-00513R000927810003-1"

KURSANOV, D.N.

62-12-20/20

AUTHORS: Vol'pin, M.Ye., Akhrem, I.S., Kursanov, D.N.

TITLE: Letters to the Editor (Pis'ma redaktoru)
New Reactions of Tropyl Salts (Novyye reaktsii soley tropiliya).

PERIODICAL: Izvestiya AN SSSR Otdeleniye Khimicheskikh Nauk, 1957, Nr 12, pp. 1501-1502 (USSR)

ABSTRACT: It was shown that the salts of cycloheptatrienyl very easily alkylate the compounds with mobile hydrogen. Tropyl salts react with the same ease with various aliphatic aldehydes. Aliphatic and aromatic ketones when heated also enter into reaction with the salts of tropyl. The latter easily alkylates numerous aromatic compounds. Propyl differs from the other simple esters by the fact that it alkylates the esters of β-keto acids, β-diketones, and β-dicarbonic acids easily in the case of soft conditions. Thus, cycloheptatrienylacetine acid ester is formed with aceto acid ester. The tropyl salts easily attach themselves to the compounds with activated short bonds (like vinyl esters, cyclopentadien, phenyl acetylene, and others). The reactions investigated offer new possibilities for the synthesis of the derivatives of cycloheptatrien and tropyl. There are 4 references, 3 of which are Slavic.

Card 1/2

"APPROVED FOR RELEASE: 03/13/2001 CIA-RDP86-00513R000927810003-1

Letters to the Editor. New Reactions of Tropyl Salts 62-12-20/20

ASSOCIATION: **Institute for Elemental-organic Compounds AS USSR (Institut** elementoorganicheskikh soyedineniy Akademii nauk SSSR).

SUBMITTED: October 9, 1957

AVAILABLE: Library of Congress

Card 2/2 1. Tropyl salts-Reactions

USCOMM-DC-54782

APPROVED FOR RELEASE: 03/13/2001 CIA-RDP86-00513R000927810003-1"

KURSANOV, D.N.

KURSANOV, D.N., PARNES, Z.N.

Studying the mechanism of pinacolone rearrangement by means of deuterium exchange. Zhur. ob. khim. 27 no.3:668-671 Mr '57. (MIRA 10:6)

1. Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR.
(Pinacolone) (Deuterium)

Kursanov, D.N.

19

Use of oxygen-18 in the study of the mechanism of alkaline transesterification of esters. R. V. Kudryavtsev and D. N. Kursanov (Inst. Heteroörg. Compds., Moscow). *Zhur. Obshchei Khim.* 27, 1680-7(1957).—Slow distn. of EtCO(O^{18}Et)-BuOH mixt. in the presence of Na resulted in recovery of O^{18} in EtOH and none being found in the ester. Thus, the reaction proceeds through acyl-O fission, as does the hydrolysis. G. M. Kosolapoff

Distr: 4E4j/4E2c(j)

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KURSHNOV, D.N.

VOL'PIN, M.Ye.; ZHDANOV, S.I.; KURSANOV, D.N.

New tropilium salts. Tropilium ion polarography. Dokl. AN SSSR 112
no.2:264-266 Ja '57. (MLRA 10:4)

1. Chlen-korrespondent AN SSSR (for Kursanov). 2. Institut elemento-organicheskikh soyedineniy i Institut fizicheskoy khimii Akademii nauk SSSR.

(Cycloheptatrienyl)

KURSANOV, D. N.

6

Reaction of benzylpyridinium chloride with cyclopentadienyllithium. D. N. Kursanov, N. K. Baranetskaya, and V. N. Setkina (Inst. Hetero-Org. Compounds, Acad. Sci., Moscow). *Doklady Akad. Nauk S.S.S.R.* 113, 116-19 (1957).—Treatment of 29.18 g. BuLi with 33.1 g. cyclopentadiene with cooling gave after standing 2 hrs. 71.9% C_5H_5Li, as detd. by carbonation. This, suspended in Et_2O was added to a similar suspension of 102.0 g. $C_5H_5N.CH_2PhCl$ and stirred 20 hrs., after which the mixt. was treated with H_2O yielding a ppt. of 6.55 g. compd. (I), $C_{17}H_{15}N$, augmented by 12.14 g. from the Et_2O soln.; the product is golden yellow, stable in air, sol. in Me_2CO, $PhNO_2$, $CHCl_3$ and pyridine; it decomps. above 160°. It dissolves in acid and is pptd. by bases. It takes up 5 moles H over Pt, indicating 5 double bonds, confirmed by iodine no. The hydrogenated product, $C_{17}H_{25}N$, forms a *methiodide*, decomp. 160-70°, and chloroplatinate, $C_{17}H_{25}N.0.5H_2PtCl_6$, decomp. 140°. The amine cannot be acetylated. I has a dipole moment of 9.7 D. The structure of I appears to be a bipolar ionic structure with a cyclopentadienyl ring on the 2-atom of pyridine, the N carrying a pos. charge and the dienyl ring a neg. charge. G. M. Kosolapoff

