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[illegible], A. [illegible].

"The Addition of -Halogen Ethers and Butadiene, and Allyl Isomerization of the Resultant Additional Compounds," work compiled with [illegible].A.Arbuzov, and presented at the June session of the Dept of Chem Sci, AS USSR, 28-29 June 1946.

Vestnik AS USSR 8/9, 1946

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PROCESSES AND PROPERTIES INDEX

Allylic rearrangements. I. Isomerization of some methoxychloropentenes in the presence of metal chlorides. A. N. Pudovik and B. A. Arbuzov. *Izvest. Akad. Nauk S.S.S.R., Otdel Khim. Nauk* **1946**, 427-37 (in Russian); cf. *C.A.* **42**, 4973*b*.—The addn. of $ClCH_2OMe$ to butadiene was improved over the procedure given by Strauss and Thiel (*C.A.* **31**, 3038). Butadiene (230 g.) cooled to −15° was treated with 310 g. $ClCH_2OMe$, followed by 4-5 g. powd. $ZnCl_2$, the flask closed with a stopper provided with an outlet tube and pinch-clamp, and the mixt. carefully mixed by shaking and allowed to stand in an ice-bath 5-6 hrs., then 15-20 hrs. at room temp. When the pressure drops the reaction is complete; the residual butadiene is removed and the residue, dild. with Et_2O, is washed with H_2O and distd. to give 135 g. *1-methoxy-3-chloro-4-pentene*, b. 31-5°, d_4^{20} 0.9890, n_D^{20} 1.4361, 105 g. *1-methoxy-5-chloro-3-pentene*, b. 58-9°, d_4^{20} 1.0089, n_D^{20} 1.4540, and 75 g. high-boiling products. The addn. does not go without the catalyst, even after 1 yr. standing. Neither the 3-(I), nor the 5-Cl isomer (II) shows isomerization on standing 1 yr. at room temp. in sealed tubes. When I and II were heated to 100° in sealed tubes, I isomerized to the extent of 16% in 27 hrs., while II gave but 3% isomerization, as detd. by *n*. If the temp. was raised to 140° the reaction was speeded up, but incipient decompn. limited the duration to 15 hrs., at which point I was 65.9% isomerized and II 7.9%. The isomerization was also studied in the presence of catalysts: 1% and 10% $ZnCl_2$, and 10% $SnCl_4$. $ZnCl_2$ (10%) enabled equil. to be reached in 24 hrs.; the mixt. then contained 80% II (equil. reached from both sides); when 1% $ZnCl_2$ is used the reaction is slower and even after 600 hrs. II is only 11.3% isomerized, while I is 63.1% isomerized. The results are given graphically. $SnCl_4$ (10%) caused a somewhat less extensive isomerization, but the reaction could not be followed accurately because of tar formation. Use of 10% $AlCl_3$ gave a greater heat evolution on mixing than was observed with the other catalysts, but its isomerization efficiency is poor: after 24 hrs. II is isomerized 11%, and I 43%; 1% $AlCl_3$ is much less effective. If the addn. of butadiene to $ClCH_2OMe$ is conducted using 1% $AlCl_3$ catalyst, the reaction mixt. gives a 36% total yield, composed of 23% II and 77% I. The problem of the possibility of primary addn. being at the 1,2-positions only cannot be solved from the available data; there is an indication that the 1,2-addn. is favored. The metal chloride-catalyzed isomerization probably proceeds similarly to the Friedel-Crafts reaction, involving formation of mesomeric ions of the methoxypentene and $ZnCl_2$-type ions, the isomerization being based on the common resonant ion. The lack of attainment of equil. when low percentages of the catalysts were used is explained by secondary reactions which give products incapable of isomerization. II. **Action of sodium acetate on isomeric methoxychloropentenes and hydrolysis of the resulting acetates.** *Ibid.* 511-8.—The reaction of NaOAc with isomeric methoxychloropentenes is best interpreted on the customary basis of allylic reactions, with the secondary chloride reacting by the S_N^i reaction mechanism, while the primary chloride reacts by both S_N^i and to some extent by S_N^2 mechanisms. 1-Methoxy-5-chloro-3-pentene (50 g.), 21 g. AcOH, and 25 g. dry NaOAc heated 2 hrs. at 120-30° gave 23 g. *1-methoxy-4-penten-3-ol ace*

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tate (I), b_9 63–5°, n_D^{20} 1.4264, d_4^{20} 0.9660, and 25.7 g. *1-methoxy-3-penten-5-ol acetate* (II), b_9 82–5°, n_D^{20} 1.4360, d_4^{20} 0.9789. 1-Methoxy-3-chloro-4-pentene (30 g.), 23 g. AcOH, and 25 g. AcONa heated 2 hrs. at 120–30° gave 10.7 g. I and 16 g. II. II (10 g.), 10 g. AcOH, and 10 g. NaOAc heated 2 hrs. at 120–5° produced no change; the same result was obtained with I. I and II were likewise unaffected by boiling with Ac_2O 3 hrs. Hydrolysis of II by hot alc. KOH gave only *1-methoxy-3-penten-5-ol*, b_{16} 97°, n_D^{20} 1.4485, d_4^{20} 0.9523; similar hydrolysis of I gave *1-methoxy-4-penten-3-ol*, b_{10} 60–1°, n_D^{20} 1.4373, d_4^{20} 0.9390. Hydrolysis of the chlorides by alkali also goes without isomerization.

G. M. Kosolapoff

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PUDOVIK, A. N.

"Allylic Rearrangements. Part 2. The Action of Sodium Acetate of the Isomeric Methoxychlorpentenes and the Hydrolysis of the Resulting Acetates," Iz. Ak. Nauk SSSR, Otdel Khim. Nauk, No. 5, 1946.

"Allylic Rearrangements. Part I. On the Isoverization of Some Methoxychloropentenes in the Presence of Metal Chlorides," Iz. Ak. Nauk SSSR, Otdel Khim. Nauk, No. 4, 1946.

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B

Allylic Rearrangement. Part III. The Action of Alcoholic Solutions of Alkali and of Sodium Dithionite on the Isomeric Methoxychloropentenes. (In Russian.) A. N. Pudovik and B. A. Arbuzov. *Bulletin of Academy of Sciences of the U.S.S.R., Section of Chemical Sciences*, July-Aug. 1947, p. 377-386.

Experimental results are given for a number of cases and discussed in terms of reaction mechanisms.

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

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CA

Allylic rearrangements. IV. Action of the sodium and magnesium derivatives of malonic acid ester and of the sodium derivative of acetoacetic acid ester on isomeric methoxychloropentenes. A. N. Pudovik and B. A. Arbuzov. *Bull. acad. sci. U.R.S.S., Classe sci. chim.* 1947, 501-8(in Russian); cf. *C.A.* 42, 1556g.—Na (4.3 g.) in 120 cc. abs. EtOH treated with 30 g. $CH_2(CO_2Et)_2$, followed by 25 g. $MeOCH_2CH_2CH:CHCH_2Cl$ (I), the mixt. heated on a steam bath 3 hrs., then the EtOH distd., the residue dild. with H_2O and extd. with Et_2O, and the ext. distd., gave 2.5 g. *di-Et 1-methoxy-3-hexene-6,6-dicarboxylate* (II), b_4 132°, n_D^{20} 1.4450, d_4^{20} 1.0213. Na (2.6 g.) in 70 cc. abs. EtOH treated with 18 g. $CH_2(CO_2Et)_2$, followed by 15 g. $MeOCH_2CH_2CHClCH:CH_2$ (III), and worked up as above, yielded 5.8 g. unreacted III, 6.7 g. unreacted $CH_2(CO_2Et)_2$, and 2 g. II. Mg shavings (5 g.), 32 g. $CH_2(CO_2Et)_2$, and 40 cc. abs. EtOH heated to boiling were treated with several drops CCl_4, the formation of the Mg deriv. allowed to proceed with occasional cooling, then the mixt. heated 3 hrs. with stirring until the Mg dissolved, treated dropwise with 28 g. I, and heated 4 hrs. at 110–20°; on cooling, the mixt. was treated with H_2O and HCl and the org. layer sepd. and combined with the Et_2O ext. of the aq. layer; distn. gave 12 g. II ($b_{0.5}$ 130–2.5°) and 14 g. *di-Et 1,11-dimethoxy-3,8-hendecadiene-6,6-dicarboxylate* (IV), $b_{0.5}$ 186–8°, n_D^{20} 1.4590, d_4^{20} 1.0250. A similar reaction using 5 g. Mg, 32 g. $CH_2(CO_2Et)_2$, 40 cc. abs. EtOH, and 28 g. III gave 4.7 g. unreacted III, 10 g. $CH_2(CO_2Et)_2$, 14.7 g. II, and 3.3 g. IV (b_{11} 208–10°, n_D^{20} 1.4585, d_4^{20} 1.0259). IV (11 g.) slowly added to 5.5 g. KOH in 50 cc. EtOH and boiled 3 hrs. gave the *free acid*, m. 86–7° (from benzene), purified through the *Ca salt* (by boiling with concd. $CaCl_2$ soln.) and acidification with HCl. Na (5.14 g.) in 50 g. abs. EtOH treated with 29 g. $AcCH_2CO_2Et$, followed by 30 g. I, boiled 3 hrs., freed of EtOH by distn., dild. with H_2O, and extd. with Et_2O, gave on distn. of the ext. 30 g. *Et 1-methoxy-3-octen-7-one-6-carboxylate*, b_{11} 151–3°, n_D^{20} 1.4507, d_4^{20} 1.0047, and 3.5 g. *Et 3-acetyl-1,11-dimethoxy-3,8-hendecadiene-6-carboxylate*, b_4 173°, n_D^{20} 1.4654, d_4^{20} 1.0077. The former ester (9 g.) was added to 2.4 g. KOH in 47 g. H_2O, stirred 2 hrs. at room temp., extd. with Et_2O, and the aq. layer was treated with 8 g. 50% H_2SO_4; warming 10–15 min. on a water bath and extn. with Et_2O gave 5.2 g. *1-methoxy-3-octen-7-one*, b_{11} 102°, n_D^{20} 1.4434, d_4^{20} 0.9149; addn. of the ester (15 g.) to 22.5 g. cooled KOH in 15 g. H_2O and 20 g. EtOH, followed by heating 3 hrs. on a steam bath, gave 1.5 g. of the above ketone (from the Et_2O ext.) and 6.4 g. *1-methoxy-3-hexene-6-carboxylic acid*, b_{11} 158°, n_D^{20} 1.4535, d_4^{20} 1.0174 (from the acidified aq. layer). The latter acid with aq. $KMnO_4$ in the cold (1 hr.) gave methoxypropionic acid, b_{11} 108–9°, n_D^{20} 1.4177. Na (7 g.) in 100 cc. abs. EtOH was treated with 39 g. $AcCH_2CO_2Et$, followed by 39 g. III; after heating 3 hrs. on a steam bath, followed by the usual working up of the org. components, no individual product was isolated and the over-all mixt. obtained b_{11} 35–b_6 200°. Thus, I gave the normally expected reaction products, whereas III apparently reacted in the form of the resonating ion ($MeOCH_2CH_2\overset{+}{C}HCH:CH_2 \rightleftarrows MeO\text{-}CH_2CH_2CH:CH\overset{+}{C}H_2$) to give "anomalous" products.

G. M. Kosolapoff

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PUDOVIK, A. N. 53T11

USSR/Chemistry - Allyl Groups Sep/Oct 1947
Chemistry - Esters

"Allyl Regroupings," A. N. Pudovik, B. A. Arbuzov, Kazan' State U, 8 pp

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

Describes action of sodium and magnesium malonic esters on isomeric methoxychloropentanes, and shows that reaction of esters with a secondary chloride gives same products as with a primary chloride.

[redacted] 53T11

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Organophosphorus-tin compounds. I. Synthesis of compounds $R_3SnPO_3R'_3$. B. A. Arbuzov and A. N. Pudovik (Chem. Inst. Acad. Sci., Kazan). *J. Gen. Chem.* (U.S.S.R.) 17, 2158-65(1947).—The Arbuzov reaction was used to prep. compds. of the type $R_3SnPO_3R'_3$ by the interaction of R_3SnX with $P(OR')_3$. The compds. suffer rapid hydrolysis on heating or standing with 5-20% HCl, with rupture of the P—Sn bond; similar cleavage occurs with alk. solns. or with halogens, as well as with AcCl. When 16 g. Me_3SnI and 7 g. $(MeO)_3P$ were heated to 105° a vigorous reaction took place and MeI distd. from the mixt.; the collected distillate was returned and the distn. was repeated at a max. temp. of 110°; 6.2 g. MeI was collected (7.7 g. theoretical); the residue, remaining in the flask, crystd. on standing and represented a 95% yield of *$Me_3SnPO(OMe)_3$*, m. 96° (from EtOH), sol. in Et_2O, $CHCl_3$, Me_2CO, EtOH, and H_2O. This, on heating 3 hrs. with concd. HCl to 100°, gave Me_3SnCl_3, m. 107°; standing at room temp. in 5% HCl gave Me_3SnCl, m. 42°, b_{10} 45-7°; boiling 3 hrs. with distd. H_2O did not change the product, however; treatment with Cl in $CHCl_3$ soln. for 24 hrs. also gave Me_3SnCl, as did similar treatment with AcCl; boiling with 10% aq. KOH gave Me_3SnOH, m. 118°. Heating 23 g. Et_3SnI and 12 g. $(EtO)_3P$ 15 min. to 150° gave 9 g. crude *$Et_3SnPO(OEt)_3$*, which on distn. gave 3 g. pure product, viscous liquid, $b_{0.4}$ 210-20°, n_D^{20} 1.4858; this heated with 20% HCl 10 hrs. at 160-70° in a sealed tube gave Et_3SnCl_3, m. 84.5-85°, while treatment with AcCl and 2 days' standing gave Et_3SnCl, b_{11} 98-100°, and a small amt. of unidentified product, b_5 142-5°, which reduces Fehling soln. $(EtO)_3PONa$, from 4 g. $(EtO)_3POH$, in 30 ml. Et_2O was treated with 8 g. Me_3SnI, boiled 1 hr., the heavy white ppt. sepd., and the Et_2O evapd., to give a yellow oil, which on standing 24 hrs. deposited 0.88 g. *$(Me_3SnOH)_3.Me_3SnI$*, decomp. 145-55°, which apparently was formed from the free radical Me_3Sn, produced in the initial reaction with the sodium phosphite. The $(EtO)_3PONa$ from 4.2 g. $(EtO)_3POH$ in abs. EtOH was treated with 10 g. Et_3SnI (no NaI pptn. was observed), the EtOH was distd. and was replaced by MeI'h, the mixt. boiled, and the soln. decanted from the white solid ppt. and distd. to give a colorless product, b_{11} 82-4°, n_D^{20} 1.4842, d_4^{20} 1.3042, which appeared to be *Et_3SnOEt*. Heating Ph_3SnBr with $(EtO)_3P$ 0.5 hr. to 170° gave only Ph_6Sn, m. 222°; similarly, when $(EtO)_3PONa$ (from 0.26 g. Na) in Et_2O was mixed with 4.5 g. Ph_3SnBr in benzene, heated 2 hrs., freed of Et_2O, and heated 4 hrs. on a steam bath, the filtered soln. on concn. had an odor of $(EtO)_3P$; addn. of Et_2O pptd. 3.7 g. *Ph_6Sn*, m. 222°. Heating Ph_3PbI with $(EtO)_3P$ gave only the disproportionation product, *Ph_6Pb*, m. 224°. Heating 8.5 g. Et_3PbBr and 4.5 g. $(EtO)_3P$ 6 hrs. at 100° gave some $(EtO)_3P$ and a white amorphous solid, insol. in org. solvents. A similar product is obtained on heating a PhMe soln. of Et_3PbBr, apparently a disproportionation product of Et_3PbBr. Thus, the org.-Pb compds. were incapable of the normal Arbuzov reaction. **II. Synthesis of compounds of the type $R_2Sn(PO_3R'_3)_2$.** B. A. Arbuzov and N. P. Grechkin. *Ibid.* 2166-77.—The Arbuzov reaction with R_2SnX_2 gave the expected phosphono-tin compds. of type $R_2Sn(PO_3R'_3)_2$, solids or semisolids, which in most cases could be crystd. from org. solvents. They were sol. in hot BuOH and $CHCl_3$, almost insol. in other solvents, and their crystn. led to severe losses. The high m.p. and poor soly. of the products is explained by their apparent dimeric structure, as shown by Rast mol. wt. detns. of the Et and the Pr compds. The P—Sn bond is readily cleaved on treatment with dil. HCl even at room temp., giving R_2SnCl_2, while HBr gives R_2SnBr_2; 10% NaOH gives R_2SnO, while Cl or Br in $CHCl_3$ soln. give R_2SnX_2. The study was extended briefly to reactions of $RSnX_3$ and SnX_4, which will be reported later. However, the reaction of $MeSnI_3$ with $2(EtO)_3P$ gave, on heating to 85-90°, followed by cooling,

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USSR/Chemistry - Phosphoric Acids, Esters Jul 1947
Chemistry - Synthesis

"Synthesis of the Esters of Tin Trialkyl-Phosphone," B. A. Arbuzov, Corr Mem, Acad Sci; A. N. Pudovik, Chem Inst, Kazan Br, Acad Sci USSR, 2 pp

"Dok Akad Nauk SSSR, Nova Ser" Vol LVII, No 2

Reaction for formation of esters of alkylphosphonic acids in metallo-organic unions, containing haloids. Presents some basic facts concerning chemical reactions. Describes tests which produced subject esters as a result of tin trialkyl-haloid and trialkylphosphite relationship. Submitted, 14 May 1947.

