SHOSTAKOVSKIY, M. G.

USSR/Chemistry - Vinyl Alkyl Esters Sep 48
Chemistry - Hydrolysis, of Vinyl Alkyl Esters

"Hydrolysis of Vinyl Alkyl Esters in Aqueous Dioxane Solution," Ye. N. Prilezhayeva, E. S. Shapiro, M. F. Shostakovskiy, Inst Org Chem, Acad Sci USSR, 11 pp

"Zhur Obshch Khimii" Vol XVIII, No 9

Tabulated data shows that rate of hydrolysis of vinyl butyl and vinyl ethyl esters and of dibutylacetal by hydrochloric acid decreases with increased content of dioxane in water used a as solvent. Discusses mechanism of this reaction. Submitted 21 Jun 47.

PA 30/49T10

SHOSTAKOVSKII, M. F.

E. N. Prilezhaeva, E. S. Shapiro, M. F. Shostakovskii, Hydrolysis of vinyl-alkyl ethers in water-dioxane solutions. p. 1663

The hydrolysis rate of hydrochloric acid in water-dioxane solutions was measured: Vinyl-butyl ether, vinyl-ethyl ether and di-butyl-acetal were found. It is shown that the rate of hydrolysis drops from water to water-dioxane solutions. An hypothesis was examined which explains the mechanism of hydrolysis of vinyl ethers and a reaction scheme is given which takes into account the interaction of the hydronium ion with ether-oxygen as well as with the β-carbon atom.

Institute of Organic Chemistry
Acad. of Sci. USSR
June 21, 1947

SO: Journal of General Chemistry (USSR) 28, (80) No. 9 (1948)

SHOSTAKOVSKII, M. F.

N.A. Gershtein and M.F. Shostakovskii, To the transformations of simple vinyl ethers. III. Interaction of simple vinyl ethers and organic acids. p. 1989.

The reaction of simple vinyl ethers and organic acids in the absence of a catalyst was studied. It is shown that the organic acids of the aliphatic series attach themselves to the simple vinyl ethers at room temperature but to complete the reaction a longer time is needed. A new method of synthesis of alkoxy-derivatives of complex ethers (acylales) with a yield of 90 percent and more is established.

Inst. of Organic Chemistry
Academy of Sciences, USSR
Lab of Vinyl Compounds
December 1, 1947

SO: Journal of General Chemistry (USSR) 28, (80) No. 11, 1948

SHOSTAKOVSKIY, M. F.

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Mechanism of activation of vinyl compounds in polymerization processes. M. ~~F. Shostakovskiĭ~~ (Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Issledovaniya v Oblasti Vysokomolekul. Soedinenii, Doklady 6-oi Konf. Vysokomolekul. Soedineniyam, Akad. Nauk S.S.S.R.* 1949, 34-44.—Vinyl alkyl ethers can polymerize by either radical chain or ionic mechanisms. They are not prone to polymerization under the action of atm. O or peroxides. The action of peroxides consists of activation of vinyl esters for various reactions. Thus, keeping 86 g. $CH_2:CHOAc$ in 400 ml. BuOH with 0.4 g. Bz_2O_2 several days at 40° gave among other substances, 95.5 g. MeCH(OBu)OAc, b_{12} 50–1°, d_{20} 0.9200, n^{20}_D 1.4060. Treatment of $CH_2:CHOAc$ with 30% H_2O_2 at 60° 12–15 hrs. gave 89.1% AcOH. Heating 22.4 g. $CH_2:CHOEt$ and 77.61 g. $CH_2:CHCl$ with 0.5 g. Bz_2O_2 in an ampul for 10 days at 60° gave 23.62% hard polymer, which on reptn. from benzene-EtOH gave 9.8 g copolymer having mol. wt. 4920. G. M. Kosolapoff

SHOSTAKOVSKIY, M. F. FA 43/49T29

USSR/Chemistry - Vinyl Ethers Mar/Apr 49
Chemistry - Chlorohydrins

"Interaction of Vinylalkyl Ethers and Halohydrins," M. F. Shostakovskiy, N. A. Gershteyn, A. K. Gorban', Inst of Org Chem, Acad Sci USSR, 8 pp

"Iz Ak Nauk SSSR, Otdel Khim Nauk" No 2

Studies reaction of vinylethyl and vinylbutyl ethers with ethylene chlorohydrin. Chlorine derivatives of the corresponding acetals were obtained. Submitted 16 Apr 48.

[redacted] 43/49T29

1ST AND 2ND ORDERS

3RD AND 4TH ORDERS

PROCESSES AND PROPERTIES INDEX

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A-II-I

Vinylation of glycerol. M. F. Shostakovsky and E. P. Gracheva (*J. gen. Chem., U.S.S.R.*, 1949, 19, 1250—1256 [*U.S. transl.*, 1243—1249]).—Reaction of glycerol with C_2H_2–10% KOH at 180—190° affords the trivinyl ether, with small amounts of mono- and di-vinyl ether if insufficient C_2H_2 is used. The mono- and di-vinyl ethers are cyclised to cyclic acetals; the mechanism of this reaction is discussed.