424 g

Some peculiarities of 2,6-dichloro derivatives of pyridine. L. N. Yakhontov (S. Ordzhonikidze All-Union Chem.-Pharm. Research Inst., Moscow). *Doklady Akad. Nauk*

Some peculiarities of 2,6-dichloro derivatives of pyridine. L. N. Yakhontov (S. Ordzhonikidze All-Union Chem.-Pharm. Research Inst., Moscow). *Doklady Akad. Nauk S.S.S.R.* 113, 1088-9(1957).—2,6-Dichloropyridines do not form picrates or salts with mineral acids. 2-Chloro-4-methyl-3-(2-chloroethyl)pyridine forms a moderately stable HCl salt. 2,6-Dichloropyridines do not form quaternary salts with MeI and do not form *N*-oxides; heating with SeO_2 does not change these compds. while 3-(2-acetoxyethyl)-4-methylpyridine is oxidized readily to 3-(2-acetoxyethyl)isonicotinic acid, m. 155-6°. 2,6-Dichloro-3-(2-acetoxyethyl)-4-methylpyridine is unchanged after many hours of heating with SeO_2 in MePh or alone even at 250°. Heating 2,6-dichloro-4-methylnicotinic acid with excess $SOCl_2$ gave its acyl chloride which gave 91% Et ester.

G. M. Kosolapoff

20-2-27/67

AUTHOR KURSANOV D.N., Corresponding Member of the Academy
VOLPIN M.Ye.

TITLE A New Method For Production of Tropilium And Metatropilium Compounds.
(Novyy put'polucheniya soyedineneiy tropiliya i metatropiliya -Russian)

PERIODICAL Doklady Akademii Nauk SSSR, 1957, Vol 113, Nr 2, pp 339-342 (U.S.S.R.)
Received 6/1957 Reviewed 7/1957

ABSTRACT At present two fundamentally different ways of producing the 7-term aromatic tropilium-system are knwon: 1.method: tropiliumdibromide (including small quantities of salts of the carboxyltropilium) is obtained by separating HBr dibromal cycloheptadiene. 2.method: This method is based on the slight isomerization of a norkadiene-system into a tropilium-system. However, it would doubtlessly be interesting to investigate the possibility of a direct transition from the cycloheptatriene-system (IV) (tropilidene) with 3 double bonds to the aromatic tropilium-system. A conjugation of all of the six double bond-π-electrons must be possible which is realized in consequence of the separation in any way of a hydrogen atom together with an electron pair from the CH_2-group of the cycloheptatriene and then at the same time the transition of the 7th carbon atom from the sp^3-hybridization condition into the sp^2- hybridization condition must be possible, which would lead to the formation of the aromatic tropilium-system. Here a nonbenzoid

Card 1/3

A New Method For Production of Tropilium And Metatropilium Compounds.

20-2-27/67

aromatic system $\sigma\pi$-electrons would develop. When studying this direct transformation from cyclopentadienes into tropilium salts the authors investigated the influence of a number of electrophile reagents, strong acids, oxidation agents, haloid derivatives etc. on tropilium salts. On the occasion of an influence of concentrated sulphuric acid on cycloheptatrienes an exothermic reaction accompanied by formation of resin develops. However, a tropilidene oxydation together with formation of considerable quantities of tropilium salts (18%) takes place. Acids without any oxidizing properites (concentrated phosphoric acid, hydrochloric acid) do not lead to a formation of tropilium. Concentrated nitiric acid reacts very turbulently with cycloheptatriene, and small quantities of tropilium develop. Other oxidation agents in acid media effect a slighter or stronger transformation of cycloheptatriene into tropilium (CrO_3 - 14%, SeO_2-7% yield of tropilium salt). Phosphorus pentachloride very slightly reacts with cycloheptatriene at normal room temperature. Tropilium chloride develops and PCl_5 is reduced to PCl_3. This reaction can serve as a good preparation method for producing tropilium salts. It is better to prepare tropilium as a more continuous, not very hygroscopic, not easily soluble perchlorate, chloroplatinate or iodide. The same

Card 2/3

"APPROVED FOR RELEASE: 03/13/2001 CIA-RDP86-00513R000927810003-1

A New Method For Production of Tropilium And Metatropilium Compounds.

20-2-27/67

method is applicable for the preparation of methyltropilium salts (II,R=CH$_3$) by the influence of phosphorus pentachloride on methylcycloheptatriene. On the other hand neither phosphorus trichloride nor phosphorus tribromide is able to effect this transformation. Similar to the reaction with phosphorus pentachloride the other proceeds with suluryl chloride. 25% tropilium salt develop with considerable resinification. Thienyl chloride does not react with cycloheptatriene. In the experimental part experimental conditions are described in detail.
(With 6 citations from publications).