[redacted]

60T1

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Allylic rearrangements. V. Action of phenylmagnesium bromide on isomeric methoxychloropentenes. A. N. Pudovik and B. A. Arbuzov. *Bull. acad. sci. U.R.S.S., Classe sci. chim.* 1948, 246–9; cf. *C.A.* 42, 1887*b*.—To the PhMgBr from 6 g. Mg and 35 g. PhBr in ether was added with cooling 30 g. $MeOCH_2CH_2CH:CHCH_2Cl$; after heating 1 hr., the mass was treated with ice and HCl to give 7.7 g. *1-methoxy-3-phenyl-4-pentene* (I), b_4 96–8°, n_D^{20} 1.5032, d_4^{20} 0.9390, and 17 g. *1-methoxy-5-phenyl-3-pentene* (II), $b_{4.5}$ 103–4°, n_D^{20} 1.5125, d_4^{20} 0.9467. A similar reaction with $MeOCH_2CH_2CHClCH:CH_2$ gave 8.8 g. I and 15.5 g. II. Oxidation of I by $KMnO_4$ gave BzOH and *α-phenyl-γ-methoxybutyric acid*, b_{12} 175–8°. Oxidation of II gave BzOH, $PhCH_2CO_2H$, and *β-methoxypropionic acid*, b_{12} 108–12°, n_D^{20} 1.4190. The results indicate that the reaction proceeds by ionic mechanism through the intermediate ion, $[MeOCH_2CH_2CH:CHCH_2 \rightleftarrows MeOCH_2CH_2CHCH:CH_2]Cl^-$. G. M. Kosolapoff

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Allylic rearrangements. VI. Catalytic isomerization of methoxychloropentenes in the presence of halogen salts of metals. A. N. Pudovik. *Izvest. Akad. Nauk S.S.S.R., Otd. Khim. Nauk* 1948, 321-9; cf. P. and Arbuzov, *C.A.* 42, 4973b. The isomerization of 1-methoxy-3-chloro-4-pentene (I) and 1-methoxy-5-chloro-3-pentene (II) in the presence of $ZnCl_2$ and other halide salts was studied. At equil. the mixt. consists of 25-6% I and 74.5% II. It was shown that $MeOCH_2CH_2Cl$ adds to bivinyl at the 1,4-positions in 23-5% yields; the addn. proceeds not ionically but molecularly or by an ionomol. mechanism. The results of isomerization studies are given graphically. I b_{10} 51.5°, n_D^{20} 1.4364, d_4^{20} 0.9660; II b_{10} 58.9°, n_D^{20} 1.4540, d_4^{20} 1.0088. The typical isomerization results were: I with 0.4% $ZnCl_2$ at 85° gave 20.5% II in 0.08 hr., 40.3% in 1 hr., 48.8% in 9 hrs., 60.2% in 20 hrs., and 73.8% in 50 hrs.; with 1% $ZnCl_2$, 54.5, 63.1, 74.4, —, —; under the same conditions, II with 1% $ZnCl_2$ at 85° gave 20.5% I in 0.08 hr. At 17° I with 0.47% $ZnCl_2$ gave 3.4% II in 0.12 days, 6.2 in 1 day, 10.0 in 3 days, 37.5 in 33 days, 55.6 in 72 days, 71.5 in 120 days; with 0.6% $ZnCl_2$ the values were: 6.2, 17.6, 29.5, 51.7, 59.1, and 71.5%, resp.; with 1% $ZnCl_2$, 23.3, 47.1, 54.5, 63.1, —, 73.8%, resp.; II with 1% $ZnCl_2$ gave 92.1% I in 0.12 days, 81.3% in 33 days, 75.6% in 120 days. Similar results were obtained with nonequil. mixts. At 0° the isomerization is very slow and only with 1% $ZnCl_2$ does it approach 60.2% II (from I) in 100 days. Using 0.0088 mol. of a salt per 1 mol. I at 17°, the following results were obtained: $ZnBr_2$, 20.4% II in 0.12 day, 48.8% in 1 day, 57.3% in 6 days, 60.2% in 20 days, 65.9% in 45 days; ZnI_2, 51.7% in 1 day, 65.9% in 6 days, 70% in 20 days, 72.1% in 45 days; $FeCl_3$, 17.6% in 10 days, 37.5% in 35 days; $FeCl_3.6H_2O$, 10% in 6 days, 10% in 20 days, 31.8% in 45 days; $HgCl_2$, 3.4% in 0.12 day, 6.2% in 1 day, 9.1% in 6 days, 20.4% in 45 days; $CuBr_2$, 3.4% in 6 days, 14.7% in 20 days, 20.1% in 45 days; $PbCl_2$, 3.4% in 10 days, 14.7% in 20 days, 14.7% in 35 days. Slow distn. of a 1% soln. of $ZnCl_2$ in II at 100° bath temp. gave a distillate contg. 84% I. Addn. of $MeOCH_2CH_2Cl$ to bivinyl was done at equimol. proportions in a closed vessel; the amt. of II in the distillates was detd. by refractive index; 0.5% $ZnCl_2$ in 2 days at 0° gave 37.5% II (with 10% isomerization of I being corrected for, this gives 27.5% true % addn. at the 1,4-positions); 1% $ZnCl_2$ gave 43.2% II (23.2% true); at −10° 0.2% $ZnCl_2$ gave 23.3% II (23.3%), while 0.5% $ZnCl_2$ gave 31.8% (24.5%), $FeCl_3$ (amt. unstated), in 10 days at 17° gave 40.3% (25.0%), while $HgCl_2$ gave 30.7% II (21.0%).

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PUDOVIK, A. N.

USSR/Chemistry - Allyl Compounds
Chemistry - Magnesium Compounds

Mar/Apr 1948

"Allyl Rearrangement," A. N. Pudovik, B. A. Arbuzov, Kazan State Univ., 4 pp.

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

Discusses action of magnesium bromobenzene on isomeric methoxi-chloropentene. A similar mixture 1-metoxi-5-phenolpentene-3 and 1-metoxi-3-phenolpentene-4 was obtained from both metoxichloropentene. Results show x "ion" nature of reaction. Submitted 3 Jun 1946

63T3

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"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

PUDOVIK, A. N.

PA 7/49T9

USSR/Chemistry - Isomerization, of Metoxychlorpentane May/Jun 48
Chemistry - Catalysis

"Regrouping of Allyl Compounds," A. N. Pudovik, Kazan State U imeni Ul'yanov (Lenin), 8½ pp

"Iz Ak Nauk SSSR, Otdel Khim Nauk" No 3

Pudovik has studied catalytic isomerization of isomeric metoxychlorpentanes in the presence of zinc chloride and other halogen salts. In the equilibrium condition, 1-metoxy-5 chlorpentane constitutes 74 - 75% of the isomer mixture. Submitted 3 Jul 1946.

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7/49T9

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"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

PUDOVIK, A. N.

[redacted]

USSR/Chemistry - Rearrangements, Allyl Sep/Oct 48
Chemistry - Ether, α, β-Dichlorethyl,
Addition to Divinyl

PA 27/49T34

"Allyl Regroupings: VII, The Addition of α, β-Dichlorethyl Ether to Divinyl and the Action of Alkali Alcohols on Addition Products," A. N. Pudovik, Kazansk Affiliate, Acad Sci USSR, 8 pp

"Iz Ak Nauk SSSR, Otdel Khim Nauk" No 5

Shows that α,β-dichlorethyl ether joins with divinyl in the presence of a catalyst, zinc chloride. Separates and classifies the 1,2 and 1,4-products of the joining, 1,6-dichloro-5-ethoxyhexene-2 and 3,6-

[redacted]

27/49T35

USSR/Chemistry - Rearrangements, Allyl Sep/Oct 48
(Contd)

dichloro-5-ethoxyhexene-1. Obtains good yield of the corresponding simple ethers with the action of caustic potash on 1,6-dichloro-5-ethoxyhexene-2 in methyl, ethyl and butyl alcohols. Submitted 3 Jul 46.

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PUDOVIK, A. N.

"Silicon Phosphororganic Derivatives," Dok. Akad. Nauk SSSR, Nova Ser., 59, no. 8, 1948

"Determination of Aliphatic Alcohols by Oxidation of Calcium Bichromate in the Presence of Some Organic Compounds," Zhur. Prik. Khim., Vol. XXI, No. 8, 1948.

"Determination of Aliphatic Alcohols by Oxidation with Potassium Bichromate in the Presences of Some Organic Compounds," Journal Applied Chem., 21, No. 8, August, 1948, p. 862.

It has been found that oxidation coefficients of n-butyl, n-propyl alcohol and diethyl ether are constant only in definite limits of sulfuric acid concentration in the reaction mixture. The possibility is shown of applying the proposed method of joint oxidation for the analysis of binary and ternary mixtures containing ethyl, propyl, butyl alcohols, diethyl ether and acetaldehyde. (Kazan State Univ. and Central Scientific Research Lab. of the Chemical Plant, October 23, 1947)

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"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

PUDOVIK, A. N.

USSR/Chemistry - Phosphorous Compounds, Organic Chemistry - Silicon

Mar 1948

"Silicon Phosphororganic Derivatives," B. A. Arbuzov, A. N. Pudovik, Chem Inst, Kazan Branch, Acad Sci USSR, 3 pp

"Kok Akad Nauk SSSR, Nova Ser" Vol LIX, No 8

Describes experiment designed to examine the reaction between triethylophosphite and haloid silicon phosphororganic derivatives: led to obtaining compounds with phosphorous-silicon connection.

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USSR/Chemistry - Rearrangements, Allyl Jan/Feb 49
Chemistry - Electron Theory

"Allyl Regroupings: VIII, Action of KOH and Na-Alcoholate of Tertiary Butyl Alcohol on Isomeric Methoxychlorpentenes and Ethoxychlorhexenes in Tertiary Butyl Alcohol," A. N. Pudovik, Kazan State U imeni Ul'yanov-Lenin, 7 pp

"Iz Ak Nauk SSSR, Otdel Khim Nauk" No 1

Finds marked difference in the course of the reactions between the primary allyl haloid compounds and KOH, and also Na-alcoholates in a solution of tertiary butyl alcohol and solutions of primary and

27/49T23

USSR/Chemistry - Rearrangements, Allyl (Contd) Jan/Feb 49

secondary alcohols. Explains this phenomena from standpoint of electron theory. Submitted 6 Dec 46.

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PUDOVIK, A. N.

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PUDOVIK, A.N.

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Allylic rearrangements. IX. Action of sodium salts of dialkyl phosphorous acids and esters of phosphorous acid on isomeric methoxychloropentenes. A. N. Pudovik and B. A. Arbuzov (Lab. Org. Khim., Kazan Gosudarst. Univ.). *Izvest. Akad. Nauk S.S.S.R., Otdel Khim. Nauk* 1949, 522-38; cf. *C.A.* 43, 5737*a*.—The reactions of $(RO)_2PONa$ with $MeOCH_2CH_2CH{:}CHCH_2Cl$ (I) proceed normally without allylic rearrangement. Addn. of 30 g. I to $(EtO)_2PONa$ [from 40 g. $(EtO)_2POH$ and 6.6 g. Na in 300 ml. Et_2O] and heating 3 hrs. gave, upon filtration, 5 g. I, 8 g. unknown matter, b_{10} 90-127°, and 38 g. *1-methoxy-5-diethylphosphono-3-pentene* (II), b_6 146-7°, n_D^{20} 1.4480, d_4^{20} 1.0880, sol. in H_2O, and extractable by Et_2O unchanged. Heating the ester (10 g.) 3 hrs. to 120° with concd. HCl in a sealed tube, followed by release of the EtCl, reheating 6 hrs., and repeated evapn. of the soln. with H_2O gave an oil, $C_4H_{10}O_4P$, apparently *$MeOCH_2CH_2CH{:}CHCH_2PO_3H_2$*, which gave a poorly sol. *Ca salt*; II added almost the theoretical amt. of Br in $CHCl_3$; oxidation of II with $KMnO_4$ (22 g. per 12 g. ester) at 10-12° gave 3.6 g. *$MeOCH_2CH_2CO_2H$*, b_{10} 108-8°, n_D^{20} 1.4185; similarly oxidation of II with peroxyphthalic acid gave nearly theoretical results. A similar reaction of 20 g. I with $(iso\text{-}BuO)_2PONa$ (from 3.5 g. Na and 30 g. ester) in 200 ml. Et_2O gave 5 g. I and 20 g. *1-methoxy-5-diisobutylphosphono-3-pentene* (III), b_6 145-6°, n_D^{20} 1.4455, d_4^{20} 0.9819. The reaction with $(MeO)_2ONa$ was slow because of poor soly. of the Na deriv. in Na; prolonged warming of 20 g. $(MeO)_2POH$ with 4.2 g. Na in 200 ml. Et_2O with stirring (some Na was unreacted), followed by addn. of 24 g. I and heating 10 hrs., gave little action and almost all the I was recovered (1.2 g. product, b_{10} 136-40°, was isolated); addn. of 20 g. $(MeO)_2POH$ to 4.3 g. Na in 50 ml. MeOH, followed by 25 g. I, after cooling, and heating 3 hrs. on a steam bath gave 14.4 g. *1,5-dimethoxy-3-pentene*, b_{11} 57-8°, n_D^{20} 1.4272, d_4^{20} 0.8840, and 14.3 g. *1-methoxy-5-dimethylphosphono-3-pentene*, b_{10} 144°, n_D^{20} 1.4530, d_4^{20} 1.0950. Reaction of I with $P(OR)_3$ also proceeds normally. Thus, 12 g. $(MeO)_3P$ and 13 g. I after 5 hrs. at 110-50° in a sealed tube gave 9.1 g. of the above ester, b_6 140-1°, and much unreacted I and $(MeO)_3P$; similarly, 14 g. $(EtO)_3P$ and 11.3 g. I after 10 hrs. at 110-50° gave [illegible] g. unreacted materials and [illegible] g. II, b_4 133-4°, n_D^{20} 1.4480, d_4^{20} 1.0885. Similar reactions of $(RO)_3P$ with $MeOCH_2CH_2CHClCH{:}CH_2$ (IV), however, yield the same products as those obtained with I; the reactions are slow and incomplete and the high temps. required do not permit detg. of whether or not there occurs an allylic rearrangement or the usual isomerization on heating which takes place with I and IV. Thus 14 g. $(EtO)_3P$ and 11.3 g. IV, after 10 hrs. at 140-50°, gave 20 g. unreacted materials and but 3.1 g. II, b_4 148-9°, n_D^{20} 1.4480, while 12 g. $(MeO)_3P$ and 13 g. IV, after 5 hrs. at 140-50°, gave but 1.4 g. of the *dimethylphosphono analog*, b_6 140-2°, n_D^{20} 1.4580. The course of the reactions of IV with $(RO)_2PONa$ depends upon the presence or absence of excess free $(RO)_2POH$; in the 1st instance the reaction proceeds with complete allylic shift and yields 60-85% $MeOCH_2CH_2CH{:}CHCH_2PO(OR)_2$ (described above) and no isomers could be detected; in the 2nd instance, however, the reactions yielded as the main product high-boiling substances which were shown to be diphosphonates of the type $MeOCH_2CH_2CH(PO_3R_2)CH_2CH_2PO_3R_2$ and $MeOCH_2CH_2CH_2CH(PO_3R_2)CH_2PO_3R_2$, apparently formed by the 2 possible modes of addn. of $(RO)_2PONa$ to the double bond of the primary compds. of type II or III, and the adducts, reacting with unused IV, yield the above diphosphonates, NaCl, and methoxypentadiene (which was isolated in all cases). Thus, addn. of 40 ml. dry C_6H_6 and 14 g. IV to $(EtO)_2PONa$ (from 2.5 g. Na and 30 g. $(EtO)_2POH$) in Et_2O, followed by distn. of the Et_2O (the reaction is too slow at the b.p. of Et_2O) and refluxing 3 hrs., gave upon filtration of the NaCl, 3.1 g. IV, 12.8 g. $(EtO)_2POH$, 1.9 g. intermediate fraction, and 12.6 g. II, b_7 144-7°; repetition with 40 g. $(EtO)_2POH$, 3.3 g. Na, and 19 g. IV gave similarly 11.8 g. II, b_{10} 150-1°. Similarly, 30 g. $(iso\text{-}BuO)_2POH$, 1.7 g. Na, and 10 g. IV in C_6H_6 gave 2.8 g. IV, 14.3 g. $(iso\text{-}BuO)_2POH$, 1.7 g. intermediate fraction, and 11.5 g. III, b_4 173-5°. A similar reaction of 30 g. $(EtO)_2POH$, 5 g. Na, and 25 g. IV in C_6H_6 (3 hrs. refluxing), gave 11 g. NaCl, 4 g. IV, 3 g. $(EtO)_2POH$, 13.8 g. (probably) *$MeOCH_2CH_2CH_2CH(PO_3Et_2)CH_2PO_3Et_2$* (IX), b_{11} 222°, b_{11} 216-17°, n_D^{20} 1.4478, d_4^{20} 1.1080, and 14 g. glassy residue. Repetition with 8.5 g.