Addition of excess of C_2H_2 to pure glycerol, containing 10% KOH, at 180—190°/10 atm., affords *glycerol trivinyl ether* [1 : 2 : 3-*trivinyloxypropane*], $C_9H_{14}O_3$ (I) (90·3%), b.p. 164—166°/760 mm., d_4^{20} 1·0355, n_D^{20} 1·4381. A similar reaction, using only 60% of the theoretical amount of C_2H_2, affords a mixture of I with small amounts of *glycerol* 1 : 3-*divinyl ether* [1 : 3-*divinyloxypropan*-2-*ol*], $C_7H_{12}O_3$ (II), b.p. 83—84°/7 mm., d_4^{20} 1·0521, n_D^{20} 1·4430, and *glycerol* 1-*vinyl ether* [1-*vinyloxypropane*-2 : 3-*diol*], $C_5H_{10}O_3$ (III), b.p. 128—130°/5 mm., d_4^{20} 1·1253, n_D^{20} 1·4521. Reduction of II or III with H_2–Raney Ni in EtOH gives, respectively, OEt·CH_2·CH(OH)·CH_2·OEt, b.p. 191—192°, d_4^{20} 0·9221, or OEt·CH_2·CH(OH)·CH_2·OH, b.p. 230—236°, n_D^{20} 1·4282. Treatment of III or II with a trace of HCl at room temp. affords the cyclic 1 : 2-acetals, b.p. 97—99°/9 mm., d_4^{20} 1·1304, n_D^{20} 1·4441, or b.p. 75—76°/9 mm., d_4^{20} 1·0780, n_D^{20} 1·4397, respectively.

M. DAVIS.

COMMON ELEMENTS

MATERIALS INDEX

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

PA2/50T78

USSR/Chemistry - Glycerin Jul 49
Vinylation, With Acetylene

"Vinylating Glycerin," M. F. Shostakovskiy, Ye. P. Gracheva, Lab of Vinyl Compounds, Inst of Org Chem, Acad Sci USSR, 7 pp

"Zhur Obshch Khim" Vol XIX, No 7 - p.1250

Exhaustive vinylation at 180-190° C with an excess of acetylene and 10% KOH results in 90% of theoretical yield of trivinylglycerol ether. With a deficiency of acetylene, both complete ether and incomplete ethers are formed. In an alkali medium, mono- and 1,3-divinyl ether of glycerin are stable, but during distillation of products of vinylation they cyclize to form corresponding cyclic acetals. Isomerization of incomplete vinyl ethers of glycerin is catalyzed by a hydrogen ion. Cyclization of these latter ethers to form cyclic acetals is explained by formation of a hydrogen bond between oxygen of original vinyl ether and hydrogen of mineral acid. In absence of latter, an intermolecular hydrogen bond is established. Submitted 28 Mar 48.

2/50T48

C 7

13

Comparative characteristic properties of α-chloroalkyl alkyl ethers. M. F. Shostakovskiĭ and A. V. Bogdanova (Acad. Sci. U.S.S.R., Moscow). *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* **1950**, 321-6. Satn. of 89 g. BuOH with HCl at 1-3°, addn. of 51 g. polyoxymethylene and 20 g. Na_2SO_4, and continued passage of HCl gave 60% *$BuOCH_2Cl$*, b_{14} 55-6°, n_D^{20} 1.4208, d_4^{20} 0.9885; the product, like other $ROCH_2Cl$ analogs, can be stored indefinitely and is hydrolyzed, yielding CH_2O (detd. by $NaHSO_3$ method), only in acid or basic solns.; it can be titrated with NaOH to give the Cl content and $AgNO_3$ titration also can be used; complexes with tertiary amines are stable in contrast to those of MeCHClOR. Heating on a water bath 10 hrs. with BuOH readily yields $(BuO)_2CH_2$. Addn. of 17.5 g. $ClCH_2OBu$ at 5° to 17.5 g. $Na_2S.9H_2O$ in 20 ml. Et_2O and stirring 2 hrs. gave a little H_2S and 7 g. NaCl, while distn. of the soln. gave 8.5 g. material, b. 90-178°, which gave an aldehyde test, and 9 g. *$(BuOCH_2)_2S$*, b_{12} 98-9°, n_D^{20} 1.4410, d_4^{20} 0.8853, which gives an insol. ppt. with $HgCl_2$. Other products formed included *$(BuO)_2CH_2$*, b_{12} 83-4°, n_D^{20} 1.4060, d_4^{20} 0.8393, *trithioformaldehyde*, m. 210-20°, and a product, b_4 157-8°, n_D^{20} 1.4530, d_4^{20} 0.9871, which was not identified. Heating $BuOCH_2Cl$ to 200-10° gave, from 33.5 g. ether, 20 g. BuCl and paraformaldehyde, which coated the app.