ASSOCIATION Institute for element-organic Compounds of the Academy of Science of the U.S.S.R.
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SUBMITTED 16.10.1956
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APPROVED FOR RELEASE: 03/13/2001 CIA-RDP86-00513R000927810003-1"

PA - 3157

AUTHOR KURSANOV, D.N., corresponding member of the Academy of Science and VITT, S.V

TITLE On the Mechanism of the Alkylation of Alcohols by N-Trimethyl-α-phenethylammonium iodide.
(Issledcvaniye mekhanizma alkilirovaniya spirtov iodistym N-tri-metil-α-fenetilammoniyem - Russian)

PERIODICAL Doklady Akademii Nauk SSSR,1957, Vol 113, Nr 3, pp 607-609,(U.S.S.R.)
Received 6/1957 Reviewed 7/1957

ABSTRACT The alkylation of methyl-, ethyl- and H-butyl alcohols was investigated with the optically-active salt of d-N-trimethyl-α-phenethylammonium. It was found that in all cases investigated the ethers ontained had no optical activity. It remained unclear, however, whether racemization takes place with alkylation or in the initial salt of ammonia as a result of heating with alcohol at high temperatures. In order to clear this up, reaction was carried out in such a manner that the d-N-trimethyl-α-phenethylammonium iodide did not enter into reaction as a whole. That part, which did not enter into reaction was then separated from the salt mixture by fractioned crystallization. It was found that the separated salt retained nearly its entire original optical activity, whereas the α-phenethylmethyl ether obtained showed no optical activity. From the data obtained it can be seen that the alkylation of alcohols with N-trimethyl-α-phenethylammonium takes place by the formation of α-phenethylcarbonium, i.e. in accordance with the asynchronous

Card 1/2

PA - 3157

On the Mechanism of the Alkylation of Alcohols by N-Trimethyl-α-phenethylammonium Iodide.

process. The experiments are described.
(With one table and three citations from Slavic publications)

ASSOCIATION Institute for Element-Organic Compounds of the Academy of Science of the U.S.S.R.

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Card 2/2

KURSANOV, D N.

AUTHOR	KURSANOV D.N., Corresponding Member of the Academy 20-5-34/67 VITT S.V.
TITLE	The Study of the Mechanism of Alkylation of Phenols by N-trimethyl-α-phenylethylammonium iodide. (Issledovanniye mekhanizma alkilirovaniya fenolov iodistym N-trimetil-α-fenetilammoniem -Russian)
PERIODICAL	Doklady Akademii Nauk SSSR, 1957, Vol 113, Nr 5, pp 1066-1069 (U.S.S.R.) Received 7/1957 Reviewed 8/1957
ABSTRACT	A number of research workers already studied the alkylation of phenols and phenolate anions which contain a benzyl- or substituted benzyl radical. It was found that on the occasion of interaction between chlorid-N-benzylpyridinium and phenol a mixture of C- and O-alkylation products is produced. It ought to be believed that this reaction, like other alkylation processes previously studied belongs to the heterolytic reactions of the substitution of the Sn type. Phenol alkylation shoud develop either according to the synchronous mechanism A or to the asynchronous mechanism B, the latter including the intermediate formation of a free carbonium ion. The authors investigated the interaction between iodine-N-trimethyl-α-phenathylammonium and resorcin and fluoroglucin. During heating of these phenols with ammonium salt a substitution of the hydrogen atoms of the phenol kernel by α-phenethylradical (C-alkylation reaction) takes place at 150° and more. The same alkylation of the two above phenols through the optically active N-

Card 1/2

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The Study of the Mechanism of Alkylation of Phenols
by N-trimethyl-α-phenylethylammonium iodide. 20-5-34/67

trimethyl-α-phenethylammonium was carried out at 155-175° with an abundance of the corresponding phenol. If the reaction develops according to schedule A, the produced α-phenethylphenols must be optically active, in the other case (B), they must be inactive. It was found that the α-phenethylphenols are optically inactive and also the α-phenylpropion acid produced from their oxidation. Herefrom it may be concluded that in phenol alkylation ammonium decay first to the accompaniment of the formation of α-phenethylcarbonium. The latter reacts with phenol and therefore reaction develops according to (B). This was also confirmed by the reaction with deuteroresorcin instead of resorcin. Reactions, methods, yields, etc. are described in detail. (With 6 Slavic references).

ASSOCIATION Institute for Element-Organic Compounds of the Academy
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Card 2/2

APPROVED FOR RELEASE: 03/13/2001 CIA-RDP86-00513R000927810003-1"

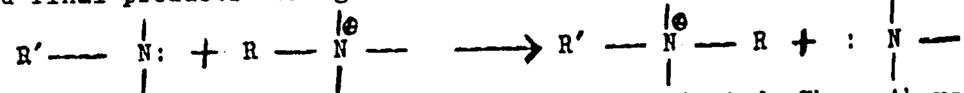
20-6-27/59

AUTHOR: KURSANOV, D.N., VITT, S.V.