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K instead of Na (5 hrs.' refluxing) gave 3.6 g. $MeOCH_2CH{:}CHCH{:}CH_2$, 1.6 g. IV, 14.3 g. of the above diphosphonate, b_{10} 214-16°, n_D^{20} 1.4400, 1.6 g. diphosphonate, probably $MeOCH_2CH_2CH(PO_3Et_2)CH_2CH_2PO_3Et_2$ (X), b_{10} 238-46°, n_D^{20} 1.4600, and 7.5 g. undistillable residue. IX is a viscous greenish liquid, sol. in org. solvents and H_2O, unchanged after 1 hr. in H_2O at 100° or after 3 hrs. at 150-60° with MeI, forms no adducts with CuCl, does not add Br, and is not oxidized by peroxyphthalic acid; heating with concd. HCl 2 hrs. at 120°, and reheating 6 hrs. after release of the EtCl, gave on evapn. with H_2O a sirup which was a tetrabasic acid (7 g. required 5.8 g. KOH for neutralization). A similar reaction of 29 g. $(iso\text{-}BuO)_2POH$, 3.5 g. Na, and 20 g. IV gave 4.8 g. methoxypentadiene, 8.3 g. liquid, b_7 100-200°, and 15.3 g. *tetra-iso-Bu analog* of IX, b_7 225-9° (crude), b_{10} 237°, n_D^{20} 1.4470, d_4^{20} 1.0203. $(MeO)_2POH$ 20 g., 4.3 g. Na, and 25 g. IV, even after 7 hrs.' refluxing, gave largely unreacted materials and only 0.4 g. methoxypentadiene and 3.2 g. substance, b_{10} 30-80°. No reaction took place on heating 10 g. II with 12 g. $(EtO)_2POH$ in the presence of a small amt. of either MeONa or $(EtO)_2PONa$ 3 hrs. to 150° in a sealed tube. To $(EtO)_2PONa$ (from 12 g. $(EtO)_2POH$ and 2 g. Na in Et_2O) was added 40 ml. C_6H_6 and 20 g. II, Et_2O distd., and the mixt. treated with stirring and heating with 12 g. IV and refluxed 3 hrs. (pptn. of colloidal NaCl); distn. gave 1.5 g. methoxypentadiene and 2.7 g. IV, and the viscous residue, treated with H_2O and Et_2O and the org. layer distd., gave 2.1 g. liquid, b_{11} 140-215°, 8.3 g. IX, b_{11} 215-18°, n_D^{20} 1.4495, and 4.9 g. X, b_{10} 235-45°, n_D^{20} 1.4595. When $(EtO)_2PONa$ (from 12 g. $(EtO)_2POH$ and 2 g. Na in Et_2O) was similarly heated in C_6H_6 3 hrs. with 20 g. II and 12 g. I, there was obtained only 28 g. II and no other products. A similar 3-hr. reaction of $(iso\text{-}BuO)_2PONa$ (from 15 g. $(iso\text{-}BuO)_2POH$ and 1.8 g. Na) with 22 g. III and 10 g. IV gave 2.4 g. methoxypentadiene, 1.7 g. IV, 5.1 g. intermediate fraction, b_7 110-220°, and 11.6 g. *tetra-iso-Bu analog* of IX, b_7 236-8°, n_D^{20} 1.4470. Similarly $(EtO)_2PONa$ (from 6 g. $(EtO)_2POH$ and 1 g. Na) and 10 g. II in C_6H_6 on distn. of the Et_2O and part of C_6H_6 gave 1.1 g. product, b_{10} 214-16°, n_D^{20} 1.4478 (apparently IX), 1.3 g. intermediate fraction, and 3.1 g. X, b_{10} 237-43°, n_D^{20} 1.4590.

X. Action of alcoholic solutions of alkali on isomeric butoxychloropentenes. A. N. Pudovik and V. I. Nikitina. *Zhur. Obshchei Khim.* (J. Gen. Chem.) 19, 75-82(1949).—The reaction of KOH with *1-butoxy-5-chloro-3-pentene* (I) in MeOH or EtOH follows the bimol. S_N^2 route with formation of RO derivs.; in PrOH, BuOH, and *tert*-BuOH there is concurrent formation of *1-butoxy-2,4-pentadiene* (III) and dibutoxypentenyl ether by the monomol. S_N^1 route, made possible by lesser dissocn. of these alcs. into RO and a proton. With *1-butoxy-3-chloro-4-pentene* (II), both S_N^1 and S_N^2 mechanisms are operative. Boiling 15 g. I and 7 g. KOH in 80 ml. MeOH 3 hrs. gave 9 g. *1-butoxy-5-methoxy-3-pentene*, b_9 93°, n_D^{20} 1.4328, d_4^{20} 0.8080; 20 g. I and 10 g. KOH in 100 g. EtOH gave 12.7 g. *1-butoxy-5-ethoxy-3-pentene*, $b_{8.5}$ 90-7°, n_D^{20} 1.4336, d_4^{20} 0.8677; 18 g. I and 9 g. KOH in 80 g. PrOH gave 0.6 g. *1-butoxy-2,4-pentadiene*, b_{10} 59-60°, n_D^{20} 1.4490, d_4^{20} 0.8230, and 10.8 g. *1-butoxy-5-propoxy-3-pentene*, b_9 110°, n_D^{20} 1.4342, d_4^{20} 0.8600; 30 g. I and 20 g. KOH in 200 g. BuOH gave 4.2 g. III, b_{11} 65°, 10.3 g. *1,5-dibutoxy-3-pentene* (IV), b_{10} 116°, n_D^{20} 1.4352, and 1.3 g. *bis(butoxypentenyl) ether*, b_7 180°, n_D^{20} 1.4535; 20 g. I and 10 g. KOH in 120 g. *tert*-BuOH gave 4.7 g. III and 5.9 g. bis(butoxypentenyl) ether, as well as 5.2 g. intermediate unseparable mixt.; 27 g. I and 14 g. KOH in 200 g. dioxane after 9 hrs. gave 6 g. III and 1 g. of the above ether, as well as 12.5 g. I. Heating 20 g. I with 10 g. KOH in 100 g. 70% EtOH 3 hrs. gave 11.8 g. *1-butoxy-5-ethoxy-3-pentene* (V), b_{10} 107-9°, and 2 g. *1-butoxy-3-penten-5-ol*, b_{10} 125-6°, n_D^{20} 1.4480, d_4^{20} 0.9039. I (40 g.) and 2.5 g. Na in 195 g. BuOH after 4 hrs. at 100° gave 14.8 g. III and 6.2 g. IV, b_{10} 121°, n_D^{20} 1.4363, d_4^{20} 0.8583. Heating 9 g. I and 5 g. powd. KOH 7 hrs. on a steam bath gave 0.8 g. III and 5.5 g. I. II (40 g.) and 20 g. KOH in 120 g. EtOH refluxed 3 hrs. gave 10.2 g. III, 9.3 g. *1-butoxy-3-ethoxy-4-pentene*, b_{10} 78°, n_D^{20} 1.4280, d_4^{20} 0.8832, and 3.2 g. V. Heating 2 g. maleic anhydride and 3 g. III gave a liquid adduct, $C_{13}H_{18}O_4$, b_{11} 192°.

XI. Action of isomeric methoxychloropentenes on sodioalkylacetoacetic esters. A. N. Pudovik. *Ibid.* 1031-45.—Heating 2.5 g. Mg, 13 g. $AcCH_2CO_2Et$, and 20 g. EtOH with a little CCl_4 initiator until the Mg dissolved, followed by addn. of 15 g. $ClCH_2CH{:}CHCH_2CH_2OMe$,

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analog (III). 9,10-Dihydro-1,2-benzanthracene gave, under a 1:1.1 molar relation, a mixt. of predominantly monocarboxylic acid, with about 3.3% of dicarboxylic acid admixt. Anthracene (1 g.), 0.2 g. Li, and 10 ml. Et_2O were shaken 140 hrs. and poured on solid CO_2, giving 96.6% *dicarboxylic acid*, m. 270-300°, after allowance for 10 mg. unreacted hydrocarbon. The above reaction mixt. treated with 1 g. I in Et_2O and let stand 40 hrs., then poured on CO_2, gave 2.04 g. II and 7.4% III; the mixt. m. 200-7°. To BuLi from 1.95 g. BuCl and 0.3 g. Li in 25 ml. Et_2O was added 3 g. I, the mixt. let stand in a closed ampul 20 hrs., and an ethylene oxide stream then passed into it; after aq. treatment, the org. layer was evapd., yielding, on soln. in a little 85% EtOH and standing, 0.36 g. I, while diln. of the mother liquor gave 0.9 g. *9-hydroxyethyl-9,10-dihydroanthracene*, m. 93-5° (from C_6H_6-petr. ether); chromatography of the residues on Al_2O_3 gave addnl. small amts. of this substance, as well as 2.5% *9,10-bis(hydroxyethyl)-9,10-dihydroanthracene*, m. 137-9° (from 50% EtOH). Treatment of BuLi (from 1.2 g. BuCl and 0.2 g. Li in Et_2O) with 2 g. 9,10-dihydro-1,2-benzanthracene 40 hrs. at room temp., followed by passage of MeCl, gave, upon treatment of the mixt. with picric acid, 0.13 g. *picrate* of *cis*(or *trans*)-*9,10-dimethyl-9,10-dihydro-1,2-benzanthracene*, m. 172-3°; the mother liquors, freed of picric acid, were dehydrogenated by S at 220-30° 0.5 hr. and chromatographed on Al_2O_3 in petr. ether; the products isolated included *10-methyl-1,2-benzanthracene*, isolated as the *picrate*, m. 171.5-3.5° (from C_6H_6) (0.18 g.), and *9-methyl-1,2-benzanthracene*, isolated as the *picrate*, m. 114-15° (0.41

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g.). I with 1 mole PhLi gave in 3 hrs. (after CO_2 treatment) 24.4% II and 3.1% III; in 24 hrs. the amts. were 63% and 8.5%, while in 50 hrs. they were 78.4% and 7.0% resp.

G. M. Kosolapoff

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PUDOVIK, A. N.

Addition of chlorine to butadiene and reactions of isomeric dichlorobutenes. A. N. Pudovik. *Zhur. Obshchey Khim.* (J. Gen. Chem.) 19, 1179–92(1949).—Chlorination of butadiene (I) at −10° to −15° in $CHCl_3$ always yields some Cl_4 compds., whose amt. increases from 20–30% in cases of large excess of I to higher values with higher amts. of Cl; without solvent no addn. takes place and the I is merely polymerized to a gelatinous mass; the ratio of 1,2- and 1,4-di-Cl compds. varies but little upon variation of the Cl ratio, and generally 55–60% of the 1,2-isomer forms; Et_2O or C_6H_6 solns. give similar results. The di-Cl compds. isomerize in the presence of $ZnCl_2$ (curves are given for 17°) and the rate is much slower than that of alkoxychloropentenes; at equil. the mixt. contains 67–70% 1,4- and 30–3% 1,2-isomer. The difference from the results of chlorination of I thus is beyond exptl. error and must be assigned to a complex nature of the chlorination, which proceeds both by ionic and by mol. routes (polarization does not reach ionization). Passage of Cl (3–2 bubbles/sec.) into 200 g. $CHCl_3$ and 200 g. 90% I with ice-cooling until a 30-g. gain was reached gave 10 g. *1,2-dichloro-3-butene*, b_{14} 43–4°, n_D^{20} 1.4605, and 8.2 g. *1,4-dichloro-2-butene*, b_{40} 75–6°, n_D^{20} 1.4888, as well as 8.1 g. residual *tetra-Cl compds.*, from which some cryst. product, m. 73° (from $CHCl_3$), was obtained. Repetition until a 35-g. gain in wt. was reached gave 36.3 g. 1,2- and 28 g. 1,4-di-Cl, and 31.5 g. tetra-Cl compds., while addn. of 180 g. Cl gave 85 g. 1,2- and 78 g. 1,4-di-Cl isomer, and 143 g. tetra-Cl compds. Passage of Cl into 200 g. I in 400 ml. dry Et_2O in 6 hrs. with cooling gave 44 g. 1,2- and 40 g. 1,4-isomer; similar reaction in C_6H_6 gave 23 and 18.5 g., resp., as well as 18.3 g. tetra-Cl compds. Passage of Cl at −15° into I for 5 hrs. at 2–3 bubbles/sec. gave no Cl compds. and only 10–12 g. I polymers. Addn. of 3 l. Cl to 20 g. (:$CHCH_2Cl)_2$ in 40 ml. $CHCl_3$ with cooling in 0.5 hr. (5/6 of the Cl was absorbed), gave 9 g. unreacted material and 16 g. Cl_4 compds. [0.6 g. liquid and 14.6 g. solid form (crude, b_{10} 110–30°)]; similar chlorination of the 1,2-isomer gave 7.7 g. solid and 6.1 g. liquid tetra-Cl compds. Neither the 1,2- nor the 1,4-di-Cl compd. isomerizes in 5 hrs. at 130° and a slight change of *n* occurs in the 1st instance after 10 hrs. at 200°; however, isomerization occurs at room temp. with 1% $ZnCl_2$ (results cited above). Heating 16 g. 1,4-isomer with 20 g. AcOH and 30 g. KOAc 5 hrs. to 130–40° gave 1.8 g. *3-butene-1,2-diol diacetate*, b_{10} 86–8°, n_D^{20} 1.4305, d_4^{20} 1.0603, and 18.3 g. *2-butene-1,4-diol diacetate*, b_{12} 116°, n_D^{20} 1.4435, d_4^{20} 1.0826; similar reaction of the 1,2-isomer gave 6.1 g. and 3.3 g., resp. Hydrolysis of the 1,4-isomer by heating 50 g. with 430 g. H_2O contg. 64 g. calcined soda 16 hrs. on a steam bath with stirring gave 9.2 g. *3-butene-1,2-diol*, b_{11} 95°, n_D^{20} 1.4610, d_4^{20} 1.0400, and 9.9 g. *2-butene-1,4-diol*, b_{11} 132°, n_D^{20} 1.4467, d_4^{20} 1.0603; similar hydrolysis of 50 g. 1,2-isomer even after 120 hrs. showed much unreacted Cl compd. and no diols could be isolated. Addn. of 20 g. 1,4-isomer to 20 g. KOH in 100 g. MeOH and heating 3 hrs. on a steam bath gave 7.7 g. *1,4-dimethoxy-2-butene*, b_{760} 142°, n_D^{20} 1.4210, d_4^{20} 0.8967, which with $KMnO_4$ gave *methoxyacetic acid*, b_9 92°, n_D^{20} 1.1170; similar reaction of 15 g. 1,4-isomer with KOH in PrOH gave 0.4 g. *1-chlorobutadiene*, b_{760} 65–6°, and 7.1 g. *1,4-dipropoxy-2-butene*, b_9 83°, n_D^{20} 1.4310, d_4^{20} 0.8631; similar reaction of 20 g. 1,4-di-Cl compd. with 25 g. KOH in 150 g. BuOH gave 0.7 g. *chlorobutadiene* and 7.3 g. *1,4-dibutoxy-2-butene*, b_5 98–100°, n_D^{20} 1.4365, d_4^{20} 0.8618, while the use of *tert*-BuOH (with 15 g. di-Cl compd.) gave 4.7 g. crude chlorobutadiene and material of wide boiling range, b_9 40–80°, which was not identified. Warming 12 g. powd. KOH with 12 g. 1,2-di-Cl compd. gave 6 g. *chloroprene*, b. 59°, n_D^{20} 1.4572, in a vigorous reaction; repetition in EtOH gave largely chloroprene and a very small amt. of crude *1,2-diethoxy-3-butene*, b_{760} 150–65°, n_D^{20} 1.4280. Addn. of 40 g. $(EtO)_3POH$ to 6.7 g. Na in Et_2O, followed by addn. (after soln. of the Na) of 40 g. dry C_6H_6 and 15 g. 1,4-di-Cl compd., distn. of

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2/2 A. N. Pudovik

the Et_2O, heating the residual mixt. 3 hrs. on a steam bath, decantation, and distn. gave 2.9 g. $((EtO)_2P(O)CH_2CH:)_2$, b_{11} 226°, n_D^{20} 1.4547, d_4^{20} 1.1247, and a glassy distn. residue; repetition with the 1,2-Cl_2 compd. gave only a viscous, undistillable mass. Heating the 1,4-di-Cl compd. (7 g.) with 20 g. $(EtO)_3P$ in a sealed tube 10 hrs. at 200° gave 6.5 g. product, b_{16} 80–8°, n_D^{20} 1.4240 (which on redistn. gave 3 g. $(EtO)_2P(O)Et$, b_{16} 87–8°, n_D^{20} 1.4150), and 9.6 g. diphosphonate, identical with that above; similar reaction of the 1,2-di-Cl compd. gave 8 g. $EtPO(OEt)_2$, 2.5 g. product b_{16} 120–60°, and 10 g. distn. residue as a glassy resin. Thus, the 1,4-isomer reacts with KOAc mainly by S_N2 (2nd-order nucleophilic substitution) mechanism, while the 1,2-isomer reacts solely by the S_N1 (1st order) mechanism.

G. M. Kosolapoff

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USSR/Chemistry - Alcohols Jan 49
Chemistry - Rearrangement, Allyl

"Allyl Rearrangements: Action of Alcoholic Alkali on Butoxylchloropentene Isomers," A. N. Pudovik, V. I. Nikitina, Lab of Org Chem, Kazan State U, 7 1/4 pp

"Zhur Obshch Khim" Vol XIX, No 1

In methanol and ethanol solutions, potassium hydroxide converts 1-butoxy-5-chloro-3-pentene into corresponding ethers. In the case of normal propyl, normal butyl, and tertiary butyl alcohols 1-butoxy-2, 4-pentadiene and

[redacted] 58/49T14

USSR/Chemistry - Alcohols (Contd) Jan 49

dibutoxypentene in yields of 5 - 17% were also obtained. With tertiary butyl alcohol, formation of dibutoxypentene was principal reaction. Mechanism of reactions involved is explained by the drop in dissociation of alcohols used into alkoxy groups and a proton. Submitted 22.Oct 47.

[redacted] 58/49T14

PUDOVIK, A. N.

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"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

Feb 49

USSR/Chemistry - Butadiene
Chemistry - Hydrolysis

"Addition of Alpha-Halogen (Chlorine) Ethers to Butadiene," A. N. Pudovik, V. I. Nikitina, S. Kh. Aygistova, Lab Org Chem, Kazan State U, 3 pp

"Zhur Obshch Khim" Vol XIX, No 2

Studies addition of chloromethylethyl, chloromethylbutyl and chloromethylisobutyl ethers to butadiene. Separates and lists characteristics of 1.2 and 1.4 addition products. Shows that hydrolysis of alpha-halogen ethers proceeds in various forms in dependence upon molecular weight of halogen ether radical. Studies isomerization of ethoxychloropentenes and butoxychloropentenes at various temperatures and concentrations of zinc chloride. Submitted 22 Oct 47.