G. M. Kosolapoff

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Synthesis and transformations of 2-chlorovinyl ethers. I Synthesis and properties of 2-chlorovinyl alkyl ethers M. F. Shostakovskiĭ and E. P. Sidel'kovskaya. *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* **1950**, 394-401. Heating 100 g. $ClCH_2CHClOBu$ and 130 g. Et_2NPh 35 hrs. at 70-80°, filtration, and extn. with Et_2O gave 60% *2-chlorovinyl Bu ether*, b_{14} 48-50°, d_4^{20} 0.9883, n_D^{20} 1.4428, this heated 15 hrs. with 10% H_2SO_4 gave a small amt. of an aldehyde, BuOH, and *$ClCH_2CH(OBu)_2$*, b_{11} 174°, n_D^{20} 1.4310; the use of 18% H_2SO_4 (2 hrs. at 85-90°) permitted isolation of some *$ClCH_2CHO$* (*semicarbazone*, m. 130-1°) hydrolysis at room temp. is slow with 15% H_2SO_4 (26-32% in 3 hrs.). A similar reaction yielded 74% $(MeO)_2CHCH_2Cl$, b_{760} 133-4°, n_D^{20} 1.4180, d_4^{20} 1.0980, from $ClCH_2CHClOMe$. Addn. of a drop of HCl to the *Et analog* in EtOH readily gave 100% *$ClCH_2CH(OEt)_2$*, b. 150-8°, n_D^{20} 1.4170, d_4^{20} 1.0180; the *$EtOCH{:}CHCl$*, obtained in 35% yield from the *di-Cl deriv.*, as above, b_{60} 47.5-8.0°, d_4^{20} 1.0380, n_D^{20} 1.4385 [some 15% *$(EtO)_2CHCH_2Cl$* was also formed]. *iso-$PrOCH{:}CHCl$*, b_{60} 44-5.7°, d_4^{20} 1.0240, n_D^{20} 1.4390, was obtained similarly in 25% yield, along with 20% *(iso-$PrO)_2CHCH_2Cl$*, b_{11} 80-3°. The 2-chlorovinyl ethers polymerize with $SnCl_4$ or $FeCl_3$ catalysts, but not with Bz_2O_2. The iso-Pr member is completely hydrolyzed to $ClCH_2CHO$ by 18% H_2SO_4 in 0.5 hr. at 60-5°. G. M. Kosolapoff

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Theoretical bases of chemistry of vinyl ethers. I. Oxonium properties of vinyl alkyl ethers. M. F. Shostakovskiĭ (Acad. Sci. U.S.S.R., Moscow). *Zhur. Obshchei Khim.* (J. Gen. Chem.) 20, 608-19(1950).—The chem. properties of vinyl alkyl ethers are reviewed and are explained by conjugation of a double bond and the O atom, which acquires oxonium character in the various reactions. The 1-haloethyl alkyl ethers also exhibit tautomerism involving a CH_2:CHO(HX)R structure and their reactions involve the mesomeric ion, MeCH $\dot{O}$R ⟷ Me$\dot{C}$H–OR. Vinyl ethers are polymerized by mineral acids in contrast to CH_2:CHOAc, CH_2:CHCl, styrene, and acrylates, all of which polymerize with peroxides, heat, light, and atm. O only, and not with acids. Satn. of 37.5 g. MeOCH:CH_2 with HBr yielded 85% *MeCHBrOMe*, b_{100} 56.5-7.0°, n^{20}_D 1.4480, d^{20}_4 1.4253. Bromination of MeOCH:CH_2 at −3° to −10° gave 99.7% *CH_2BrCHBrOMe* (crude), 83.3% pure, b_{18} 56°, d^{20}_4 1.9701, n^{20}_D 1.5300, a strong lacrimator, b. 160° with much decompn., can be indefinitely stored in a closed flask. PhOH (48 g.) and 56.5 g. BuOCH:CH_2 treated with 0.05 g. 33% HCl (spontaneous reaction) and allowed to stand 1 day gave 80 g. *MeCH(OBu)OPh*, b_9 107.0-7.5°, d^{20}_{20} 0.9605, d^{20}_4 0.9588, n^{20}_D 1.4830, also obtained in 59.1-g. yield on heating 60 g. PhOCH:CH_2 and 40 g. BuOH 10 hrs. to 170-80° in an autoclave; some MeCH$(OBu)_2$, PhOH, and 9 g. *MeCH$(OPh)_2$*, b_{12} 148.5-9.5°, d^{20}_4 1.087, n^{20}_D 1.5568, are formed concurrently. The repetition of the former synthesis with 2-$C_{10}H_7OH$ gave some unreacted BuOCH:CH_2 and 90.3% *2-$C_{10}H_7$OCH(OBu)Me*, b_{11} 187.2-7.4°, d^{20}_{20} 1.0513, d^{20}_4 1.0521, n^{20}_D 1.5548. Distn. of MeCH(OBu)OPh at atm. pressure gave BuOCH:CH_2, PhOH, and MeCH$(OBu)_2$, as well as BuOH. Heating 95 g. EtOCH:CH_2 and 124 g. PhOH 7 hrs. to 125-30° gave 180 g *MeCH(OEt)OPh*, b_{11} 91-2°, $n^{21.5}_D$ 1.5050, $d^{21.5}_4$ 0.99; distn. of this at atm. pressure gave EtOCH:CH_2, EtOH, PhOH, and some *MeCH$(OPh)_2$*, b_{10} 128-30°, n^{20}_D 1.5500, d^{20}_4 1.0857. In 2-3 months in a sealed vessel 50 g. BuOCH:CH_2 and 2 g. MeCHClOBu yield a polymer with av. mol. wt. 1200 (from Me_2CO-EtOH); the same mixt. polymerizes to this extent in several hrs. at 100°, while 3-4 days' exposure to sunlight gives complete polymerization. Exposure of 19.8 g. MeCHBrOPh, 10 g. BuOCH:CH_2, and 20 g. dioxane to sunlight for 3 days gave on distn., after removal of solids, 27.9 g. liquid, b. 93-101°, composed of BuBr, H_2O, and dioxane, thus indicating the halogenated ether is the activator in the polymerization process.