TITLE: The Study of the Mechanism of the Alkylation of Amines by N-Tri-Methyl-α-Phenylethylammonium Iodide.
(Isseledovaniye mekhanizma alkilirovaniya aminov yodistym N-tri-metyl-α-fenetilammoniem. Russian).

PERIODICAL: Doklady Akademii Nauk SSSR, 1957, Vol 113, Nr. 6, pp 1283 - 1285 (U.S.S.R.)

ABSTRACT: It is known that the ammonium salts of the type $Ar{-}{-}{-}CH_2{-}{-}{-}\overset{+}{N}\equiv$ can alkylate primary and secondary amines by the transfer of the radical $ArCH_2$ from one nitrogen atom to the other. This process is also interesting by the fact that in this reaction the initial and final products belong to the same class of compounds:



$$R'{-}\underset{|}{\overset{|}{N}}{:} + R{-}\underset{|}{\overset{|\oplus}{N}}{-} \longrightarrow R'{-}\underset{|}{\overset{|\oplus}{N}}{-}R + {:}\underset{|}{\overset{|}{N}}{-}$$

The mechanism of this reaction remains uninvestigated. The authors investigated the alkylations of piperidine and morpholine by the optically active N-trimethyl-α-phenylethylammonium iodide. This reaction can develop either according to a synchronous or according to an asynchronous mechanism with an intermediate formation of a free carbonion. In the first case the developing N-α-phenylehtyl-piperdin has to be optically active. In the second case (with car-

Card 1/3

The Study of the Mechanism of the Alkylation of Amines by N-Trimathyl-α-Phenylethylammonium Iodide. 20-6-27/59

con ion formation) the optically activity would be lacking. It was found that in the substitution process this activity of the phenylethylradical is conserved: the N-α-phenylethylpiperdine obtained from the d-salt turned to the right side whereas the N-α-phenylethylmorpholine resulted from the l-salt turned to the left. Therefore the reaction passes according to a synchronous mechanism. It was necessary to determine the configuration of the leftturning substance. In so far as in the here applied reaction the asymmetrical centre is not concerned it can be stated that the leftturning substance belongs to the l-series. From this it results that in the case of the mentioned reaction with piperdine (and obviously also with morpholine) the inversion of the reversal of the α-phenylradical takes place. Since in the case of heating of longer duration optical purity was reduced, a secondary reaction of the symmetrical substitution seems to have taken place. Apparently the repetition of this process is bound to lead to ramification. In the experimental part the reactions with yields and constants are described in detail. (4 Slavic references).

Card 2/3

20-6-27/59

The Study of the Mechanism of the Alkylation of Amines by N-Tri-Methyl-α-Phenylethylammonium Iodide.

ASSOCIATION: Not given
PRESENTED BY:
SUBMITTED: 14 November 1956
AVAILABLE: Library of Congress

Card 3/3

KURSANOV, D. N., SETKINA, V. N., PARNES, Z. N. and BYKOVA, Ye. V., (Inst. of Element-Organic Compounds AS USSR) ,

"Study of Severl Heterolytic Reactions by the Hydrogen-Exchange Method." p, 13.

Isotopes and Radiation in Chemistry, Collection of papers of 2nd All-Union Sci. Tech. Conf. on Use of Radioactive and Stable Isotopes and Radiation in National Economy and Science, Moscow, Izd-vo AN SSSR,1958, 380pp.

This volume published the reports of the Chemistry Section of the 2nd AU Sci Tech Conf on Use of Radioactive and Stable Isotopes and Radiation in Science and the National Economy, sponsored by Acad Sci USSR and Main Admin for Utilization of Atomic Energy under Council of Ministers USSR Moscow 4-12 Apr 1957.

KURSANOV, D.N.; VOL'PIN, M.Ye., kand. khim. nauk; PARNES, Z.N., kand. khim. nauk.

New aromatic systems. Report No.1: Tropylium cation and cyclopentadienyl anion as nonbenzene aromatic systems. Khim. nauka i prom. 3 no.2:159-173 '58. (MIRA 11:6)

1. Chlen-korrespondent AN SSSR (for Kursanov).
(Organic compounds)
(Cycloheptatrienylium compounds)
(Cyclopentadienyl)

KURSANOV, D.N.; BYKOVA, Ye.V.; SETKINA, V.N.

Hydrogen exchange in the process of heterolytic reactions. Exchange of hydrogen atoms during substitution of iodine in alkyl iodides. Izv. AN SSSR Otd. khim. nauk no.7:809-813 Jl '58. (MIRA 11:8)

1. Institut elementoorganicheskikh soyedineniy AN SSSR.
(Hydrogen) (Alkyl iodides)

5(3)

SOV/62-58-12-18/22

AUTHORS: Kursanov, D. N., Parnes, Z. N., Kononova, R. G.