46/49T21

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3RD AND 4TH ORDERS

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Addition of α-halo ethers to butadiene. A. N. Pudovik, V. I. Nikitina, and S. Kh. Algistova. *Zhur. Obshchei Khim.* (J. Gen. Chem.) 19, 279-80(1949).—Butadiene (160 g.) cooled in a Dry Ice bath was mixed with 200 g. $EtOCH_2Cl$ and 4 g. $ZnCl_2$; shaking the closed vessel in an ice bath 10-15 hrs., letting stand 10-15 hrs. at room temp., washing with water, and extn. with Et_2O gave 170 g. *1-ethoxy-3-chloro-4-pentene*, b_{10} 28°, n_D^{20} 1.4345, d_4^{20} 0.9400, and 150 g. *1-ethoxy-5-chloro-3-pentene*, b_{10} 43°, n_D^{20} 1.4510, d_4^{20} 0.9707. Similarly, 370 g. butadiene and 825 g. $BuOCH_2Cl$ with 1% $ZnCl_2$ gave 100 g. *1-butoxy-3-chloro-4-pentene*, b_{10} 77°, n_D^{20} 1.4307, d_4^{20} 0.9200, 385 g. *1-butoxy-5-chloro-3-pentene*, b_{10} 93.4°, n_D^{20} 1.4500, d_4^{20} 0.9161, and 56 g. *di-Bu formal*, b_{10} 70°, n_D^{20} 1.4040, d_4^{20} 0.8622. Iso-$BuOCH_2Cl$ (235 g.), 100 g. butadiene, and 3.4 g. $ZnCl_2$ similarly gave 36 g. *diiso-Bu formal*, b_{10} 50.1°, n_D^{20} 1.4033, d_4^{20} 0.8274, 122 g. *1-isobutoxy-3-chloro-4-pentene*, b_{10} 71°, n_D^{20} 1.4350, d_4^{20} 0.9146, and 108 g. *1-isobutoxy-5-chloro-3-butene*, b_{10} 93.4°, n_D^{20} 1.4460, d_4^{20} 0.9342. The acetal formation is caused by the reaction of unreacted halo ether with water during the aq. washing, with formation of ROH, which reacts with residual halo ether. This was confirmed by the fact that pure $MeOCH_2Cl$ hydrolyzes completely in water to CH_2O, HCl, and MeOH, but the Et deriv. gives 14% $HCH(OEt)_2$, the Pr deriv. gives 65% $HCH(OPr)_2$, while Bu and iso-Bu derivs. give 70-80% of the corresponding formals. Catalytic isomerization of the alkoxychloropentenes in the presence of 0.002-0.01 mole $ZnCl_2$ at −10°, 0°, and 17° was done as described earlier (P. and Arbuzov, C.A. 42, 6311b). The results are given graphically. At −10° almost no isomerization of $EtOCH_2CH_2CHClCH:CH_2$ takes place with 0.18% $ZnCl_2$ in 2 days, and only 8% with 0.55% $ZnCl_2$; at 17° it is isomerized 10.3% in 5 days and 25.4% in 63 days with 0.002 mole $ZnCl_2$, 28.1% and 53.0% with 0.006 mole $ZnCl_2$, and 58.2 and 67.1% with 0.01 mole $ZnCl_2$. $EtOCH_2CH_2CH:CHCH_2Cl$ is isomerized 14.1% in 63 days with 0.01 mole $ZnCl_2$, correspondingly slower isomerization occurs at 0°. $BuOCH_2CH_2CHCl:CHMe$ is isomerized 22.5% in 5 days and 53.2% in 100 days at 17° with 0.006 mole $ZnCl_2$, with 0.01 mole the values are 58.6 and 80.1%; $BuOCH_2CH_2CH:CHCH_2Cl$ is isomerized 7.5% in 5 days with 0.01 mole $ZnCl_2$ and 12.7% in 30 days (final value). Equil. in a mixt. of the BuO derivs. with $ZnCl_2$ at 17° is reached at 85.7% 5-Cl isomer. Correction for the attendant isomerization in the actual amts. of isomers obtained in the butadiene reaction shows 28-35% addn. in 1,4 sense and 65-72% in 1,2 sense, hence the addn. is not ionic but ionoanol. or mol. G. M. K.

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

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PUDOVIK, A. N.

USSR/Chemistry - Butadiene Jun 49
Chemistry - Isomerization

PA 64/49T15

"The Addition of Chlorine to Butadiene and the Isomerization of the Dichlorobutenes," A. N. Pudovik, Lab of Org Chem, Kazan State U, 13½ pp

"Zhur Obshch Khim" Vol XIX, No 6

The addition was studied in solutions of chloroform, ether, and benzene and without solution. In the first case, 1,2-dichloro-butene-3 composed 55-60% of the isomeric dichlorobutenes formed. In the second, the butadiene was partially polymerized, but products were not detected. Additions of chlorine to the several dichlorobutenes produced reactions with practically identical speeds. Butadiene tetrachloride was formed in small quantities even during very slow passage of the chlorine in the presence of a large surplus of butadiene in the mixture. Thermal and catalytic isomerization of the dichlorobenzenes were carried out, determining that in a state of equilibrium the mixture consists of 30-33% of 1,2- and 76-70% of 1,4-dichlorobutene, and that CH_2Cl groups have greater positive inductive effect than the $ROCH_2$ - CH_2 group. Details effects of other substances on the dichlorobenzenes. Submitted 13 Mar 48.

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PUDOVIK, A. N.

PA 64/49T11

USSR/Chemistry - Allyl Rearrangements Jun 49

"Allyl Rearrangements: XI, The Action of Isomeric Methoxychloropentenes on Na-Alkylacetoacetic Esters," A. N. Pudovik, Lab of Org Chem, Kazan State U, 11½ pp

"Zhur Obshch Khim" Vol XIX, No 6

No allyl rearrangements occur in the reaction of primary methoxychloropentene with Na-derived methyl, ethyl, propyl, and butylacetoacetic esters, but they do occur when secondary methoxychloropentene (1-methoxy-3-chloropentene-4) is used. Shows that di-substituted derivatives of acetoacetic esters were obtained

64/49T11

USSR/Chemistry - Allyl Rearrangements Jun 49
(Contd)

by the ester decomposition during heating with sodium ethylate in an alchohol medium. As a result of the reaction between n-octylchloride and Na-ethylacetoacetic ester is obtained the product of the ester decomposition which originally forms the ethyl esters of ethyloctylacetoacetic and ethyloctylacetic acids. Submitted 6 Jan 48.

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"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

Allylic rearrangements. XII. Action of organomagnesium compounds and of magnesium upon isomeric ethoxy- and butoxychloropentenes. A. N. Pudovik and G. M. Vinokurova (Kazan State Univ.). *J. Gen. Chem. U.S.S.R.* 19, No. 10, 2315-54(1949)(English translation).—See *C.A.* 44, 1896g.

E. J. C.

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1ST AND 2ND ORDERS

3RD AND 4TH ORDERS

PROCESSES AND PROPERTIES INDEX

BC

A2

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E. GLYNN.

Allyl rearrangements. XI. Action of isomeric chloromethoxypentenes on sodioallylacetoacetic esters. A. N. Pudovik (*J. gen. Chem., USSR*, 1949, 19, 1034—1046 (*U.S. transl.*, A 1025—1026)).—The reactions between primary chloromethoxypentene and CRAcNa·CO_2Et (R = Me, Et, Pr, or Bu) proceeds normally without rearrangements giving the corresponding disubstituted derivatives of CH_2Ac·CO_2Et, 5-Chloro-1-methoxypent-4-ene and the corresponding acetoacetoxyacetate, mainly or exclusively, the esters of disubstituted acetoacetate. These result from ester-cleavage of disubstituted derivatives of CH_2Ac·CO_2Et in the presence of NaOEt or CRAcNa·CO_2Et and EtOH. The rate of formation of disubstituted acetoacetic esters in the case of *sec.*-chloromethoxypentene depends on the slow, unimol. reaction of dissociation of the chloride into ions which is considerably slower than the reaction of ester-cleavage of the disubstituted derivatives of CH_2Ac·CO_2Et formed. The reaction of *sec.*-chloromethoxypentene occurs with a complete allyl rearrangement. Disubstituted derivatives of CH_2Ac·CO_2Et undergo ester-cleavage when heated with NaOEt in EtOH. n-C_6H_{17}Cl and CRtAcNa·CO_2Et give a product, C_6H_{17}·CHEt·CO_2Et, of the ester cleavage of Et ethyloctylacetoacetate first formed.

Adding 5-chloro-1-methoxypent-5-ene (I) to a solution of Mg and CH_2Ac·CO_2Et in EtOH containing a little CCl_4 and heating the mixture at 100° for 5 hr. gives Et 2-keto-5-methoxyoct-5-ene-3-carboxylate [5-methoxypent-3-enylacetoacetate], b.p. 151—155°/13 mm., d_4^{20} 1·0040, n_D^{20} 1·4511. COMe·CMeNa·CO_2Et and I in boiling EtOH afford *Et 7-methoxyhept-4-ene-2-carboxylate*, $C_{11}H_{20}O_3$ (II), b.p. 118·5°/16 mm., d_4^{20} 0·9942, n_D^{20} 1·4370, and (preponderantly) *Et 8-methoxy-3-methylcet-5-en-2-one-3-carboxylate* (*methyl-*

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5-*methoxypent-2-enylacetoacetate*], $C_{13}H_{20}O_4$ (III), b.p. 148°/8 mm., d_4^{20} 0·9964, n_D^{20} 1·4500. 3-Chloro-1-methoxypent-4-ene (IV) and COMe·CMeNa·CO_2Et furnish chiefly III and much smaller quantities of II. III and NaOEt in boiling EtOH furnish II. I and COMe·CEtNa·CO_2Et in boiling EtOH furnish *Et* 8-*methoxy-3-ethylcet-5-en-2-ene-3-carboxylate*, $C_{15}H_{26}O_4$ (V), b.p. 169°/18 mm., d_4^{20} 0·9916, n_D^{20} 1·4515, with a small quantity of more volatile products. With IV and NaOEt in EtOH, COMe·CEtNa·CO_2Et furnishes mainly *Et* 8-*methoxyoct-5-ene-3-carboxylate*, $C_{13}H_{22}O_3$ (VI), b.p. 128—129°/17 mm., d_4^{20} 0·9287, n_D^{20} 1·4380, with a little V. COMe·CEtNa·CO_2Et and IV in boiling C_6H_6 afford mainly V with a small amount of more volatile substance. NaOEt in boiling EtOH converts V into VI. I, CHPrAc·CO_2Et, and NaOEt in boiling EtOH furnish almost exclusively *Et* 9-*methoxy-4-acetylnon-6-ene-3-carboxylate* [*propyl-5-methoxypent-2-enylacetoacetate*], $C_{15}H_{26}O_4$, b.p. 147°/5 mm., d_4^{20} 0·9768, n_D^{20} 1·4520, with a very small proportion of *Et* 10-*methoxynon-6-enyl-4-carboxylate*, $C_{15}H_{26}O_3$, b.p. 129°/5·5 mm., d_4^{20} 0·9218, n_D^{20} 1·449, also obtained with much unreacted material when IV, CHPrAc·CO_2Et, and NaOEt are heated in EtOH at 100° for 5 hr. CHBuAc·CO_2Et, I, and NaOEt in boiling EtOH (5 hr.) give a small volatile fraction and *Et* 10-*methoxy-5-acetyldec-7-ene-5-carboxylate* [*n-butyl-5-methoxypent-2-enylacetoacetate*], $C_{16}H_{28}O_4$ (VII), b.p. 135°/14 mm., d_4^{20} [illegible], n_D^{20} 1·4[illegible]. Under similar conditions IV furnishes much initial material and *Et* 10-*methoxydec-7-ene-5-carboxylate*, $C_{15}H_{26}O_3$ (VIII), b.p. 145—146°/12 mm., d_4^{20} 0·9180, n_D^{20} 1·4415. VII is scarcely attacked by aq. KOH (at room temp. and then at 100°), is resistant towards 10% H_2SO_4 at 100°, but is converted by KOH in boiling aq. MeOH into 8-*methoxy-3-butylcet-5-en-2-ene*[1-*methoxy-6-acetyldec-3-ene*], $C_{15}H_{26}O_3$, b.p. 145—146°/17 mm., d_4^{20} 0·8942, n_D^{20} 1·4460, and 10-*methoxydec-7-ene-5-carboxylic acid*, $C_{15}H_{26}O_3$, b.p. 165°/8 mm., d_4^{20} 0·9493, n_D^{20} 1·4510. NaOEt in boiling EtOH partly transforms VII into VIII. Oxidation of VII by $KMnO_4$ gives OMe·$[CH_2]_2$·CO_2H, b.p. 106—107°/15 mm., n_D^{20} 1·4170. Analogously, VIII yields OMe·$[CH_2]_2$·CO_2H and *Et* 1-*carboxyhexane-2-carboxylate* [*butylsuccinate*], $C_{10}H_{18}O_4$, b.p. 140—142°/4 mm., d_4^{20} 1·0510, n_D^{20} 1·4424. COMe·CEtNa·CO_2Et and n-$C_5H_{11}Cl$ in anhyd. EtOH at 100° furnish *Et undecane-3-carboxylate* [*ethylcetylacetate*], $C_{16}H_{30}O_2$, b.p. 107—110°/3 mm., d_4^{20} 0·8701, n_D^{20} 1·4325, with much unchanged material.

H. Wren.

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C A

Addition of chlorine to butadiene and reactions of isomeric dichlorobutenes. A. N. Pudovik. *Zhur. Obshchei Khim.* (J. Gen. Chem.) 19, 1179–92(1949).—Chlorination of butadiene (I) at −10° to −15° in $CHCl_3$ always yields some Cl_2 compds., whose amt. increases from 20–30% in cases of large excess of I to higher values with higher amts. of Cl_2; without solvent no addn. takes place and the I is merely polymerized to a gelatinous mass; the ratio of 1,2- and 1,4-di-Cl compds. varies but little upon variation of the Cl ratio, and generally 55–60% of the 1,2-isomer forms; Et_2O or C_6H_6 solns. give similar results. The di-Cl compds. isomerize in the presence of $ZnCl_2$ (curves are given for 17°) and the rate is much slower than that of alkoxychloropentenes; at equil. the mixt. contains 67–70% 1,4- and 30–33% 1,2-isomer. The difference from the results of chlorination of I thus is beyond exptl. error and must be assigned to a complex nature of the chlorination, which proceeds both by ionic and by mol. routes (polarization does not reach ionization). Passage of Cl (3–2 bubbles/sec.) into 200 g. $CHCl_3$ and 200 g. 90% I with ice cooling until a 30-g. gain was reached gave 10 g. *1,2-dichloro-3-butene*, b_{10} 43–4°, n_D^{20} 1.4605, and 8.2 g. *1,4-dichloro-2-butene*, b_{10} 75–6°, n_D^{20} 1.4888, as well as 8.1 g. residual *tetra-Cl compds.*, from which some cryst. product, m. 73° (from $CHCl_3$), was obtained. Repetition until a 65-g. gain in wt. was reached gave 36.3 g. 1,2- and 28 g. 1,4-di-Cl, and 31.5 g. tetra-Cl compds., while addn. of 180 g. Cl gave 85 g. 1,2- and 78 g. 1,4-di-Cl isomer, and 143 g. tetra-Cl compds. Passage of Cl into 200 g. I in 400 ml. dry Et_2O in 6 hrs. with cooling gave 44 g. 1,2- and 40 g. 1,4-isomer; similar reaction in C_6H_6 gave 23 and 18.5 g., resp., as well as 18.3 g. tetra-Cl compds. Passage of Cl at −15° into I for 5 hrs. at 2–3 bubbles sec. gave no Cl compds. and only 10–12 g. I polymers. Addn. of 3 l. Cl to 20 g. (:$CHCH_2Cl$)$_2$ in 40 ml. $CHCl_3$ with cooling in 0.5 hr. (5/6 of the Cl was absorbed), gave 9 g. unreacted material and 16 g. Cl_2 compds. (0.6 g. liquid and 14.6 g. solid form (crude, b_{10} 110–30°)); similar chlorination of the 1,2-isomer gave 7.7 g. solid and 6.1 g. liquid tetra-Cl compds. Neither the 1,2- nor the 1,4-di-Cl compd. isomerizes in 5 hrs. at 130° and a slight change of n occurs in the 1st instance after 10 hrs. at 200°; however, isomerization occurs at room temp. with 1% $ZnCl_2$ (results cited above). Heating 15 g. 1,4-isomer with 20 g. AcOH and 30 g. KOAc 5 hrs. to 130–40° gave 1.8 g. *3-butene-1,2-diol diacetate*, b_{10} 86–8°, n_D^{20} 1.4305, d_4^{20} 1.0603, and 18.3 g. *2-butene-1,4-diol diacetate*, b_{10} 116°, n_D^{20} 1.4435, d_4^{20} 1.0826; similar reaction of the 1,2-isomer gave 6.1 g. and 3.3 g., resp. Hydrolysis of the 1,4-isomer by heating 50 g. with 430 g. H_2O contg. 64 g. calcined soda 16 hrs. on a steam bath with stirring gave 0.2 g. *3-butene-1,2-diol*, b_{10} 95°, n_D^{20} 1.4610, d_4^{20} 1.0166, and 0.9 g. *2-butene-1,4-diol*, b_{10} 132°, n_D^{20} 1.4467, d_4^{20} 1.0800; similar hydrolysis of 50 g. 1,2-isomer even after 120 hrs. showed much unreacted Cl compd. and no diols could be isolated. Addn. of 20 g. 1,4-isomer to 20 g. KOH in 100 g. MeOH and heating 3 hrs. on a steam bath gave 7.7 g. *1,4-dimethoxy-2-butene*, b_{10} 142°, n_D^{20} 1.4210, d_4^{20} 0.8967, which with $KMnO_4$ gave *methoxyacetic acid*, b_{10} 92°, n_D^{20} 1.1170; similar reaction of 15 g. 1,4-isomer with KOH in PrOH gave 0.4 g. *1-chloro-butadiene*, b_{760} 65–6°, and 7.1 g. *1,4-dipropoxy-2-butene*, b_{10} 83°, n_D^{20} 1.4310, d_4^{20} 0.8831; similar reaction of 20 g. 1,4-di-Cl compd. with 25 g. KOH in 150 g. BuOH gave 0.7 g. *chlorobutadiene* and 7.3 g. *1,4-dibutoxy-2-butene*, b_{10} 98–100°, n_D^{20} 1.4365, d_4^{20} 0.8618, while the use of *tert*-BuOH (with 15 g. di-Cl compd.) gave 4.7 g. crude chlorobutadiene and material of wide boiling range, b_{10} 40–80°, which was not identified. Warming 12 g. powd. KOH with 12 g. 1,2-di-Cl compd. gave 6 g. *chloroprene*, b. 59°, n_D^{20} 1.4572, in a vigorous reaction; repetition in EtOH gave largely chloroprene and a very small amt. of crude *1,2-diethoxy-3-butene*, b_{760} 150–65°, n_D^{20} 1.4280. Addn. of 40 g. $(EtO)_3POH$ to 6.7 g. Na in Et_2O, followed by addn. (after soln. of the Na) of 40 g. dry C_6H_6 and 15 g. 1,4-di-Cl compd., distn. of

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the Et_2O), heating the residual mixt. 3 hrs. on a steam bath, decantation, and distn. gave 2.9 g. $((EtO)_2P(O)CH_2CH:)_2$, b_{10} 220°, n_D^{20} 1.4547, d_4^{20} 1.1247, and a glassy distn. residue; repetition with the 1,2-Cl_2 compd. gave only a viscous, undistillable mass. Heating the 1,4-di-Cl compd. (7 g.) with 20 g. $(EtO)_3P$ in a sealed tube 10 hrs. at 200° gave 6.5 g. product, b_{10} 80–8°, n_D^{20} 1.4240 (which on redistn. gave 3 g. $(EtO)_2P(O)Et$, b_{10} 87–8°, n_D^{20} 1.4150), and 9.6 g. diphosphonate, identical with that above; similar reaction of the 1,2-di-Cl compd. gave 8 g. $EtPO(OEt)_2$, 2.5 g. product b_{10} 120–60°, and 10 g. distn. residue as a glassy resin. Thus, the 1,4-isomer reacts with KOAc mainly by S_N2 (2nd-order nucleophilic substitution) mechanism, while the 1,2-isomer reacts solely by the S_N1 (1st order) mechanism.