G. M. Kosolapoff

CH

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Action of inorganic bases on 1,2-dichloroethyl alkyl ethers. M. F. Shostakovskii and F. P. Sidel'kovskaya (Acad. Sci. U.S.S.R., Moscow). *Zhur. Obshchei Khim.* (J. Gen. Chem.) 20, 620-6(1950).—The reaction of alk. reagents with $CH_2ClCHClOR$ proceeds by cleavage of H and Cl ions, followed by decompn. of the unstable residue, yielding an alc., which reacts with the initial ether, forming chloroacetal. $BuOCHClCH_2Cl$, b_7 51-2°, n_D^{20} 1.4475, d_4^{20} 1.1020 (20 g.), treated with 9 g. KOH and kept 16 hrs. at 70-80° gives 1 g. unreacted ether and 10 g. $(BuO)_2CHCH_2Cl$ (I), b_{11} 113-14°, d_4^{20} 0.9820, n_D^{20} 1.4320; at 30° the reaction is the same, but its progress is slower; in BuOH, the reaction yields 53% I and BuOH; in heptyl alc. it gives 39% $ClCH_2CH(OBu)OC_7H_{15}$, b_7 157-60°, b_4 159°, d_4^{20} 0.9837, n_D^{20} 1.4387, some crude I, and 11% $ClCH_2CH(OC_7H_{15})_2$, b_7 187-90°, b_7 188-8.5° (pure), n_D^{20} 1.4420, d_4^{20} 0.9247. Reaction with CaO after 15 hrs. at 70-5° gives 51% I and 20% unreacted ether, while dry K_2CO_3 gives 65% I and 21.6% unreacted ether in 20 hrs. at 70-80°. Passage of dry NH_3 into the dichloro ether at 50° (spontaneous) gives 17% unreacted ether and 33% I. The reaction with Na is sluggish at room temp., while heating leads to violent interaction; in C_6H_6 for 6 hrs. at 70-80° it gives 21% I and 25% unreacted ether.

G. M. K.

CA

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Synthesis and transformations of β-chlorovinyl alkyl ethers. II. Reaction of β-chlorovinyl alkyl ethers with potassium hydroxide and sodium. M. F. Shostakovskii and F. P. Sidel'kovskaya. *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* **1950**, 641-6; cf. C. A. **45**, 2851i.—Rapid addn. of 10 g. powd. KOH to 18 g. CHCl:CHOEt and subsequent distn. gave 57% KCl, 6 g. unreacted ether, and 16% *HC:COEt*, b. 50-2°, d_4^{20} 0.800, n_D^{20} 1.3726, giving a yellow ppt. with NH_4OH-CuCl. The Bu analog (12.7 g.) similarly gave 6 g. unreacted ether and 8.1% *HC:COBu*, b. 106-8°, n_D^{20} 1.4020, d_4^{20} 0.8280, also giving a yellow Cu deriv. Neither ether could be analyzed for C and H because of their explosive combustion. Addn. of 13 g. CHCl:CHOBu to 1 g. Na dust in 25 ml. dry Et_2O (spontaneous reaction) and refluxing 1.5 hrs. gave 1 g. tar, some BuONa, NaCl, a trace of C_2H_2, 1.6% HC:COBu, and 60% CH_2:CHOBu. No Wurtz-type products were found. The vinyl ether may arise by hydrogenation of the acetylenic analog or by halogen displacement with H from the starting material.