TITLE: The Case of a Retarded Hydrogen Exchange in the > N-H Group (Sluchay zamedlennogo vodorodnogo obmena v gruppe > N-H)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1958, Nr 12, pp 1493-1494 (USSR)

ABSTRACT: In this brief report the authors mention that the isotope exchange of hydrogen in the NH-group of dimethyl carbethoxy pyrrole takes place comparatively slowly. It turned out to be possible to measure the kinetics of this reaction at different temperatures. The velocity constants were calculated by a first order equation. The experiments were carried out at 12, 15, 20, and 25°. $K_{12} = 3.2.10^{-5}$; $K_{15} = 5.6.10^{-5}$; $K_{20} = 1.07.10^{-4}$; $K_{25} = 2.21.10^{-4}$ in sec^{-1}. Apparent activation energy = 25500 cal. The retarded hydrogen exchange which took place in this case is interpreted from the viewpoint of the theory developed by A. I. Brodskiy. There are 2 references, 1 of which is Soviet.

Card 1/2

The Case of a Retarded Hydrogen Exchange in the > N-H Group SOV/62-58-12-18/22

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR (Institute of Elementorganic Compounds, Academy of Sciences, USSR)

SUBMITTED: May 22, 1958

Card 2/2

KURSANOV D. N.

79-2-10/61

AUTHORS: Vol'pin, M. Ye., Akhrem, I. S., Kursanov, D. N.

TITLE: The Influence Exerted by the Nucleophilia of the Anion Upon the Nature of Linkage in Tropilium Compounds (Vliyaniye nukleofil'nosti aniona na kharakter svyazi v soyedineniyakh tropiliya)

PERIODICAL: Zhurnal Obshchey Khimii, 1958, Vol. 28, Nr 2, pp. 330 - 333 (USSR)

ABSTRACT: A number of salts of the aromatic 7-member cation of cycloheptatrienyl (tropilium) was recently produced (references 1 to 3). They are all salts of sufficiently strong acids ($X = Cl, Br, J, ClO_4$, $PtCl_6$, $B(C_6H_5)_4$, NCO). On the other hand the tropiliumoxide, methoxytropilium, tropilium cyanide, tropiliumthioether (references 1 and 2), where the X^- is an anion of sufficiently weak acids, are covalent compounds of type (II). Here and further the authors leave open the question whether the covalent tropilium derivatives possess a cycloheptatriene- or norcadiene structure (cf. reference 4). The authors made it their task to determine the boundary where the ionic compound $C_7H_7+X^-$ transforms into the covalent compound C_7H_7--X. For this purpose they synthesized tropilium derivatives of acetic and benzoic acids ($K_a = 1.75.10^{-5}$ and $6.5.10^{-5}$). As well the tropilium acetate as the tropilium benzoate (more exactly the cycloheptatrienylacetate and -benzoate) proved to be typically covalent

Card 1/4

79-2-10/[illegible]

The Influence Exerted by the Nucleophilia of the Anion Upon the Nature of Linkage in Tropilium Compounds

compounds - liquids - which can be solved in nonpolar solvents. Thus the transition from the ionic salts of tropilium to the covalent derivatives lies in the interval K_a of the corresponding acids. These results agree with the data by Doring (reference 1) that the tropilium ion behaves in water like the acid $K_a = 1.8.10^{-5}$ and reacts according to the scheme

$$C_7H_7 + 2H_2O \longrightarrow C_7H_7OH + H_3O^+ \quad .$$

The results obtained point to the assumption that the acids with $K_a \geqslant 1.2.10^{-4}$ will yield ionic salts with tropilium: the acids $K_a \leqslant 1.8 - 1.75.10^{-5}$ must yield covalent compounds with tropilium. This result is confirmed by the results of the interaction of tropilium bromide or tropilium perchlorate and cyclopentadienillithium. The formation of the covalent compound is explained by the weak acid properties of cyclopentadiene and consequently by the considerable nucleophilia of the anion C_5H_5. The tropilium acetate and -benzoate were synthesized by means of acylation of tropilium oxide (dicycloheptatrienylether) with corresponding acetic and benzoic anhydrides. This method of ether production may have quite a general importance. The attempts to produce tropilium acetate by means of an exchange reaction of tropilium perchlorate and potassium

Card 2/4

The Influence Exerted by the Nucleophilia of the Anion Upon the Nature of Linkage in Tropilium Compounds

7.-2-10/3

acetate in water and in alcohol were unsuccessful. Neither was it possible to produce tropilium benzoate by the exchange of potassium benzoate and tropilium perchlorate in water, nor by an exchange reaction of silver benzoate and tropilium bromine in alcohol or nitromethane. This indicates the instability of the cycloheptatrienyl ether and the inclination to hydrolysis. The covalent compound C_7H_7-X in tropilium cyanide and tropiliumcyclopentadienyl proved to be considerably stabler. It is interesting that in the acid process of the hydrolysis of tropilium cyanide a partial isomerization supposedly takes place and that phenylacetic acid is formed. Conclusions: 1) Tropilium acetate, -benzoate and cyclopentadienylcycloheptatriene which proved to be covalent compounds were produced. 2) It was shown that the nature of linkage of the cycloheptatrienyl residue with the anion depends on the nucleophilia of the anion. The transition from ionic to covalent tropilium derivatives lies in the range of K_a from $1.2 \cdot 10^{-}$[illegible] to [illegible].3 - $1.75.10^{-5}$. 3) It was shown that in the case of an acid hydrolysis of tropilium cyanide a regrouping with the formation of phenylacetic acid takes place. There are 6 references, 2 of which are Slavic.