G. M. Kosolapoff

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PUDOVIK, A.N.; ARBUZOV, B.A.

Addition of dialkylphosphorous acids to unsaturated compounds. Part 1: Addition of dialkylphosphorous acids to β,β-dimethyldivinylketone. Izv.Kazan.fil.AN SSSR Ser.khim.nauk no.1:45-52 '50. (MLRA 10:5)

(Phosphorous acids) (Vinyl compounds)

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PUDOVIK, A.N.

PUDOVIK, A.N.; ARBUZOV, B.A.

Addition of dialkylphosphorous acids to unsaturated compounds. Part 2: Addition of dialkylphosphorous acids to the nitrile of acrylic acid and methylmethacrylate. Izv.Kazan.fil.AN SSSR Ser. khim.nauk no.1:53-58 '50. (MLRA 10:5)
(Phosphorous acids) (Methacrylic acid)

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Acetylene allene rearrangements. I. The action of esters of phosphorous acid on 2-methyl-2-chloro-3-butyne. A. N. Pudovik (Kazan State Univ.). *Zhur. Obshchei Khim.* (J. Gen. Chem.) **20**, 92-9(1950); cf. C. A. **44**, 1886g. $Me_2CClC:CH$ (10 g.) and 10 g. $(EtO)_3P$ after 10 hrs. in a sealed tube at 150° gave 7.5 g. $Me_2C:C(PO(OEt)_2)CH(Et)PO(OEt)_2$ (I), b_4 183-5°, b_4 177-8°, n_D^{20} 1.4508, d_4^{20} 1.1171, about 1 g. unidentified substances, b_4 185-215°, and 8.7 g. tar. I's sol. in H_2O and may be recovered unchanged even after 4 hrs. at 140°; its hydrolysis with concd. HCl gave a sirupy *free acid* contg. 2 PO_3H_2 groups (confirmed by analysis of the Ba salt, which is not described). The results are similar when the reaction is run at 130-40° or even 120°, although it is less complete; no reaction took place at 90° after 10 hrs. However, 9 g. chloride and 14 g. phosphite heated in 17 ml. dry C_6H_6 6 hrs. to 130° gave 3.1 g. $Me_2C:C(PO(OEt)_2)_2$, b_{10} 120-2°, n_D^{20} 1.4555, d_4^{20} 1.0237, 5.9 g. diphosphonate identical with I, and 6 g. residue. The allene deriv. does not yield ppts. with ammoniacal Ag or Cu. The initial chloride is unchanged after 6 hrs. at 130°. I with $KMnO_4$ gave Me_2CO, confirming its structure, while 1.5 g. allene deriv. heated 7 hrs. to 150-60° gave 0.4 g. liquid, b_5 97-120°, n_D^{20} 1.4190, and 0.7 g. *dimer* of the allene deriv., b_4 205-6°, n_D^{20} 1.4795, d_4^{20} 1.0992. The allene deriv. (3 g.) heated with 5 g. $(EtO)_3P$ 10 hrs. to 140° gave 2 g. $(EtO)_3P$, 3 g. crude products, b_5 45-190°, and 1.3 g. I, b_4 187-8°, n_D^{20} 1.4589, d_4^{20} 1.1166. Heating 16 g. $(EtO)_3P$ with 10 g. $Me_2C:C:CHCl$ 10 hrs. to 150° gave much EtCl, 8.5 g. crude $(EtO)_3P$, and unidentified products. $(BuO)_3P$ (50 g.) and 20 g. $Me_2CClC:CH$ after 10 hrs. at 150° gave 12 g. BuCl, 2.3 g. $(BuO)_3P$, 1.3 g. $Me_2C:C(PO(OBu)_2)_2$, b_{10} 131-2°, n_D^{20} 1.4110, d_4^{20} 0.9594, 4.3 g. $Me_2C:C(PO(OBu)_2)CH(Bu)PO(OBu)_2$, b_5 207-10°, n_D^{20} 1.4612, d_4^{20} 1.0505, and 3 g. unidentified product, b_5 210-227°, n_D^{20} 1.4652. Repetition with 15 g. chloride, 20 g. $(MeO)_3P$, and 20 g. CaH_2 gave after 8 hrs. at 120° 9.8 g. $MeP(O)(OMe)_2$, b_{10} 70°, n_D^{20} 1.4112, 3.1 g. $Me_2C:C(PO(OMe)_2)CH(Me)PO(OMe)_2$, b_4 180-2°, n_D^{20} 1.4782, d_4^{20} 1.2218. $Me_2CClC:CH$ (20 g.) with $(EtO)_2PONa$ [from 27 g. $(EtO)_2POH$] in Et_2O refluxed 2 hrs. gave a mixt. of unidentified products, b_5 115-80°.

G. M. Kosolapoff

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Allylic rearrangements. XIII. Preparation of mercaptans of allyl type and their transformation into thio ethers. A. N. Pudovik and N. N. Kudryavtseva (Kazan State Univ.). *Zhur. Obshchei Khim.* (J. Gen. Chem.) **20**, 848-54(1950); cf. C.A. **42**, 1559g; **44**, 1806g.—Methods were developed for the formation of either mercaptans or thio ethers from allylic halides and metal hydrosulfides. Allylic mercaptans are converted to thio ethers with evolution of H_2S on heating. Primary methoxy-, ethoxy-, or butoxychloropentenes react with hydrosulfides normally without allylic shift, while the secondary derivs. react with a full allylic rearrangement. A soln. of 5 g. Na in 100 ml. abs. EtOH was satd. with H_2S and refluxed 3 hrs. with 25 g. $EtOCH_2CH_2CH:CHCH_2Cl$; distn. of the org. products gave 32% *1-ethoxy-3-penten-5-thiol*, b_4 70-1°, n_D^{20} 1.4725, d_4^{20} 0.9530, and 20% $(EtOCH_2CH_2CH:CHCH_2)_2S$, b_{14} 172.5°, n_D^{20} 1.4830, d_4^{20} 0.9400; the latter forms slowly from the former on heating, such as is encountered during distn. Repetition of the synthesis at room temp. (24 hrs.) gave 10.1 g. mercaptan and 3.9 g. thio ether. Similarly $EtOCH_2CH_2CH_2CHClCH:CH_2$, refluxed 3 hrs., gave 3.2 g. *1-ethoxy-3-penten-5-thiol* and 7.6 g. thio ether. The thiol forms the thio ether at a rate which is appreciable even at 85°, and becomes rapid at 130°. The structures of the products were confirmed by $KMnO_4$ oxidation to *β-ethoxypropionic acid*, b_{14} 109°, n_D^{20} 1.4215. $Me(CH_2)_3SH$ heated 8 hrs. to 130° showed no detectable reaction. $BuOCH_2CH_2CH:CHCH_2Cl$ (25 g.) and 9.5 g. KOH in 100 ml. 81% EtOH, previously satd. with H_2S, gave after 24 hrs. 42.5% *1-butoxy-3-penten-5-thiol*, b_{10} 107-10°, n_D^{20} 1.4675, d_4^{20} 0.9232, and 22.5% *corresponding thio ether*, b_4 185-7°, n_D^{20} 1.4770, d_4^{20} 0.9234. $BuOCH_2CH_2CHClCH:CH_2$ did not react at room temp. but after 3 hrs. on a steam bath it gave (from 50 g. chloride) 3.1 g. thiol (identical with the above) and 17.2 g. thio ether. The *MeO analog* gave 55% *1-methoxy-3-penten-5-thiol*, b_{14} 63-6°, n_D^{20} 1.4775, d_4^{20} 0.9783, and a trace of a higher-boiling fraction from the primary chloride, while the secondary chloride, which reacted only at reflux, gave 3.4 g. *thio ether*, b_{10} 161°, n_D^{20} 1.4940, and 2 g. thiol. $CH_2:CHCH_2Br$ (25 g.) yielded 9.3 g. crude *allyl mercaptan* (pure, b. 63-6°, n_D^{20} 1.4080, d_4^{20} 0.9304), and 3.2 g. *thio ether*, b. 138-40°, n_D^{20} 1.4805; the former polymerizes on standing and is gradually converted to the thio ether on heating.

G. M. Kosolapoff

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No. 2

Addition of dialkyl phosphites to unsaturated ketones, nitriles, and esters. A. N. Pudovik and B. A. Arbuzov (A. E. Arbuzov Inst., State Univ., Kazan). *Doklady Akad. Nauk S.S.S.R.* **73**, 327-30(1950); cf. *C.A.* **44**, 1893g.—The addn. of $(RO)_2PONa$ to unsatd. compds., discovered earlier (cf. above ref.) in reactions of secondary allylic chlorides, was extended to other unsatd. compds. with an active unsatd. link; compds. contg. CO, CN, or CO_2R groups which by their electron-attractive properties produce a pos. charge on the β-C atom of the ethylene link and the addn. of nucleophilic reagents to the unsatd. link, as the addn. to the carbonyl group itself is correspondingly repressed. These unsatd. derivs. readily add $(RO)_2POH$ in the presence of alcoholates of alkali metals, the reaction being run by dropwise addn. of a satd. alc. soln. of RONa to an equimolar mixt. of $(RO)_2POH$ and the unsatd. deriv. The action is exothermic (the effect is smaller with larger compds.) and the products are isolated by distn. after an unstated period required for completion. Usually the phosphites of the higher alcs. require larger amts. of RONa for satisfactory action; it is advisable to use the same R in RONa and the phosphite to avoid transesterifications. $Me_2C:CHCOCH:CH_2$ yields products contg. 1 double bond (Br titration), while hydrolysis of the product obtained with $(EtO)_2P'OH$ by means of HCl yielded EtCl (in an amt. corresponding to an equimolar adduct); no H_3PO_4 was detected (H_3PO_4 would form if the phosphono group attached itself to the α-C atom in respect to the CO group), and the product showed an active keto group by qual. reactions with Na nitroprusside and $2\text{-}C_{10}H_7OH$, and by formation of a phenylhydrazone. On this basis the structures of the following products, $Me_2C:CHCOCH_2CH_2PO(OR)_2$, were established (R given): *Me* (59%), b_{10} 169-71°, n_D^{20} 1.4711, d_4^{20} 1.1130; *Et* (52%), b_3 149°, d_4^{20} 1.0658, n_D^{20} 1.4669; *iso-Bu* (48.5%), b_{10} 188-9°, n_D^{20} 1.4511, d_4^{20} 1.0013; *Bu* (57%), b_{10} 198-200°, n_D^{20} 1.4623, d_4^{20} 1.0111(?). The addns. to $CH_2:CHCN$ are much more energetic and addn. of a few drops of RONa soln. to the mixt. causes spontaneous boiling, unless the mixt. is cooled; hydrolysis of the adducts gave phosphonopropionic acid, m. 164-5°, thus confirming the structure $(RO)_2P(O)CH_2CH_2CN$: R = *Me* (86.3%), b_{10} 158°, n_D^{20} 1.4432, d_4^{20} 1.1064; *Et* (83%), b_{10} 159-60°, n_D^{20} 1.4388, d_4^{20} 1.1089; *iso-Pr* (46.4%), b_{10} 160°, n_D^{20} 1.4345, d_4^{20} 1.0500; *iso-Bu* (71%), b_{10} 171°, n_D^{20} 1.4386, d_4^{20} 1.0059; *Bu* (71.5%), b_{10} 177-8°, n_D^{20} 1.4395, d_4^{20} 1.0155. With $CH_2:CMeCO_2Me$ the reaction is much more sluggish and the action begins only after addn. of considerable amts. of RONa; the products obtained, $(RO)_2P(O)CHMeCO_2Me$, were: R = *Me* (77.7%), b_{10} 137-8°, n_D^{20} 1.4377, d_4^{20} 1.1761; *Et* (74.5%), b_{10} 152-3°, n_D^{20} 1.4350, d_4^{20} 1.1212; *iso-Pr* (61%), b_{10} 153-4°, n_D^{20} 1.4298, d_4^{20} 1.0612. The reactions appear to proceed by addn. of $(RO)_2PO^-$ and Na^+ to the unsatd. link, with subsequent replacement of Na by H supplied by a 2nd mole of $(RO)_2POH$, thus regenerating $(RO)_2PONa$.

G. M. Kosolapoff

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FULL TRANSLATION AVAILABLE - W215599, 4 Dec 1950

Addition of dialkyl phosphites to unsaturated compounds. A new method of synthesis of β-ketophosphonic and unsaturated α-hydroxyphosphonic esters. A. N. Pudovik (A. E. Arbuzov Chem. Inst., Kazan Sec. Acad. Sci. U.S.S.R.). *Doklady Akad. Nauk S.S.S.R.* **73**, 499–502(1950); cf. *C.A.* **45**, 2853*a*. —The addn. of $(RO)_2POH$, under the catalytic influence of RONa, to unsatd. electrophilic compds., described in the previous paper (*loc. cit.*), was extended to the simplest α,β-unsatd. ketones, with the vinyl group substituted in various ways. MeCH:CHAc (I), PhCH:CHAc, and furfurylideneacetone (II) gave 70-80% yields of adducts. The most vigorous addn. takes place with I, the least vigorous with II. The products prepd. included: *$AcCH_2CHMePO(OMe)_2$*, b_{10} 134-5°, n_D^{20} 1.4411, d_4^{20} 1.1313; *di-Et ester*, b_{12} 139-40°, n_D^{20} 1.4387, d_4^{20} 1.0850; *di-iso-Bu ester*, b_{10} 156-8°, n_D^{20} 1.4400, d_4^{20} 1.0221; *di-Bu ester*, b_{10} 172-3°, n_D^{20} 1.4412, d_4^{20} 0.9985; *$AcCH_2CHPhPO(OMe)_2$*, b_{10} 189-90°, n_D^{20} 1.5095, d_4^{20} 1.1791; *di-Et ester*, b_{10} 203°, n_D^{20} 1.5050, d_4^{20} 1.1309; *di-iso-Bu ester*, b_{11} 208°, n_D^{20} 1.4900, d_4^{20} 1.0736; *di-Bu ester*, b_{11} 219-20°, n_D^{20} 1.4927, d_4^{20} 1.0737; *$AcCH_2CH(C_4H_3O)PO(OMe)_2$*, b_8 163-4°, n_D^{20} 1.4835, d_4^{20} 1.2181; *di-Et ester*, b_{14} 192-3°, n_D^{20} 1.4755, d_4^{20} 1.1616; *di-iso-Bu ester*, b_1 161°, n_D^{20} 1.4711, d_4^{20} 1.0932; *di-Bu ester*, b_1 182°, n_D^{20} 1.4730, d_4^{20} 1.0995. Addns. to unsatd. ketones with 2 substituents on the vinyl group and to various unsatd. aldehydes, by the same technique, yielded HO phosphonates, having active OH groups (Zerewitinov method). Thus, unsatd. aldehydes and mesityl oxide add the dialkyl phosphite to the carbonyl group rather than to the C:C double bond. The products included the following: *$Me_2C:CHC(OH)MePO(OMe)_2$*, b_{12} 136°, n_D^{20} 1.4457, d_4^{20} 1.1163; *di-Et ester*, b_{11} 138°, n_D^{20} 1.4400, d_4^{20} 1.0675; *di-iso-Bu ester*, b_{11} 162-3°, n_D^{20} 1.4409, d_4^{20} 1.0029; *di-Bu ester*, b_{11} 171-2°, n_D^{20} 1.4440, d_4^{20} 1.0084; *$CH_2:CHCH(OH)PO(OMe)_2$*, b_{10} 149-51°, n_D^{20} 1.4575, d_4^{20} 1.2188; *di-Et ester*, b_{10} 154-5°, n_D^{20} 1.4506, d_4^{20} 1.1225; *di-iso-Pr ester*, b_7 140-1°, n_D^{20} 1.4415, d_4^{20} 1.0405; *di-iso-Bu ester*, b_{10} 166-70°, n_D^{20} 1.4411, d_4^{20} 1.0130; *di-Bu ester*, b_{10} 168-70°, n_D^{20} 1.4348, d_4^{20} 0.9968; *$MeCH:CHCH(OH)PO(OMe)_2$*, b_8 150-2°, n_D^{20} 1.4360, d_4^{20} 1.1690; *di-Et ester*, b_8 163-4°, n_D^{20} 1.4555, d_4^{20} 1.1005; *$(C_4H_3O)CH:CHCH(OH)PO(OEt)_2$*, m. 106-7°; *$PhCH:CHCH(OH)PO(OMe_2)$*, m. 101-2°; *di-Et ester*, m. 104-5°. The addn. of $(RO)_2PONa$ to the carbonyl group was first suggested in the reaction of AcCl with $(RO)_2PONa$ (Arbuzov and Azanovskaya, *ibid.* **58**, 1961(1947)). G. M. Kosolapoff

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PUDOVIK, A. N.