G. M. Kosolapoff

CA

Syntheses and reactions of α-haloethyl alkyl ethers. II. 1-Bromoethyl alkyl ethers. M. F. Shostakovskii and A. V. Bogdanova (Acad. Sci. U.S.S.R., Moscow). *Zhur. Obshchei Khim.* (J. Gen. Chem.) **20**, 1315–25(1950); cf. *C.A.* **42**, 4519*f*. The ethers MeCHBrOR are more reactive than the Cl analogs, apparently because of a hyperconjugative effect in the Me group and consequent loosening of the Br link to the point of almost complete ionization. The elimination of HBr by means of inorg. or org. bases, in an attempt to prep. the corresponding vinyl derivs., was shown to be impossible. These ethers with aq. alkali (NaOH) yield AcH and ROH at a rate comparable to that of neutralization, while PhNEt$_2$ gave acetals, MeCH(OR)$_2$, originating from the attack by the amine-HBr on the ether O, which liberates ROH, which, in turn, reacts with the original ether, yielding the final acetal; NH$_3$ reacts even more smoothly, while the Na reaction confirms the ionic state of the Br by yielding acetals, as above, instead of Wurtz reaction products. Passage of HBr into 100 g. CH$_2$:CHOBu, b. 93–3.5°, n_D^{20} 1.4020, d_4^{20} 0.7788, at 0° until an 82.5 g. wt. gain was reached gave 88.9% *MeCHBrOBu*, b_{16} 62–8°, n_D^{20} 1.4485, d_4^{20} 1.2080. Similarly, CH$_2$:CHOEt, b. 35.5–6.0°, n_D^{20} 1.3785, d_4^{20} 0.7512, gave 84% *MeCHBrOEt*, b_{12} 40–1°, n_D^{20} 1.4465, d_4^{20} 1.2770; CH$_2$:CHOMe, b_{760} 5.0–5.2°, n_D^{0} 1.3730, d_4^{0} 0.7723, gave 85% *MeCHBrOMe*, b_{760} 56.5–7.0°, n_D^{20} 1.4480, d_4^{20} 1.4256. Titration with 0.1 N NaOH to methyl orange at room temp. immediately gives 98.5–9.8% ionizable HX, i.e. Br ion; the results are similar to a Volhard titration. Treatment with aq. NaHSO$_3$ gives essentially quant. amts. of AcH (iodometric detn.). Addn. of 26 g. MeCHBrOBu to 21.4 g. PhNEt$_2$ at 5° gave 90% *MeCH(OBu)$_2$*. BuOH as solvent gave the same result, while passage of dry NH$_3$ into the ether in Et$_2$O (max. temp. 42°) gave 71% MeCH(OBu)$_2$, some BuOH, and a little polymer; addn. of 9 g. MeCHBrOBu to 1.1 g. Na in Et$_2$O and heating 2 hrs. gave 5 g. NaBr, 1 g. MeCH(OBu)$_2$, and a small amt. of EtOBu or CH$_2$:CHOBu. Addn. of MeCHBrOEt to satd. EtOH-NaOH and heating 1 hr. at 70° gave 11.9 g. NaBr and 5 g. MeCH(OEt)$_2$, while MeCHBrOMe similarly gave *MeCH(OMe)$_2$*, b. 63.5–4.0°, n_D^{20} 1.3760, d_4^{20} 0.8578. MeCHBrOEt (18.5

g.) in petr. ether added to 11 g. powd. NaOAc at 5-8° and heated 2 hrs. gave 11 g. NaBr and 60% *MeCH(OAc)OEt*, b_{16} 58-9°, n_D^{20} 1.3920, d_4^{20} 0.9158; dioxane as solvent gave 47% of the latter product; a similar reaction with MeCHBrOBu in petr. ether gave a little BuOH and AcOH, while in dioxane 45% *MeCH(OAc)OBu*, b_{16} 60-?°, n_D^{20} 1.4100, d_4^{20} 0.9187, was obtained. Passage of dry HCl into MeCHBrOEt at room temp. failed to cause any reaction. The MeCHBrOR ethers are generally poorly stable, the instability being greater in higher homologs; all are effective catalysts for vinyl polymerizations. III. **2-Haloethyl phenyl ethers.** *Ibid.* 1320-32. The ethers MeCHXOPh are less reactive and more stable than the aliphatic analogs, as a result of the opposing mesomeric effects introduced by the Ph nucleus, which increases the covalent link with the halogen. Slow passage of dry HX into $CH_2:CHOPh$ below 0° readily gave *MeCHClOPh* (95.5%), b_{16} 97-8°, n_D^{20} 1.5225, d_4^{20} 1.1150, and *MeCHBrOPh* (95.4%), b_2 87-9°, n_D^{20} 1.5580, d_4^{20} 1.3010. Shaking MeCHClOPh 45 min. with 0.2 *N* $NaHSO_3$ gave a quant. amt. of AcH, titration with 0.1 *N* NaOH also gave 99.5% removal of Cl, as did the Volhard detn. A soln. of the ether in BuOH gave a polymeric product (viscous red mass), and no true reaction with BuOH took place; the result was similar even at −12° in a N atm.; EtOH-KOH at 5° readily gave 88% MeCH(OEt)OPh, b_6 70-1°, n_D^{20} 1.4930, d_4^{20} 0.9932, while KOH-BuOH gave *MeCH(OPh)OBu*, b_{13} 125-7°, n_D^{20} 1.4825, d_4^{20} 0.9595. Heating the ether with AcOH gave HCl and a red polymer; no reaction occurred with NaOAc in Et_2O, nor with Br at 4°; HCl had no effect at 20°, while $PhNEt_2$ gave $CH_2:CHOPh$, some PhOH, and *MeCH(OPh)₂*, b_3 116-8°, n_D^{20} 1.5540, d_4^{20} 1.0808. G. M. Kosolapoff