Card 3/4

The Influence Exerted by the Nucleophilia of the Anion Upon the Nature of Linkage in Propilium Compounds 79-2-10/61

ASSOCIATION: Institute for Elemental-organic Compounds AS USSR (Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR)

SUBMITTED: April 15, 1957

AVAILABLE: Library of Congress

Card 4/4

SOV/20-120-4-31/67

AUTHORS: Setkina, V. N., Kursanov, D. N., Corresponding Member, Academy of Sciences, USSR

TITLE: Hydrogen Exchange Reactions of Alkyl Chlorides With Hydrochloric Acid and of Tertiary Butyl Alcohol When the Hydroxyl is Substituted by Chlorine (O reaktsiyakh vodorodnogo obmena alkilkhloridov s solyanoy kislotoy i tretichnogo butilovogo spirta pri zamene gidroksila na khlor)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol. 120, Nr 4, pp. 801-804 (USSR)

ABSTRACT: The reactions of tertiary aliphatic alcohols with a saturated HCl solution proceed very rapidly and practically irreversibly under the formation of alkyl chlorides. Reliable data on the mechanism of this reaction are lacking in publications. It might be assumed that the mentioned reaction proceeds according to the carbonium-ion-mechanism. The authors attempted to decide whether in connection with it an exchange of hydrogen takes place. They have found that the number of hydrogen atoms exchanged for deuterium corresponds only to the number of α-hydrogen atoms. For this purpose the reaction of tertiary

Card 1/3

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butyl alcohol with a saturated HCl solution was investigated. The solution was enriched by deuterium. The rapidly formed tertiary butyl chloride contained only a small amount of deuterium. During a further contact between chloride and deutero-chloric acid this amount increased (Table 1). Other tertiary chlorides behaved in the same way. A primary alkyl chloride, that is to say, butyl chloride did not enter the reaction under the same conditions (Table 2). Numerous investigations (Ref 4) of the mechanism of various solvolytic reactions of tertiary halide alkyls showed that all these reactions proceed according to the S_N1-mechanism. Their velocity is determined by the ionisation velocity of tertiary halogenides. Obviously the mentioned reaction with deutero-chloric acid is a special case of solvolytic monomolecular reactions. Thus it may be concluded that the initially mentioned hydrogen exchange reaction of tertiary alkyl chlorides is connected with their capability of being ionizable in a HCl solution which as is known has a high dielectric constant. The result of the ionisation of chlorides is their hydrogen exchange. The phenomenon that only α-hydrogen atoms of the

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SOV/20-120-4-31/67

Hydrogen Exchange Reactions of Alkyl Chlorides With Hydrochloric Acid and of Tertiary Butyl Alcohol When the Hydroxyl is Substituted by Chlorine

chlorides take part in this process can be explained by the impossibility of migration of the carbonium center along the hydrocarbon atom chain. This is impossible because of an electrostatic attraction of this center by anions or as a result of the influence exerted on the carbonium carbon by the solvate shell. In this reaction the carbonium ions are either not formed at all or they are so short-lived that they have not enough time to be exchanged for the acidous deuterium donors. The first assumption is more probable (Ref 5). There are 2 tables and 5 references, 1 of which is Soviet.

SUBMITTED: February 21, 1958

1. Hydrogen--Exchange reactions 2. Alkyl chlorides--Exchange reactions 3. Hydrochloric acid--Exchange reactions 4. Butanol--Chemical reactions 5. Chlorine--Chemical reactions 6. Substitution reactions

Card 3/3

AUTHORS: Kursanov, D. N., Bykova, Ye. V., Setkina, V. N. SOV/62-58-7-2/26

TITLE: Hydrogen Exchange in the Process of Heterolytic Reactions. Exchange of Hydrogen Atoms by the Substitution of Iodine in Alkyl Iodide(Vodorodnyy obmen v protsesse geteroliticheskikh reaktsiy. Obmen atomov vodoroda pri zameshchenii yoda v yodistykh alkilakh)

PERIODICAL: Izvestiya Akademii nauk SSSR, Otdeleniye khimicheskikh nauk, 1958, Nr 7, pp 809 - 813 (USSR)