USSR/Chemistry - Organophosphorus Compounds Feb 51

"Addition of Dialkylphosphorous Acids to Unsaturated Compounds. I. Addition of Dialkylphosphorous Acids to β,β-Dimethyldivinylketone," A. N. Pudovik, B. A. Arbuzov, Chem Inst imeni Acad A. Ye. Arbuzov, Kazan Affiliate, Acad Sci USSR

"Zhur Obshch Khim" Vol XXI, No 2, pp 382-388

Dialkylphosphorous acids shown to add easily to β,β-dimethyldivinylketone in presence of small quantities of alcoholates of alkali metals to form corr esters of phosphonic acids. Structure of products verified and mechanism of their formation proposed.

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PUDOVIK, A. N.

USSR/Chemistry - Acetylene Derivatives Aug 51

"Acetylene-Allene Rearrangements. II. Action of Alcoholic Alkali, Alcoholates, and Alkali Metal Acetates on Acetylene and Allene Chlorides," A. N. Pudovik, Lab of Org Chem, Kazan' State U

"Zhur Obshch Khim" Vol XXI, No 8, pp 1462-1471

Action of alc solns of alcoholates and alc alkalis on dimethylethinylchloromethane (I) and dimethylvinylethinylchloromethane (II) under conditions favorable to bimol mechanism yielded ethers of dimethylethinylcarbinol (III) and dimethylvinylethinylcarbinol and, resp, isopropenylacetylene (IV) and isopropenylvinylacetylene. Action of I and II

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USSR/Chemistry - Acetylene Derivatives (Contd) Aug 51

on allene chloride in MeOH soln yielded small amt of Me ether of 1-methoxy-3-methyl-butadiene-1,2. Monomol alcoholysis of I yielded simple ethers of III and small amt of IV.

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PUDOVIK, A. N.

188T17

USSR/Chemistry - Acetylene Derivatives Aug 51

"Acetylene-Allene Rearrangements. III. Action of Organomagnesium Compounds on Dimethylvinylchloromethane," A. N. Pudovik, L. A. Mukhamedova, Lab of Org Chem, Kazan' State U

Zhur Obshch Khim" Vol XXI, No 8, pp 1472-1476

Examd reaction of dimethylvinylethinylchloromethane with MgEtBr and MgPhBr. On basis of results of oxidation of reaction products, concluded that both reactions proceed with partial acetylene-allene rearrangement. Proposes explanation of rearrangement mechanism.

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PUDOVIK, A. N.

191T43

USSR/Chemistry - Allyl Rearrangement Sep 51

"Allyl Rearrangements. XIV. Action of Amines on Isomeric Methoxychloropentenes," A. N. Pudovik, Lab Org Chem, Kazan' State U imeni V. I. Ul'yanov-Lenin

"Zhur Obshch Khim" Vol XXI, No 9, pp 1642-1648

Action of isomeric methoxy-, isopropoxy-, butoxy-chloropentenes on diethylamine, ethylaniline, aniline showed that primary halogen-allyl isomers react with secondary amines by normal scheme to form products structurally like initial chlorides. In reaction of secondary isomers with diethylamine there was complete allyl rearrangement,

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USSR/Chemistry - Allyl Rearrangement (Contd) Sep 51

with aniline partial rearrangement, evidently by combined ionic and mol mechanism. Nature of amine affects reaction mechanism.

191T43

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PUDOVIK, A. N.

USSR/Chemistry - Acetylene Compounds Oct 51

"Acetylene-Allene Rearrangements. IV Ionic Theory of Acetylene-Allene Rearrangements," A. N. Pudovik, Kazan' State U imeni V. I. Ul'yanov-Lenin

"Zhur Obshch Khim" Vol XXI, No 10, pp 1811-1818

From study of reaction kinetics, shows that hydrolysis of acetylenic chlorides proceeds by monomol mech. Studies catalytic isomerization of dimethylethenylchloromethane in presence of metal halides. Proposes ionic theory for mechanism of acetylene-allene rearrangements.

194T27

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FA 194T32

USSR/Chemistry - Organophosphorus Compounds — Oct 51

"Addition of Dialkylphosphorus Acids to Unsaturated Compounds. II. Addition of Dialkylphosphorus Acids to the Nitrile of Acrylic Acid and Methylmethacrylate," A. N. Pudovik, B. A. Arbuzov, Chem Inst imeni Acad A. Ye. Arbuzov, Kazan' Affiliate, Acad Sci USSR

"Zhur Obshch Khim" Vol XXI, No 10, pp 1837-1841

Demonstrates that dialkylphosphorus acids in presence of Na alcoholate add to nitrile of acrylic acid and Me methacrylate to form

194T32

USSR/Chemistry - Organophosphorus Compounds (Contd) — Oct 51

corresponding derivs of phosphonic acids. Proves structure of obtained products and proposes explanation of mechanism of their formation.

194T32

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PUDOVIK, A. N.

"Phosphonoethylation," Doklady Akademiy Nauk SSSR, Vol. LXXX, No. 1, 1951, pp. 65-68

FULL TRANSLATION AVAILABLE IN W-23177, 10 July, 1952

APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3"

"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

PULOVIK, A.N.; YARMUKHAMETOVA, D.Kh.

New synthesis of esters of phosphonic and thiophosphonic acids. XI. Addition of dialkyl phosphites to the amide and esters of methacrylic acid. Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk '52, 721-6. (MLRA 5:9) (CA 47 no.20:10467 '53)

1. A.E.Arbuzov Chem. Inst., Kazan.

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PUDOVIK, A. N.

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

(4) Chem

Synthesis of esters of phosphonic and thiophosphonic acids. XII. Addition of dialkyl phosphites to unsaturated dibasic acids and esters. A. N. Pudovik. *Bull. acad. sci. U.S.S.R., Classe sci. chim.* 1952, 821-4 (Engl. translation). See *C.A.* 47, 10467*e*. XIII. Addition of diethyl thiophosphite to ketones and aldehydes. A. N. Pudovik and G. A. Zametaeva. *Ibid.* 825-30. See *C.A.* 47, 10467*i*. XIV. Method of synthesis of esters of amino phosphonic acids. A. N. Pudovik and M. V. Korchemkina. Ibid. 831-5. See *C.A.* 47, 10468*f*. XV. Addition of esters of phenyl- and alkylphosphonous acids to esters of methacrylic and acrylic acids. A. N. Pudovik and D. Kh. Yarmukhametova. *Ibid.* 803-6. See *C.A.* 47, 10469*c*.

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"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

PUDOVIK, A.N.; YARMUKHAMETOVA, D.Kh.

New synthesis of esters of phosphonic and thiophosphonic acids. XV. Addition of esters of phenyl- and alkylphosphonous acids to esters of methacrylic and acrylic acids. Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk '52, 902-7. (MLRA 5:11)
(CA 47 no.20:10469 '53)

APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3"

"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

PUDOVIK, A.N.; IMAYEV, M.G.

Reaction of phosphonoethylation and diene synthesis with vinylphosphonic esters. Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk '52, 916-22. (CA 47 no.20:10463 '53) (MLRA 5:11)

1. Kazan State Univ.

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"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

PUDOVIK, A.N.

New synthesis of esters of phosphonic and thiophosphonic acids. XII. Addition of dialkyl phosphites to unsaturated dibasic acids and esters. Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk '52, 926-31. (MLRA 5:11) (CA 47 no.20:10467 '53)

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"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

PUDOVIK, A. N. an G. A. Zametayeva

"Addition of diethyl thiophosphite to ketones and aldehydes," Izvest. Akad. Nauk SSSR, Otdel Khim. Nauk, 932-9, 1952.

DIGEST AVAILABLE in B-64419, 15 May 53 (Translated)

APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3"

"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

PUDOVIK, A. N. and M. V. Korchemkina

"New Method of Synthesis of Esters of Aminophosphonic Acids," Izvest. Akad. Nauk SSSR, Otdel Khim. Nauk, pp. 940-6, 1952.

DIGEST OF ARTICLE AVAILABLE (Translated)

B-64419, 15 May 53

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"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

PUDOVIK, A.N.; IVANOV, B.Ye.

Addition of dialkyl phosphites and their chlorides to α-oxides. Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk '52, 947-55. (MLRA 5:11)
(CA 47 no.20:10464 '53)

1. Kazan State Univ.

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"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

PUDOVIK, A. N.

USSR/Chemistry - Organophosphorus Compounds Jul/Aug 52

"New Method for the Synthesis of Esters of Phosphonic and Thiophosphonic Acids. 11. Addition of Dialkylphosphorous Acids to the Amide and Esters of Methacrylic Acid," A. N. Pudovik, D. Kh. Yarmukhametova, Chem Inst imeni Acad A. Ye. Arbuzov, Kazan' Affiliate, Acad Sci USSR

"Iz Ak Nauk SSSR, Otdel Khim Nauk" No 4, pp 721-726

Finds that dialkylphosphorous acids add to the amide of methacrylic acid under the formation of

229T20

amides of dialkylphosphonoisobutyric acid. Obtains and describes products of the addn of higher dialkylphosphorous acids to methylmethacrylate and of diethylphosphorous acids to esters of methacrylic acid having various ester radicals.

229T20

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"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

1. PUDOVIK, A. N., IMAYEV, M. G.

2. USSR (600)

4. Phosphonic Acid

7. Reactions of phosphonoethylation and diene synthesis with vinylphosphonic esters. Izv. AN SSSR. Otd. khim. nauk, No. 5, 1952

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

APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3"

"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

1. PUDOVIK, A. N., IVANOV, B. YE.

2. USSR (600)

4. Phosphorous Acid

7. Addition of dialkylphosphorous acids and of their chlorides to α-oxides. Izv. AN SSSR. Otd. khim. nauk, No. 5, 1952

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

APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3"

"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

1. PUDOVIK, A. N., ZAMETAYEVA, G. A.

2. USSR (600)

4. Phosphorous Acid

7. New method for the synthesis of phosphonic and thiophosphonic esters. Part 13. Addition of diethylthiophosphorous acid to ketones and aldehydes. Izv. AN SSSR. Otd. khim. nauk, No. 5, 1952

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

APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3"

"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

1. PUDOVIK, A. N., KORCHEMKINA, M. V.

2. USSR (600)

4. Phosphonic Acid

7. New method for the synthesis of phosphonic and thiophosphonic esters. Part 14. New method for the synthesis of aminophosphonic esters. Izv. AN SSSR. Otd. khim. nauk, No. 5, 1952

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

APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3"

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(3)

1-25-54

Academician Aleksandr Erminingel'dovich Arbuzov (on 75th birthday). A. N. Pudovik and K. V. Nikonorov. *Uspekhi Khim.* 21, 1137-53(1952).—Biography with portrait and 35 references to scientific work. G. M. K.

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APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3"

"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

PUDOVIK, A. N.

USSR/Chemistry - Organophosphorus Compounds Jan 52

"Allyl Rearrangements. XV. Reactions Between Sodium and Magnesium Salts of Dialkylphosphorous Acids and Isomeric Butoxychloropentenes," A. N. Pudovik, Lab of Org Chem, Kazan' State U imeni V. I. Ul'yanov-Lenin

"Zhur Obshch Khim" Vol XXII, No 1, pp 109-113

Studied action of Na and Mg salts of dialkylphosphorous acids on isomeric butoxy- and methoxychloropentenes. Showed possibility of using Mg salts for synthesis of phosphonic acids. Reactions of Na and Mg salts with primary butoxychloropentene proceed

207T22

USSR/Chemistry - Organophosphorus Compounds Jan 52
(Contd)

without rearrangement; with secondary pentenes, however, there is full allyl rearrangement, with formation of alkoxydialkylphosphono-pentenes, identical in structure with those obtained from primary chlorides.

207T22

APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3"

"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

USSR/Chemistry - Organophosphorus Compounds

Mar 52

"The Addition of Dialkylphosphorous Acids to Unsaturated Compounds. III. New Method of Synthesis of beta-Ketophosphonic Esters," A. N. Pudovik, Chem Inst imeni Acad A. Ye. Arbuzov, Kazan Affiliate, Acad Sci USSR

"Zhur Obshch Khim" Vol XXII, No 3, pp 462-467

The esters were produced by adding dialkyl phosphorous acid to α, β-unsatd ketones in presence of alcoholates of alkali metals. The addn products of

209T41

USSR/Chemistry - Organophosphorus Compounds (Contd)

Mar 52

dimethyl, diethyl, diisobutyl, and dibutyl phosphorous acids to ethyldene acetone, benzalacetone, and furfuralacetone were sepd and described.

209T41

PUDOVIK, A. N.

APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3"

"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

USSR/Chemistry - Organophosphorus Compounds Mar 52

"The Addition of Dialkylphosphorous Acids to Unsaturated Compounds. IV. Addition of Dialkylphosphonic Acids to Unsaturated Aldehydes; New Method of Synthesizing Unsaturated α-Hydroxyphosphonic Esters," A. N. Pudovik, Yu. P. Kitayev, Lab of Org Chem of Kazan Affiliate, Acad Sci USSR, and Kazan State U

"Zhur Obshch Khim" Vol XXII, No 3, pp 467-473

Dialkylphosphorous acids in presence of alcoholates of alkali metals will add to α, β-unsatd aldehydes at the carbonyl group, forming esters of unsatd

209T42

USSR/Chemistry - Organophosphorus Compounds (Contd) Mar 52

α-hydroxyphosphonic acids. The products of addn of dialkylphosphorous acids to acrolein, cinnamic aldehyde, crotonic aldehyde, furyl acrolein, and hexadiene-2,4-al-1 were sepd and described.

209T42

PUDOVIK, A. N.

APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3"

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USSR/Chemistry - Organophosphorus Compounds Mar 52

"The Addition of Dialkylphosphorous Acids to Unsaturated Compounds. V. The Addition of Dialkylphosphorous Acids to Methylacrylate, Vinyl Acetate, and Vinyl Butyl Ether," A. N. Pudovik, Chem Inst imeni Acad A. Ye. Arbuzov, Kazan Affiliate, Acad Sci USSR

"Zhur Obshch Khim" Vol XXII, No 3, pp 473-477

Dialkylphosphorous acids will add to methyl acrylate and vinyl acetate, in the presence of alcoholates of alkali metals, to form the corresponding methyl esters of β-dialkylphosphonopropionic acid

209T43

USSR/Chemistry - Organophosphorus Compounds (Contd) Mar 52

and β-dialkylphosphonoethyl acetates. Dialkylphosphorous acids will not add to vinyl butyl ether in the presence of alcoholates of alkali metals and phosphoric acid.

209T43

PUDOVIK, A. N.

APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3"

"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

PUDOVIK, A. N.

Chemical Abst.
Vol. 48 No. 5
Mar. 10, 1954
Organic Chemistry

The addition of dialkyl phosphites to unsaturated compounds. III. New synthesis of α-oxo phosphonic esters. A. N. Pudovik. *J. Gen. Chem. U.S.S.R.* 22, 525-30(1952) (Engl. translation). See *C.A.* 47, 2686*f*. IV. The addition of dialkyl phosphites to unsaturated aldehydes. New method of synthesis of unsaturated α-hydroxy phosphonic esters. A. N. Pudovik and Yu. P. Kitaev. *Ibid.* 531-5.—See *C.A.* 47, 2687*a*. V. The addition of dialkyl phosphorous acids to methyl acrylate, vinyl acetate, and vinyl butyl ether. A. N. Pudovik. *Ibid.* 537-[illegible].—See *C.A.* 47, 2687*h*. VI. The addition of dialkyl phosphites to ethyl esters of cinnamic and crotonic acids. *Ibid.* 1[illegible]9-01.—See *C.A.* 47, 4836*h*. VII. Addition of dialkyl phosphites to α,β-unsaturated ketones of the aliphatic series. *Ibid.* 1415-19.—See *C.A.* 47, 4837*b*. H. L. H.

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"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

A.N. PUDOVIK

May 52

USSR/Chemistry-Methoxychlorchexenes

"The Addition of α-Halogen Ethers of the CH_3CHCl - O - R Type to Butadiene," Lab. of Org. Chem, Kazan' State U.

Zhur Obshch Khim, Vol 22, No 5, pp 773-781

Chloroethylmethyl ether (I), chloroethylethyl ether, and chloroethylbutyl ether were added to butadiene, and the corresponding 1,2, and 1,4 addition products were isolated and studied. Catalytic isomerization of methoxychlorchexenes in the presence of zinc chloride was studied. In the state of equilibrium, 90-93 % 2-methoxy-6-chlorchexene-4 and 7-10% 2-methoxy-4-chlorchexene-5 were found to be presnet. The type of addition of (I) to butadiene was detd. From 65 to 70% of the ether is added at the 1,2 positions, and 25-35% at the 1,4 positions, In the author's opinion, the addn of halogene ethers and other halogen derivs to butadiene proceeds not ionically but innomolecularly.

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"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

Chemical Abst.
Vol. 48 No. 5
Mar. 10, 1954
Organic Chemistry
CATALYSTS

Chem. 7

The addition of α-halo ethers of the type MeCHClOR to butadiene. A. N. Pudovik (Kazan State Univ.). J. Gen. Chem. U.S.S.R. 22, 835-41(1952)(Engl. translation).—See C.A. 47, 3222f. H. L. H.