SHOSTAKOVSKII, M. F.

"Studies in the field of synthesis and transformations of a-haloethers. III. a-Haloethyl phenyl ethers." M. F. Shostakovskii and A. V. Bogdanova. (p. 1326)

SO: Journal of General Chemistry (Zhurnal Obshchei Khimii) 1950, Vol 20, No. 7.

C.A.

10

Synthesis and reactions of vinyl ethers of ethanolamines
I. Vinylation of monoethanolamine M. F. Shostakovskii,
I. A. Chekulaeva, and N. A. Gershtein (Izvest. Akad.
Nauk S.S.S.R., Otdel. Khim. Nauk **1951**, 328-33.--Heating
$HOCH_2CH_2NH_2$ (I) in N 6 hrs. to 120-40° gave 64 g. un-
changed I and 4 g. tar; in the presence of KOH some 20%
tar forms, while addn. of 10% K salt of I gives 10% tar
Heating I under C_2H_2 pressure (16 atm.) at 120-40°, in the
presence of 10% KOH (solid) gave 10-12% vinyl deriv.
and much tar; without KOH in C_6H_6, only tar formed.
The best yields were obtained when 72 g. I was treated with
2.8 g. K and the soln. dild. with 150 ml. C_6H_6 and heated
12 hrs. at 120-40° in a rotating steel autoclave under 16
atm. C_2H_2; distn. gave 57 g. pure $CH_2:CHOCH_2CH_2NH_2$,
b_{760} 114.5-15.5°, b_{750} 115-16°, n_D^{20} 1.4380, d_4^{20} 0.9018;
treated with dil. H_2SO_4 it yields AcH; distn. of the higher-
boiling fractions gave about 1 ml. each of apparently CH_2:-
$CHOCH_2CH_2NHCH:CH_2$, b_{12} 58°, n_D^{20} 1.4801, d_4^{20} 0.9550,
and $HOCH_2CH_2N(CH:CH_2)_2$, b_4 95-115°, n_D^{20} 1.5092, d_4^{20}
1.0112. Both are gradually hydrolyzed in part by dil.
H_2SO_4, yielding some 25% AcH at room temp. Some resin-
ous *acid*, m. 95-6°, also forms.
G. M. Kosolapoff

SHOSTAKOVSKIY, M. F.

183T11

USSR/Chemistry - Organic Sulfur Compounds May/Jun 51

"Synthesis of Sulfur Compounds From Acetylene and Vinyl Ethers. Communication No 1: Synthesis of alpha-Alkoxyethylmercaptanes and alpha, alpha'-Dialkoxydiethylsulfides by Reacting Hydrogen Sulfide With Vinyl Ethers," M. F. Shostakovskiy, Ye. N. Prilezhayeva, E. S. Shapiro, Inst Org Chem, Acad Sci USSR

"Iz Ak Nauk SSSR, Otdel Khim Nauk," No 3, pp 284-294

Found conditions of quant addn of hydrogen sulfide according to Markovnikov's rule to vinylether

183T11

LG.

USSR, Chemistry - Organic Sulfur Compounds (Contd) May/Jun 51

ether and vinylbutyl ether with formation of alpha-
alkoxyethanethiols and alpha, alpha'-dialkoxy-
diethylsulfides. Showed hemithioacetals, as dis-
tinguished from their oxygen analogues, are cap-
able of brief existence as free substances.
Studied some reactions of alpha-alkoxyethanethiols
and alpha, alpha'-dialkoxydiethylsulfides and
proved constitution of these substances. In syst
RO-C-C-X, there is conjugation of single bonds
leading to facilitated splitting off of OR as
anion and X as cation with simultaneous formation
of double C=S bond.

183T11

SHOSTAKOVSKIY, M. F.