ABSTRACT: In the present paper the results obtained in the investigations of some reactions of the nucleophylic iodine substitution in alkyl iodide are described. The possibility of using the reaction of hydrogen exchange in the study of the mechanism of heterolytic reactions was investigated. Furthermore the hydrogen exchange was investigated in the following cases: a)In the hydrolysis of tertiary alkyl iodide by water enriched with heavy hydrogen (deuterium). b) In the exchange of iodine atoms in alkyl iodide with a 56% H J enriched with deuterium. It was found that the hydrogen exchange in C-H bonds occurs in such reactions where according to the data supplied by kinetic inves-

Card 1/2

Hydrogen Exchange in the Process of Heterolytic SOV/62-58-7-2/26
Reactions. Exchange of Hydrogen Atoms by the Substitution of Iodine in Alkyl
Iodide

tigations they take place according to the monomolecular mechanism. It was shown in detail that the hydrolysis of tertiary iodides(C_4H_9J and $C_5H_{11}J$) and the iodide exchange in tertiary iodides are accompanied by hydrogen exchange reactions, if the hydrogen exchange does not take place in the reaction of the iodine exchange in secondary and primary iodides. This tends to show the bimolecular mechanism of these reactions. There are 2 tables and 30 references, 15 of which are Soviet.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR (Institute of Elemental-organic Compounds, AS USSR)

SUBMITTED: February 5, 1957

Card 2/2

62-58-3-19/30

AUTHORS: Kursanov, D. N., Baranetskaya, N. K.

TITLE: γ-Benzylpyridine-N-Cyclopentadienylide (γ-benzilpiridiniy-N-tsiklopentadiyenilid)

PERIODICAL: Izvestiya Akademii Nauk SSSR, Otdeleniye Khimicheskikh Nauk, 1958, Nr 3, pp. 362 - 363 (USSR)

ABSTRACT: Three representatives of a new class of bipolar compounds (which contain a negatively charged cyclopentadienyl group) were already earlier described by the authors. It was now interesting to synthesize the above-mentioned compound, where (in contrast to the ilide) the ammonia nitrogen is directly connected with the negatively charged group. On that occasion the same method was employed which Lloyd and Smizum employed in the synthesis of piperidine-cyclopentadienylide. The compound synthesized by the authors of this report possesses all properties similar to the ilides (see the diagram on absorption in the ultraviolet spectral region. There are 1 figure and 5 references, 2 of which are Soviet.

Card 1/2

γ-Benzylpyridine-N-Cyclopentadienylide 62-58-3-19/30

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR
(Institute for Elemental- organic Compounds, AS USSR)

SUBMITTED: October 12, 1957

Card 2/2

KURSANOV D.N.

79-2-28/64

AUTHORS: Parnes, Z. N., Vitt, S. V. , Kursanov, D. N.

TITLE: An Investigation of the Isomerization of Pinacoline by the Method of Traced Atoms (Issledovaniye izomerizatsii pinakolina metodom mechenykh atomov)

PERIODICAL: Zhurnal Obshchey Khimii, 1958, Vol. 28, Nr 2, pp. 410 - 413 (USSR)

ABSTRACT: At present different researchers found that the aliphatic carbon ions (iony karboniya) enter into a reaction of hydrogen exchange with acids. The hydrogen atoms are exchanged with the carbon atoms close to the carbon center (references 1 - 3). It was also shown that the carbon center of the carbon ion which was formed by the action upon carbonyl compounds by sulfuric or another strong mineral acid (at 0°C) is incapable of migrating, in contrast to the carbon ion which was obtained from the hydrocarbon with a tertiary carbon atom. Thus in the interaction of ketones , aldehydes, carboxylic acids with D_2SO_4 or D_3PO_4 the hydrogen exchange only takes place in those hydrogen atoms that are at C_α. But cases of ketone isomerization are known (references 4 - 7) which are explained by a displacement of the carbon center. Barton and Porter (reference 6) recently most exactly proved that the oxygen atom does not go over from one carbon to another in the ketone isomerization, but that

Card 1/3

79-2-23/64

An Investigation of the Isomerization of Pinacoline by the Method of Traced Atoms

only the hydrocarbon radicals migrate. For confirming this situation they used ditertiary butylketone (III) which contains C^{14} in the carbonyl group. It seemed interesting to the authors to investigate the interaction of pinacoline (V) with deuterosulfuric acid under the same conditions under which the isomerization of the above-mentioned ketones (reference 6) takes place. The isomerization of pinacoline assumed in this connection cannot be determined by the usual chemical methods, as the reaction product is not different from the initial product; but by means of labelled atoms it was hoped to discover it. On the basis of data on the regrouping of pinacoline (reference 9) it must be reckoned with the fact that the ion (VII) either only exists for such a short time that it cannot markedly enter the hydrogen-exchange reaction and that the regrouping takes place synchronously, i.e. without forming a free ion (VII). But the ions (VI) and (VII) must easily enter the hydrogen reaction. Due to the reversability of the isomerization reaction all hydrogen atoms of pinacoline must finally be exchanged. On the basis of the data given it may be supposed that the hydrogen exchange in the hidden isomerization occurs as a consequence of a regrouping of methyl groups and is independent of the displacement of the carbon center. Summary: 1) The interaction of pinacoline with deuterosulfuric acid was investigated under the conditions