(7)

APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3"

"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

USSR/Chemistry - Organophosphorus Compounds

Jul 52

"The Addition of Dialkylphosphorous Acids to Unsaturated Compounds. VI. Addition of Dialkylphosphorous Acids to Ethyl, Esters of Cinnamic and Crotonic Acids," A. N. Pudovik, Chem Inst imeni A. Ye. Arbuzov, Kazan' Affiliate, Acad Sci USSR

"Zhur Obshch Khim" Vol 22, No 7, pp 1143-1147

Dialkylphosphorous acids, in the presence of alcoholates of alkali metals, readily add to esters of cinnamic and crotonic acids with the

229T37

formation of esters of β-dialkylphosphono-β-phenylpropionic and β-dialkylphosphonobutyric acids, resp. The sapon of the latter resulted in the formation of β-phosphono-β-phenylpropionic and β-phosphonobutyric acids.

229T37

229T37

PUDOVIK, A. N.

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"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

PUDOVIK, A. N.

Phosphorous Acids

Addition of dialkylphosphorous acids to unsaturated compounds. Part 7. Addition of dialkylphosphorous acids to -unsaturated ketones of the aliphatic series. Zhur. ob. khim. 22 No. 3, 1952.

9. Monthly List of Russian Accessions. Library of Congress, November 1952, Uncl.

APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3"

"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

PUDOVIK, A. N.

Chem (2)

Chemical Abst.
Vol. 48 No. 5
Mar. 10, 1954
Organic Chemistry

Allyl rearrangements. XVI. Formation of acetates and alcohols from isomeric butoxychloropentenes. A. N. Pudovik and V. I. Nikitina. *J. Gen. Chem. U.S.S.R.* 22, 1421-3(1952)(Engl. translation).—See *C.A.* 47, 4842b.
H. L. H.

APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3"

"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

USSR/Chemistry - Organomagnesium Compounds Sep 52

"Allyl Rearrangements. XVII. The Reactions Between Organomagnesium Compounds and Isomeric Methoxychlorpentenes," A. N. Pudovik, V. I. Nikitina, Lab of Org Chem, Kazan' State U imeni V. I. Ul'yanov-Lenin

"Zhur Obshch Khim," Vol 22, No 9, pp 1553-1559

The reactions between isomeric methoxychloropentenes and benzyl magnesium chloride (I), ethyl Mg bromide (II), and butyl Mg bromide (III) were studied. When (I) reacts with isomeric

232T22

methoxychloropentenes, mixts of isomeric methoxybenzylpentenes of identical compn are formed. This reaction proceeds by an ionic mechanism. As a result of the action of (II) and (III) on isomeric methoxychloropentenes, mixts of the corresponding 1-methoxy-5-alkylpentene-3 and 1-methoxy-6-beta-methoxyalkyloctadiene-3,7 compds are formed. The latter product also forms as a result of the direct action of magnesium on isomeric methoxychloropentenes.

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PUDOVIK, A. N.

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"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

USSR/Chemistry - Organic Sulfur Compounds Sep 52

"Allyl Rearrangements. XVIII. The Reactions Between Methoxychloropentenes and Salts of Xanthogenic Acid," A. N. Pudovik, S. V. Zotikova, Kazan' State U imeni V. I. Ul'yanov-Lenin

"Zhur Obshch Khim" Vol 22, No 9, pp 1559-1562

Reactions between isomeric methoxychloropentenams and sodium ethyl- and butylxanthogenates were studied. 1-methoxy-5-chloropentene-3 reacts with sodium ethyl- and butylxanthogenate in a normal manner under formation of

232T23

methoxypentenyl esters of ethyl- and butylxanthogenic acids, resp. As a result of the action of ethyl- and butylxanthogenates of sodium on 1-methoxy-3-chloropentene-4, dimethoxypentenyl thiophene forms. The reaction proceeds under a complete allyl rearrangement. A mechanism for the formation of dimethoxypentenyl thiophene is proposed.

232T23

PUDOVIK, A. N.

APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3"

"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

PUDOVIK, A. N.

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

(3)

Allylic rearrangements. XVII. Reaction between organomagnesium compounds and isomeric methoxychloropentenes. A. N. Pudovik and V. I. Nikitina. *J. Gen. Chem.* (U.S.S.R.) 22, 1595-9(1952)(Engl. translation).—See C.A. 47, 8032*a*. XVIII. Reactions of isomeric methoxychloropentenes with salts of xanthic acids. A. N. Pudovik and S. V. Zotikova. *Ibid.* 1601-3.—See C.A. 47, 8033*e*. H. L. H.

APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3"

"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

USSR/Chemistry - Organophosphorus Compounds Nov 52

"The Addition of Dialkylphosphorous Acids to Unsaturated Compounds: VIII. The Addition of Dialkylphosphorous Acids to Ethylidene- and Benzylidene-Malonic and Acetoacetic Esters," A. N. Pudovik, Chem Inst im Acad A. Ye. Arbuzov, Kazan Affiliate Acad Sci USSR.

"Zhur Obshch Khim" Vol 22, No 11, pp 2047-2052

It was demonstrated that dialkylphosphorous acids, in the presence of alcoholates of alkali metals, are quite readily added to ethylidene-

238T39

and benzylidene-malonic and -acetoacetic esters, forming (with yields of 65% to 80%) the corresponding α-(dialkylphosphono) -ethylmalonate, α -(dialkylphosphono) -ethylacetoacetate, phenyldialkylphosphono-methylmalonate, and phenyldialkylphosphono-methylacetoacetate.

238T39

APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3"

"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

USSR/Chemistry - Organophosphorus Compounds Nov 52

238T40

"The Addition of Dialkylphosphorous Acids to Unsaturated Compounds: IX. The Action of Sodium Diethylphosphite on Allyl Bromide and Isomeric Chlorobutenes," A. N. Pudovik and M. M. Frolova, Chem Inst im Acad A. Ye. Arbuzov, Kazan' Affiliate Acad Sci USSR

"Zhur Obshch Khim" Vol 22, No 11, pp 2052-2058

The reactions between allyl bromide or isomeric chlorobutenes and sodium diethylphosphite (I) were studied. It was shown that the presence of

238T40

an excess of diethylphosphorous acid and benzene materially affected the course of these reactions, and actually arrested the reaction at the stage of substitution, with the formation of allylphosphonic ester (II) and 1-dialkylphosphonobutene-2 (III). In the absence of free diethylphosphorous acid in the reaction medium, and in the presence only of the min quantity of benzene necessary for dissolving I, the addn of I took place at the double bond of II with the formation of di-dialkylphosphonic derivatives. The reaction between I and 3-chloro-butene-2 proceeded with full allyl regrouping. By direct expts in the presence of sodium ethylate, the addn of diethylphosphorous acid to II and III was demonstrated.

238T40

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"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

PUDOVIK, A. N.

Chem

Addition of dialkylphosphorous acids to unsaturated compounds. VIII. Addition of dialkylphosphorous acids to ethylidene- and benzylidene-malonic and acetoacetic esters. A. N. Pudovik. *J. Gen. Chem. U.S.S.R.* 22, 2103-6(1952) (Eng. translation). IX. Action of diethyl sodium phosphite with allyl bromide and isomeric chlorobutenes. A. N. Pudovik and M. M. Frolova. *Ibid.* 2107-11.—See *C.A.* 47, 9910*f*. H. L. H.

APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3"

"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

PUDOVIK, A.N.

Chem abs V48
1-25-54
Organic Chemistry

(3) Chem

Addition of phosphonoacetic ester and its homologs to unsaturated electrophilic reagents. A. N. Pudovik and N. M. Lebedeva (Kazan State Univ.). *Zhur. Obshchei Khim.* 22, 2128-32(1952).—$(EtO)_2P(O)CH_2CO_2Et$ (I) is capable of adding to strongly electrophilic unsatd. compds. in the presence of EtONa (*C.A.* 45, 2856*d*). Homologs of the phosphonoacetate react similarly. Thus, 7.5 g. I and 3.45 g. CH_2:CHCN (II) in 20 ml. abs. EtOH were treated dropwise with satd. soln. of EtONa in abs. EtOH with cooling (the reaction is very exothermic); after the completion of the reaction the mixt. yielded a little unreacted I, 2.5 g. $(EtO)_2P(O)CH(CH_2CH_2CN)CO_2Et$ (III), b_4 185-6°, n_D^{20} 1.4470, d_{20} 1.1065, and 3 g. $(EtO)_2P(O)C(CH_2CH_2CN)_2CO_2Et$ (IV), b_5 230-1°, n_D^{20} 1.4580, d_{20} 1.1307. Addn. of 10 drops EtONa-EtOH to 10.4 g. I and 4 g. CH_2:$CHCO_2Me$, under similar conditions, gave 5.85 g. $(EtO)_2P(O)CH(CH_2CH_2CO_2Me)CO_2Et$, b_4 200°, n_D^{20} 1.4510, d_{20} 1.1474. Addn. of EtONa-EtOH to 13.12 g. I and 6.7 g. CH_2:$CMeCO_2Me$ while heating on a steam bath resulted in 7.69 g. $(EtO)_2P(O)CH(CH_2CHMeCO_2Me)CO_2Et$, b_{12} 199-201°, n_D^{20} 1.4450, d_{20} 1.1172. When 4 ml. EtONa-EtOH was gradually added to 5 g. PhCH:$CHCO_2Et$ and 7 g. I no heat evolution was evident; the mixt. was kept 5 hrs. on a steam bath and gave on distn. some 3 g. $(EtO)_2P(O)CH(CHPhCH_2CO_2Et)CO_2Et$, b_4 190-2°, n_D^{20} 1.4740, d_{20} 1.1272. Similarly 8.2 g. I and [illegible] g. di-Me maleate treated with 2 ml. EtONa-EtOH then heated 2 hrs. on a steam bath gave 1.7 g. $(EtO)_2P(O)CH(CH_2CH(CO_2Me)CH_2CO_2Me)CO_2Et$, b_3 173-5°, n_D^{20} 1.4[illegible], d_{20} 1.1730. Addn. of EtONa-EtOH to 6.6 g. PhCH:CHAc and 10 g. I gave a vigorous reaction and after brief heating on steam bath yielded 8 g. $(EtO)_2P(O)CH(CHPhCH_2Ac)CO_2Et$, b_6 207-10°, n_D^{20} 1.5019, d_{20} 1.1356. Heating 10 g. I, 5 g. furfuralacetone and 2 ml. satd. EtONa-EtOH in sealed tube 10 hrs. at 130-5° (no reaction otherwise) gave 1.5 g. *Et α-diethylphosphono-β-(2-furyl)-δ-oxohexanate*, b_2 138-9°, n_D^{20} 1.4490, d_{20} 1.109, which resinified on standing. Stirring 35 g. I with 3.4 g. Na in 150 ml. Et_2O 1.5 hrs., addn. of 24 g. BuBr and refluxing 2.5 hrs., followed by coagulation of pptd. NaBr by heating with some activated C, and filtration resulted in isolation of 21.2 g. $(EtO)_2P(O)CHBuCO_2Et$ (III), b_3 154-6°, n_D^{20} 1.4360, d_{20} 1.0406. This (6 g.) and 1.5 g. II treated with ice cooling with 4 drops EtONa-EtOH; after 0.5 hr. at room temp. the mixt. was distd. yielding 5 g. $(EtO)_2P(O)CBu(CH_2CH_2CN)CO_2Et$, b_2 186-7°, n_D^{20} 1.4500, d_{20} 1.0641. From 5 g. $(EtO)_2P(O)CHMeCO_2Et$ and 3 g. II, under similar conditions, was obtained 3.6 g. $(EtO)_2P(O)CMe(CH_2CH_2CN)CO_2Et$, b_5 176-8°, n_D^{20} 1.4430, d_{20} 1.0960 (the starting material, b_3 126°). Similar reaction of 7 g. III with 2 g. CH_2:$CHCO_2Me$ gave 7.2 g. $(EtO)_2P(O)CBu(CH_2CH_2CO_2Me)CO_2Et$, b_3 179-81°, n_D^{20} 1.4510, d_{20} 1.1002; reaction with 4 g. III and 1.5 g. CH_2:$CMeCO_2Me$ gave 3.2 g. $(EtO)_2P(O)CBu(CH_2CMeHCO_2Me)CO_2Et$, b_2 169-70°, n_D^{20} 1.4490, d_{20} 1.0818.

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PUDOVIK, A. N.

3

(3) Chem

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

Addition of phosphonacetic ester and its homologs to unsaturated electrophilic reagents. A. N. Pudovik and N. M. Lebedeva. *J. Gen. Chem. U.S.S.R.* 22, 2183-6(1952) (Engl. translation).—See *C.A.* 48, 5644*h*. H. L. H.

APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3"

"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

1. PUDOVIK, A. N., LEBEDEVA, N. M.

2. USSR (600)

4. Acetic Acid

7. Addition of phosphonoacetic ester and its homologs to unsaturated electrophilic reagents. Zhur. ob. khim. 22, no. 12, 1952.

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

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"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

USSR/Chemistry - Organophosphorus Compounds, 21 Apr 52

"Addition of Dialkylphosphorous Acids to Amines. New Method of Synthesizing Esters of Aminophosphonic Acids," A. N. Pudovik, Chem Inst imeni A. Ye. Arbuzov, Kazan Affiliate, Acad Sci USSR

"Dok Ak Nauk SSSR" Vol LXXXIII, No 6, pp 865-868

Addn of dialkylphosphorous acids to benzalaniline and its derivs was carried out according to the method described in "Iz. Kazansk Filiala Ak Nauk SSSR" No 1, p 53, 1950, and "Dok Ak Nauk SSSR" Vol LXXX, No 1, 1951, for the addn of dialkylphosphorous acids to unsatd electrophilic compds. The reaction proceeds

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easily, even at room temp, supplying esters of phenylamino phenylmethyl phosphonic acids in a high yield. Addn products of dialkylphosphorous acids to o-, m-, and p-benzaltoluidines, benzalanisidine benzal-β-naphthylamine and π-dimethylaminobenzalaniline were prepd analogously and were also obtained in fairly high yields.

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PUDOVIK, A. N.

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USSR/Chemistry - Organophosphorus Compounds 21 May 52

"The Problem Concerning the Mechanism of the Arbuzov Regrouping," A. N. Pudovik, Chem Inst imeni A. Ye. Arbuzov. Kazan' Affiliate, Acad Sci USSR

"Dok Ak Nauk SSSR" Vol LXXXIV, No 3, pp 519-522

A. Ye. Arbuzov's work on the isomerization of phosphorous acid esters after their reaction with alkyl halides led to the synthesis of a whole series of phosphonic esters, e.g., esters of phosphonocarboxylic acids, cyclic esters of phosphonic acid, esters of trichloromethylphosphonic acid, esters of alkoxyalkylphosphonic acids, ketophosphonic esters

(1)

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and others. Arbuzov also introduced the reaction of phosphorous acid esters with hydrogen halides, leading to dialkylphosphorous acids. This work seeks to clarify the mechanism of the Arbuzov isomerization. The addn of a R Hal or H Hal mol to a phosphorous acid ester, as indicated by the ionic formula $(RO)_3P^+R'$ Hal^-, is followed by a reaction which can proceed through a monomol, bimol, or intramol mechanism, depending on the structure of the radical R and the conditions of the expt. Exptl data obtained in this instance show that secondary allyl radicals in $(RO)_3P^+R'$, a pos ion formed by the reaction of allyl alcs with PCl_3, react with Cl through the monomol mechanism, whereas primary allyl radicals in that ion react through the bimol mechanism. An intramol

(2)

225T6

PUDOVIK, A. N.

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"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

PUDOVIK, A.N.

RT-114 (New method of synthesis of esters of phosphonocarboxylic acids and their derivatives). Novyi metod sinteza efirov fosfonkarbonovykh kislot i ikh proizvodnykh. Doklady Akademii Nauk SSSR, 85(2): 349-352, 1952.

TRANSLATION AVAILABLE - W-27967, 23 Sep 53

APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3"

"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

PUDOVIK, A. N.

A. N. PUDOVIK and N. P. DENISOVA (Kazan State University)

"Synthesis and Properties of Vinylphosphoric Esters, III, Synthesis of Ethoxy and Butoxyvinylphosphonic Esters" Sbornik Statei po Obshchei Khim 1, 388-92 (1953)

This article is of possible significance for the reason that several new compounds are described, although it is impossible to determine by a perusal of the article whether any of the new compounds described therein are unusually toxic, because they represent a comparitively new variation of structure.

[redacted] B 76820, 7 July 1954 - Digest available

APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3"

"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

PUDOVIK, A. N. and PLAKATINA, N. I.

"Addition of Dialkyl Phosphorous Acids to Unsaturated Compounds. X. Addition of Dialkylphosphorous Acids to Unsaturated Nitriles," Sbornik Statey po Obshchey Khim No 2, pp 831-6, 1953

Summary in B-76295

APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3"

"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

PUDOVIK, A.N.

USSR.

Synthesis and properties of vinylphosphinic esters. I. Reaction of phosphonethylation of addition of dialkyl phosphorous acids, ammonia, and amines to the ethyl ester of vinylphosphinic acid. A. N. Pudovik and G. M. Denisova. *J. Gen. Chem. U.S.S.R.* 23, [illegible] (Engl. translation). —See *C.A.* 48, 2572*i*. II. Phosphonethylation reaction, addition of malonic cyanacetic, and acetoacetic ester and their homologs to vinylphosphonic ester. A. N. Pudovik and O. N. Grishina. *Ibid.* 277–81.—See *C.A.* 48, 2573*c*.

H. L. H.

APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3"

"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

FUDOVIK, A. N., GRISHINA, O. N.

Esters

Synthesis and properties of vinylphosphonate. Part 2. Reaction of phosphoethylation. Addition of malonic, cyanoacetic and acetoacetic esters and their homologs to vinylphosphonate. Zhur. Ob. khim. 23 No. 2, 1953.

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

APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3"

"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

Pudovik, A.N.