Jul/Aug 51

USSR/Chemistry - Organic Sulfur Compounds

"Synthesis of Sulfur-Containing Compounds Based on Simple Vinyl Ethers and Acetylene. Communication 2. Synthesis of β, β' - and α, β Dialkoxydiethylsulfides," Ye. N. Prilezhayeva, E. S. Shapiro, M. F. Shostakovskiy, Inst of Org Chem, Acad Sci USSR

"Iz Ak Nauk SSSR, Otdel Khim Nauk" No 4, pp 438-447

PA 192T23

Found conditions for synthesis of α,β – and β,β'-dialkoxydiethylsulfides from simple vinyl ethers and H_2S. Mixts of isomeric sulfides were analyzed and purity of products detd by method, discovered by present authors, of titration based on decompn of above sulfides in presence of $HgCl_2$.

PA 192T23

9. Monthly List of Russian Accessions, Library of Congress, ___________1953. Unclassified.

SHOSTAKOVSKIY, M. F.

USSR/Chemistry - Organic Sulfur Compounds

Sep/Oct 51

"Synthesis of Sulfur Compounds on the Base of Vinyl Ethers and Acetylene. Communication 3. Certain Properties of α, β and β, β'-Dialkoxydiethylsulfides," Ye. N. Prilezhayeva, E. S. Shapiro, M. F. Shostakovskiy, Inst of Org Chem, Acad Sci USSR

"Iz Ak Nauk SSSR, Otdel Khim Nauk" No 5, pp 560-567

Studied some characteristic reactions of α, β- and β, β'-dialkoxydiethylsulfides. Comparison of chem reactions of α, α'-, α, β-, and β, β'-dialkoxydiethylsulfides showed that introduction of alkoxyl at C atom which is in α-position with respect to S atom causes compd to react in manner different from that characteristic for dialkylsulfides, which is particularly expressed in decreased ability to form stable complex compds with Hg salts and increased tendency toward characteristic decompn reaction. Discusses causes of this behavior.

PA 195T14

SHOSTAKOVSKIY, M. F.

USSR/Chemistry - Organic Sulfur Compounds Sep/Oct 51

"Synthesis of Sulfur Compounds on the Basis of Acetylene and Vinyl Ethers. Communication 4. Synthesis of Trithioacetaldehyde," Ye. N. Prilezhayeva, E. S. Shapiro, M. F. Shostakovskiy, Inst of Org Chem, Acad Sci USSR

"Iz Ak Nauk SSSR, Otdel Khim Nauk" No 5, pp 568-570

By action of H_2S on vinyl ethers in presence of high concns of HCl, prepd with good yield cyclic trimer of thioacetaldehyde and corresponding alc. Reaction proceeds through intermediate formation of α-chloroethylalkyl ethers and α-alkoxyethylmercaptans and decompn of latter in acid medium.

PA 195T15

SHOSTAKOVSKIY, M. F.

USSR/Chemistry - Vinyl Ethers Nov/Dec 51

"Certain Methods for Quantitative Determination of Vinyl Ethers," M. F. Shostakovskiy, Ye. N. Prilezhayeva, N. I. Uvarov, Inst of Org Chem, Acad Sci USSR

"Zhur Analit Khim" Vol VI, No 6, pp 348-352

On basis of vinylpropyl and vinylisopropyl ethers, worked out methods for quant detn of vinyl ethers. Hydrolytic oximation of ether in presence of hydroxylamine chloride yields good results if ether contains < 20% alc. Greater % of alc results in lengthy procedure and incomplete detn.

LC 195T30

USSR/Chemistry - Vinyl Ethers (Contd) Nov/Dec 51

Hydroxylamine sulfate gives unsatisfactory quant detn since it does not cause total oximation. Iodometric method gives satisfactory results for mixts contg any ratio of ether to alc.

LC 195T30

PA 195T30

CA

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Decomposition of α-halo ethers. I. α-Haloethyl alkyl ethers. M. F. Shostakovskii and A. V. Bogdanova. *Zhur. Obshchei Khim.* (J. Gen. Chem.) 21, 388-93(1951). —Contrary to current ideas, α-haloethyl alkyl ethers lose HX only in contact with atm. moisture or with excess of H_2O. The decompn. induced by H_2O probably first yields HX, ROH, and *polyvinyl resinous products*, and the formation of RX is a secondary reaction of HX with the ROH. *MeCHBrOBu*, b_{11} 63.0-3.8°, n_D^{20} 1.4483, d_4^{20} 1.2981 (180 g.), was gradually distd. through a 25-cm. column, yielding 97.1% *BuBr*, 15 g. H_2O, and traces of AcH. Letting 50 g. ether stand 3 weeks in a sealed tube in diffused light gave 80.1% BuBr and H_2O upon distn. at 150 mm. Similar treatment of the ether (39.0 g.) mixed with 13 g. CH_2:$CHCH_2Br$ gave 98.7% BuBr, 2.8 g. H_2O, and 90% unchanged CH_2:$CHCH_2Br$, as well as a little dark resin and traces of AcH. Slow distn. of *MeCHBrOEt* similarly gave 89% EtBr and H_2O, along with AcH. *MeCHBrOMe*, b_{90} 56.5-7.0°, n_D^{20} 1.4486, d_4^{20} 1.4253, kept 3 weeks in diffused light in a sealed tube gave MeBr hydrate and $MeCH(OMe)_2$, b. 62-4°, as well as a little resin (C 65.5, H 6.8%) and an unstated amt. of Br. **II. α-Haloethyl phenyl ethers.** *Ibid.* 394-8.—Keeping 10 g. *MeCHBrOPh*, b_7 88-9°, n_D^{20} 1.5590, d_4^{20} 1.3040, 7 days in a sealed tube in diffused light yielded a pink porous solid which ruptured the vessel; repetition in N atm. gave the same material which is partly sol. in Me_2CO; the insol. portion analyzes as $C_{11}H_{12}O_2$, apparently a *phenol-aldehyde resin;* the sol. portion had a similar compn. If the ether is allowed to stand in moist air a similar product forms rapidly (30 min.), along with a little free PhOH. A soln. of the ether in CH_2:CHOBu and dioxane slowly (2 days) deposits small amts. of solid, the latter contains Br, while the soln. yields BuBr and H_2O. Slow distn. of MeCHClOPh gave much HCl, PhOH, and an aldehyde-phenol resin.