Card 2/3

79-2-28/64

An Investigation of the Isomerization of Pinacoline by the Method of Traced Atoms

of the ketone isomerization. It was shown that under these conditions pinacoline exchanges the hydrogen atoms in the tertiary butyl group against deuterium. 2) The mechanism of the reaction of deutero-exchange and pinacoline-isomerization were investigated. There are 1 table, and 9 references, 4 of which are Slavic.

ASSOCIATION: Institute for **Elemental-organic Compounds AS USSR**
(Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR)

SUBMITTED: January 16, 1957

AVAILABLE: Library of Congress

Card 3/3

SOV/ 20-120-3-26/67

AUTHORS: Kursanov, D. N., Corresponding Member, Academy of Sciences, USSR, Vol'pin, M. Ye., Akhrem, I. S.

TITLE: The Reaction of Tropylium Salts With Vinyl Ethers and Mercury β-Chloroacetaldehyde (Reaktsiya soley tropiliya s vinilovymi efirami i β-khlormerkuratsetal'degidom)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol. 120, Nr 3, pp. 531-534 (USSR)

ABSTRACT: A characteristic property of the stable aromatic cation of cycloheptatrienylium (tropylium) is represented by its capability to react with nucleophilic reagents. (Ref 1). It was to be expected that the electrophilic property of the tropylium cation is sufficient also for a reaction with more weakly nucleophilic reagents, as vinyl ethers. This actually was the case, as the tropylium salts react with simple vinyl ethers in aqueous or alcohol solutions even in the cold under a self-heating. This high reactivity is a result of the influence of the electron-donor ether group. Compounds with isolated or conjugated double bindings, however, without

Card 1/4

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SOV/20-120-5-26/67

The Reaction of Tropylium Salts With Vinyl Ethers and Mercury β-Chloroacetaldehyde

activating substances (as, for example, methylcyclohexene, cycloheptatriene and others), or with electron accepting substituents (cinnamic acid, acrylic acid, acrylonitrile, chloroallyl and others) do not react with tropylium salts under identical conditions. In all cases the same product results independent of the nature of the anion of the initial salt of tropylium (whether bromide or perchlorate) and independent of the character of the alkyl in the vinylalkyl ethers: cycloheptatrienyl acetaldehyde. This reaction is analogous to that of the addition of mercury salts to vinyl ethers (Ref 2). Therefore it could be assumed that the mechanism of interaction of the tropylium salts with vinyl ethers includes an attack upon the double binding of the vinyl ether by the ion $C_7H_7^+$. At the same time, or subsequently, an action of one molecule of the solvent (water or alcohol) takes place. An acetal or a semi-acetal is probably the intermediate product of the reaction. The reaction velocity with the tropylium salts is markedly reduced at the transition from the simple vinyl ether to the vinyl acetate. This apparently is connected with a partial withdrawal of electrons by the C=O group.

Card 2/4

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S0720-120-3-26/67

The Reaction of Tropylium Salts With Vinyl Ethers and Mercury β-Chloroacetaldehyde

Cycloheptatriene acetaldehyde was also obtained by a counter synthesis, that is to say by a reaction of the tropylium salts (bromide or perchlorate) with mercury β-chloroacetaldehyde. Because of an exchange of an Hg-atom with a tropylium radical an aldehyde was produced, which was identical with that produced from vinyl ethers. This is the first case to be investigated of an interaction of organomercury compounds with tropylium salts. The reaction of the tropylium salts with mercury β-chloroacetaldehyde proceeds according to the type of C-alkylation. The haloid acyls O-acylate mercury β-chloroacetaldehyde. There are 4 references, 3 of which are Soviet.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR
(Institute of **Elemental-organic** Compounds AS USSR)

Card 3/4

SOV/20-120-3-26/67

The Reaction of Tropylium Salts With Vinyl Ethers and Mercury β-Chloro-acetaldehyde

SUBMITTED: January 14, 1958

1. Tropylium salts--Chemical reactions 2. Vinyl ethers--Chemical reactions 3. Mercury compounds (organic)--Chemical reactions

Card 4/4

SETKINA, V.N.; KURSANOV, D.N.

Hydrogen exchange reactions of alkyl chlorides and tertiary butyl alcohol, when hydroxyl is replaced by chlorine, with hydrochloric acid. Dokl. AN SSSR 120 no. 4:801-804 Je '58.

(MIRA 11:8)

1. Chlen-korrespondent AN SSSR (for Kursanov).

(Organic compounds)

(Hydrochloric acid)