5

Reaction of addition and condensation of phosphonoacetone and phosphonoacetic ester. A. N. Pudovik and N. M. Lebedeva (A. E. Arbuzov Chem. Inst., Kazan). *Doklady Akad. Nauk S.S.S.R.* 90, 799–802(1953); cf. Fiszer and Michalski, *Roczniki Chem.* 26, 203(1952).—Addn. of $AcCH_2PO(OR)_2$ or $EtO_2CCH_2PO(OR)_2$ to unsatd. ketones, esters and nitriles was performed by addn. of RONa-ROH catalyst, followed by heating for several hrs. on a steam bath. Substitutions at the 2nd-C atom of the olefinic link reduce reactivity so much that mesityl oxide failed to react even after 5 hrs. at 150–200°. On the other hand CH_3:CHCN reacts vigorously. Thus were obtained the following esters: 70% $(EtO)_2P(O)CHAcCH_2CH_2CO_2Me$, b_3 160–2°, n_D^{20} 1.4488, d_{20} 1.1347; 57.4% combined yield of $(EtO)_2P(O)CHAcCH_2CH_2CN$, b_2 157°, 1.4487, 1.1100, and $(EtO)_2P(O)CAc(CH_2CH_2CN)_2$, b_1 204–7°, 1.4563, 1.1125; 47% $(EtO)_2P(O)CH(CO_2Et)CHMeCH_2Ac$, b_3 164–5°, 1.4504, 1.1045; 55% $(EtO)_2P(O)CH(CO_2Et)CHPrCH_2Ac$, b_2 169–71°, 1.4480, 1.0690; 49% $(EtO)_2P(O)CH(CO_2Et)CHPhCH_2COEt$, b_2 202°, 1.5035, 1.1186 (at 40°); 38% $(EtO)_2P(O)CH(CO_2Et)CH(CO_2Et)CH_2CO_2Et$, $b_{1.5}$ 188°, 1.4478, 1.1526; 50% $(EtO)_2P(O)CH(CO_2Et)CH_2CHMeCO_2Bu$, b_2 168–70°, 1.4428, 1.0854. Heating for several hrs. at 160–70° a mixt. of BzH, $EtO_2CCH_2PO(OEt)_2$, and Ac_2O gave 37–40% $PhCH{:}C(CO_2Et)P(O)(OEt)_2$, $b_{2.5}$ 184°, n_D^{20} 1.5179, which hydrolyzed with HCl to the *benzylidenephosphonic acid*, m. 132°. G. M. Kosolapoff

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PUDOVIK, A.N.

3

Synthesis of aminophosphinic and aminothiophosphinic esters. A. N. Pudovik (A. E. Arbuzov Chem. Inst., Kazan). ~~Doklady Akad. Nauk~~ S.S.S.R. 92, 773-6(1953); cf. C.A. 47, 4300g, 10468f.—RPH(O)OR with aromatic imines yields the corresponding amino-substituted phosphinic acids. The reaction is run with RONa as catalyst, as described earlier. In this way were formed the following esters, which are insol. in H_2O, sol. in hot BtOH and Et_2O: 63% *PhCH(NHPh)EtP(O)OEt*, m. 85°; 45.7% *p-Me₂NC₆H₄CH(NHPh)EtP(O)OEt*, m. 123°; *PhCH(NHC₆H₄-Me-m)EtP(O)OEt*, 61%, m. 111.5–12.0°; 82.3% *PhCH(NHPh)EtP(O)OBu*, m. 100°; 73.1% *PhCH(NHC₆H₄-OMe-p)EtP(O)OBu*, m. 107–8°; 52.6% *PhCH(NHPh)PhP(O)OEt*, m. 176°; 71% *PhCH(NHC₆H₄OMe-p)PhP(O)OEt*, m. 157–8°; and 56.8% *PhCH(NHC₆H₄Me-p)PhP(O)OEt*, m. 174–5°. Similar reaction of $(EtO)_2PSH$ and $(BuO)_2PSH$ gave: 43.2% *p-MeOC₆H₄NHCHPhP(S)(OEt)₂*, m. 48°; 60% *PhNHCH(C₆H₄NMe₂-p)P(S)(OEt)₂*, m. 100–100.5°; 62.3% *p-MeC₆H₄NHCHPhP(S)(OEt)₂*, m. 67°; 52.2% *m-MeC₆H₄NHCHPhP(S)(OEt)₂*, m. 77–8°; 50% *m-MeC₆H₄NHCH(C₆H₄Me-m)P(S)(OEt)₂*, m. 84–5°; 54.1%, *C₆H₅NHCHPhP(S)(OEt)₂* (position on C_6H_5 group unstated), m. 136.5°; 78.3% *PhNHCHPhP(S)(OBu)₂*, m. 83°; *p-MeOC₆H₄NHCHPhP(S)(OBu)₂*, m. 45–6°; 81.2% *p-Me₂NC₆H₄CH(NHPh)P(S)(OBu)₂*, m. 80°; *m-MeC₆H₄-NHCH(C₆H₄Me-m)P(S)(OBu)₂*, 73%, m. 57–8°; 61.3% *p-MeC₆H₄NHCH(NHPh)P(S)(OBu)₂*, m. 30°; 71.8% *p-MeC₆H₄NHCHPhP(S)(OBu)₂*, m. 75.5°; 65.6% *m-MeC₆H₄-NHCHPhP(S)(OBu)₂*, m. 47–7.5°; and 83.1% *p-ClC₆H₄CH(NHPh)P(S)(OBu)₂*, m. 67–8°. It was impossible to isolate in solid state the adducts of $(BtO)_2PSH$ with PhN:CHPh and some of its derivs., although the BuO analogs were readily crystd. The products were purified by crystn. from BtOH; compds. in the 1st group gave poor yields largely because of losses in purification.

G. M. Kosolapoff

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PUDOVIK, A.N.; MURATOVA, A.A.

Effect of the nature and structure of solvents on the rate of combination of lithium with naphthalene, acenaphthene and phenanthrene. Uch. zap. Kaz. un. 113 no.8:7-18 '53. (MLRA 10:5)
(Lithium) (Hydrocarbons) (Solvents)

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"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

PUDOVIK, A. N.

USSR/ Chemistry Synthesis

Card : 1/1 Pub. 40 - 10/27

Authors : Pudovik, A. N., and Yarmukhametova, D. Kh.

Title : New method of synthesizing phosphinic and thiophosphinic acid esters. Part 16.- Synthesis of mono-, diphosphon- and thiophosphoncarboxylic acid esters

Periodical : Izv. AN SSSR. Otd. khim. nauk 4, 636 - 645, July - August 1954

Abstract : The synthesis and physico-chemical properties of mono-, diphosphon- and thiophosphoncarboxylid acid esters are described. The physical constants and yields of the synthesized esters, are tabulated. The hitherto unknown thiophosphoncarboxylic acid esters, in pure form, were synthesized by mixing dialkylthiophosphorous acid, carboxylic acid esters and alcohol alcoholates with identical radicals in the alkoxy and carboxy groups. Eight USSR references (1952). Tables.

Institution : Acad. of Sc. USSR, Kazan Branch, The A. E. Arbuzov Chemical Institute

Submitted : April 1, 1953

ABSTRACT IN B-64414, 15 May 1953

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"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

Pudovik, A. N.

AID P - 1112

Subject : USSR/Chemistry

Card 1/1 Pub. 119 - 2/7

Author : Pudovik, A. N. (Kazan')

Title : New method for synthesizing esters of phosphonic and thiophosphonic acids

Periodical : Usp. khim., 23, no. 5, 547-580, 1954

Abstract : A brief review of the existing methods for the synthesis of esters of phosphonic acids is given. A new method which consists in the addition of dialkylphosphorous and dialkylthiophosphorous acids and acid esters of alkyl- and arylphosphinic acids to unsaturated compounds is described. Twenty tables, 95 references (62 Russian: 1905-1953).

Institution : None

Submitted : No date

APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3"

"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

PUDOVIK, A. N.

USSR/Chemistry - Reaction processes

Card 1/1 Pub. 151 - 23/38

Authors : Pudovik, A. N., and Kovyrzine, K. A.

Title : Reaction of alkyl halides and allyl bromide with dibutylthiosodium phosphide

Periodical : Zhur. ob. khim. 24/2, 307-311, Feb 1954

Abstract : The reaction between alkyl halides and dibutylthiosodium phosphide was investigated. The products obtained from above reaction and their properties are described. Displacement and the addition of the dibutylthio phosphide, according to the double bond of allylthiophosphinic ester, was observed during the reaction of dibutylthiosodium phosphide with allyl bromide. The two low- and high-boiling reaction products obtained and their chemical formulas are described. Five USSR references (1949-1953).

Institution : State University, Kazan

Submitted : September 17, 1953

APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3"

"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

PUDOVIK, A. N.

[redacted]

USSR

Action of alkyl halides and allyl bromide on dibutyl sodium thiophosphite. A. N. Pudovik and K. A. Kovyrzina. *J. Gen. Chem. U.S.S.R.* 24, 311-14(1954)(Engl. translation). See *C.A.* 49, 4498e. H. L. H.

APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3"

"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

USSR/Chemistry

Card : 1/1

Authors : Pudovik, A. N., Sabirova, R. D., and Tener, T. A.

Title : New method of synthesizing esters of phosphinic and thiophosphinic acids. Part 17- Addition of esters of ethylphosphinous, dialkylphosphorous and dialkylthiophosphous acids to unsaturated compounds.

Periodical : Zhur. Ob. Khim., 24, Ed. 6, 1026 - 1033, June 1954

Abstract : Experiments showed that esters of phosphinous acids, attach themselves to unsaturated ketones, in the presence of alcoholates of alkali metal. The addition of ethyl and butyl ethers of ethyl phosphinous acid to ethylidine acetone, benzylidene acetone, benzylidenemethyl-ethylketone, mesityl oxide and 3-methylheptene-3-one-5 was proven experimentally. Numerous new keto-phosphinic esters were obtained, through the addition of diethylphosphorous, diethylthiophosphorous and dibutylphosphorous acids to heptene-3-one-2, 1-phenylpentene-1-one-3 and 3-methylheptene-3-one-5. Nine references. Tables.

Institution : State University, Kazan

Submitted : January 7, 1954

APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3"

"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

PUDOVIK, A.N.

3

New method of synthesis of esters of phosphonic and thiophosphonic acid. XVIII. Addition of dialkylthiophosphorus acids to the ylidene derivatives of malonic and acetoacetic esters. A. N. Pudovik and L. I. Sidnikhina. *J. Gen. Chem. U.S.S.R.* [redacted] 1954 (Engl. translation).— See *C.A.* 49, 9496i. B. M. R.

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APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3"

"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

PUDOVIK, A. N.

USSR/ Chemistry Synthesis methods

Card : 1/1 Pub. 151 - 19/35

Authors : Pudovik, A. N., and Sidnikhina, L. I.

Title : New method for the synthesis of phosphinic and thiophosphinic acid esters Part 18.-Addition of dialkylthiophosphorous acids to idene-derivatives of malonic and acetoacetic esters

Periodical : Zhur. Ob. Khim. 24, Ed. 7, 1193 - 1198, July 1954

Abstract : The addition of dialkylthiophosphorous acids to ethylidenemalonic, benzylidenemalonic, isopropylidenemalonic and ethylideneacetoacetic esters, is analyzed. The addition products obtained and their chemical properties are described. Table, showing the chemical formulas, boiling points and yield of the addition products, is included. Nine USSR references.

Institution : The V. I. Ulyanov-Lenin State University, Kazan

Submitted : January 22, 1954

APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3"

"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

Pudovik, A. N.

CH

Synthesis of esters of phosphonic and thiophosphonic acids. XIX. Addition of dialkyl phosphites and esters of phosphonous acid to unsaturated nitriles and to vinylphosphonic ester. A. N. Pudovik and N. G. Poloznova (Kazan State Univ.). ~~Zhur. Obshchei Khim.~~ 25, 778-83; ~~J. Gen. Chem. U.S.S.R.~~ 25, 745-8(1955)(Engl. translation); cf. 48, 2573*e*; 49, 2406*i*.—Addn. of RONa with cooling to an equimolar mixt. of $(RO)_2POH$ or $(RO)_2PSH$ and the desired unsatd. compd., followed by heating 0.5 hr. on a steam bath resulted in the formation of the following esters (yield, b.p., n_D^{20}, d_{20} given): $(MeO)_2PSCH_2CH_2CN$, 59%, b_{14} 133-9°, 1.4860, 1.1555; $(EtO)_2PSCH_2CH_2CN$, 74%, b_7 134-5°, 1.4772, 1.1095; $(BuO)_2PSCH_2CH_2CN$, 68%, b_5 167°, 1.4741, 1.0366; $(iso\text{-}BuO)_2PSCH_2CH_2CN$, 67%, b_{14} 174°, 1.4721, 1.0245; $(EtO)_2PSCH_2CHMeCN$, 56%, b_{10} 145-6°, 1.4730, 1.0806; $(iso\text{-}BuO)_2PSCH_2CHMeCN$, 59%, b_{12} 189-9.5°, 1.4678, 1.0075; $(EtO)_2PSCHMeCH_2CN$, 75%, b_3 121-5°, 1.4750, 1.0840; $(BuO)_2PSCHMeCH_2CN$, 62%, b_{14} 176-7°, 1.4693, 1.0208; $(iso\text{-}BuO)_2PSCHMeCH_2CN$, 75%, b_{14} 178-8.5°, 1.4668, 1.0134; $(EtO)_2PSCH_2CH_2P(O)(OEt)_2$, 66%, b_{11} 163°, 1.4638, 1.1356; $(BuO)_2PSCH_2CH_2P(O)(OEt)_2$, 67%, b_3 209°, 1.4510, 1.0573. Similar reaction using $RP(O)(H)OEt$ gave: $EtP(OEt)(O)CH_2CH_2CN$, 67%, b_{12} 173-1.5°, 1.4527, 1.0794; $EtP(OBu)(O)CH_2CH_2CN$, 50%, b_{13} 192°, 1.4521, 1.0291; $PhP(OEt)(O)CH_2CH_2CN$, 48%, b_1 162-3°, 1.5245, 1.1478; $EtP(OEt)(O)CH_2CHMeCN$ 46%, b_{12} 183-5°, 1.4470, 1.0048; $EtP(OEt)(O)CHMeCH_2CN$, 68%, b_7 158-9.5°, 1.4550, 1.0597; $EtP(OEt)(O)CH_2CH_2P(O)(OEt)_2$, 59%, b_4 195°, 1.4510, 1.1235.

G. M. Kosolapoff

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"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

PUDOVIK, A.N.; POLOZNOVA, N.G.

New method for the synthesis of esters of phosphinic and thiophosphinic acids. Part 19. Addition of dialkylthiophosphorous acids and phosphinous acid esters to unsaturated nitriles and to vinylphosphinic acid ester. Zhur.ob.khim. 25 no.4:778-783 Ap '55. (MLRA 8:7)

1. Kazanskiy Gosudarstvennyy universitet. (Phosphorus acids) (Nitriles)

APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3"

"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

PUDOVIK, A. N.

New method of synthesis of esters of phosphonic and thiophosphonic acids. XX. Addition of incomplete esters of acids of phosphorus to esters of isocyanic acid. A. N. Pudovik and A. V. Kuznetsova (State Univ., Kazan). Zhur. Obshchei Khim. 25, 1369-72(1955); cf. C.A. 49, 8788i; 50, 2417e.—Equimolar mixts. of RNCO with $(RO)_2POH$, $(RO)_2PSH$, or $(RO)_2PS_2H$ were heated on a steam bath 20-40 min. with or without addn. of dry RONa. The resulting adducts were distd. or crystd. MeNCO reacts slowly without the catalyst, but with RONa the reaction is rapid and energetic; PhNCO is more reactive and reacts with $(MeO)_2PSH$ without catalyst. Good yields and sufficiently pure products were obtained only from the di-Me esters of P acids. The reaction probably occurs by preliminary addn. of the P atom to the C of the NCO group. The following esters are reported (b.p., m.p., n_D^{20}, d_{20}, yield %, given): *MeNHCOP(O)(OMe)₂*, b₂ 135-7°, —, 1.4585, 1.2929, 45%; *MeNHCOP(O)(OEt)₂*, b₁ 142°, —, 1.4525, 1.1800, 60%; *MeNHCOP(O)(OBu)₂*, b₁ 182-3°, —, 1.4448, 1.0591, 40%; *MeNHCOP(O)(OCH₂CHMe₂)₂*, b₁ 162°, m. 39-40°, —, —, 58%; *MeNHCOP(S)(OMe)₂*, b₁ 144-5°, —, 1.5118, 1.2873, 54%; *MeNHCOP(S)(OEt)₂*, b₁ 139°, m. 36-7°, —, —, 55%; *MeNHCOP(S)(OBu)₂*, b₁ 172-3°, —, 1.4838, 1.0821, 37%; *PhNHCOP(O)(OMe)₂*, —, m. 103°, —, —, 95%; *PhNHCOP(S)(OMe)₂*, —, m. 107-8°, —, —, 67%; *PhNHCOSP(S)(OMe)₂*, —, m. 93°, —, —, 66%; *PhNHCOSP(S)(OEt)₂*, —, m. 56°, —, —, 82%. Reaction of 12 g. $(MeO)_3P$ with 7 g. PhNHCOCl gave MeCl and 10 g. $PhNHCOP(O)(OMe)_2$, m. 102-3°, identical with the above described specimen, thus confirming the nature of the reaction. The above compds. showed but a very weak toxicity against the barn weevil. Also in *J. Gen. Chem. U.S.S.R.* 25, 1317-19(1955)(Engl. translation). G. M. Kosolapoff

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"APPROVED FOR RELEASE: 06/15/2000 CIA-RDP86-00513R001343520019-3

Pudovik, A.N.

500

Synthesis of esters of phosphonic and thiophosphonic acids. XXI. Addition of dialkylthiophosphites and dialkyldithiophosphoric acids to anils. A. N. Pudovik and M. K. Sergeeva. *J. Gen. Chem. U.S.S.R.* 25, 1713-18(1955) (Engl. translation).—See *C.A.* 50, 7073*i*. B. M. R.

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