G. M. Kosolapoff

1451

SHOSTAKOVSKII, M. F.

"The decomposition of a-halo ethers. II. a-Haloethyl phenylethers." by M. F. Shostakovskii and A. V. Bogdanova. (p.394)

SO: Journal of General Chemistry (Zhurnal Obshchei Khimii) 1951, Volume 21, No,2

C. a.
1951

Organic Chemistry
10

Hydrolysis of vinyl phenyl ether M. F. Shostakovskii and A. V. Bogdanova. *Zhur. Obshchei Khim.* (J. Gen. Chem.) 21, 632-4(1951).—Hydrolysis of *$PhOCH:CH_2$*, b. 155.6°, n_D^{20} 1.5225, d_4^{20} 0.9767, with 2% H_2SO_4 in sealed tubes at 100°, followed by detn. of the AcH produced, is substantially complete in 2 hrs.; 1% H_2SO_4 in 2 hrs. gives 84-5% hydrolysis. The reaction proceeds by formation of an oxonium complex by protonation of O, followed by addn. of HOH, with displacement of the proton and consequent cleavage of the hemiacetal to AcH and ROH. G. M. K.

CA

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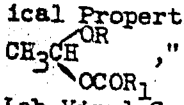
Transformations of vinyl ethers. V. Chemical properties of partial acylals of the type $CH_3CH(OR)OCOR'$. M. F. Shostakovskii and N. A. Gershtein. *Zhur. Obshchei Khim.* (*J. Gen. Chem.*) 21, 1452-60(1951); cf. *C.A.* 43, 3785*i*.—To 50 g. boiling $BuOCH:CH_2$ was added dropwise over 1.5 hrs. 23 g. HCO_2H and distn. after standing 24 hrs. gave 0.8 g. AcH, 3 g. *HCO_2Bu*, b. 106.5-7.3°, d_4^0 0.8975, d_4^{20} 0.8975, n_D^{20} 1.3912, 1.35 g. HCO_2H, 50.1 g. *$MeCH(OBu)O_2CH$*, b_{22} 62-2.5°, d_4^0 0.9340, d_4^{20} 0.9323, n_D^{20} 1.4020 (product can be distd. only in a N atm. under reduced pressure; with H_2O a rapid hydrolysis occurs), and 6.35 g. $(BuO)_2CHMe$. When the addn. of HO_2CH was more rapid (5 min.), similar results were obtained. A similar reaction with AcOH, but with reverse order of mixing, gave a little AcH, a little BuOAc, and 85% *MeCH(OBu)OAc*, b_1 42.5-3.0°, d_4^0 0.9210, d_4^{20} 0.9193, n_D^{20} 1.4040, and a trace of $(BuO)_2CHMe$. Heating 36 g. $EtOCH:CH_2$ and 44 g. $PrCO_2H$ in sealed tube 15 hrs. to 100° gave 91% *$MeCH(OEt)O_2CPr$*, b_{28} 81-1.5°, $b_{4.5}$ 37.5-8.0°, d_4^0 0.9237, d_4^{20} 0.9221, n_D^{20} 1.4030; $BuOCH:CH_2$ gave 94% *$MeCH(OBu)O_2CPr$*, b_7 71.5-5.2°, $b_{1.5}$ 59-9.1°, d_4^0 0.9032, d_4^{20} 0.9016, n_D^{20} 1.4118. Possibly the formation of acetals and esters is the result of decompn. of the acylals to vinyl ethers and vinyl esters, the former reacting with ROH to yield the acetals, the latter with free acids to form ethylidene esters, which are hydrolyzed to the aldehyde and the acids, the latter reacting with ROH to form the esters. G. M. K.

1952

SHOSTAKOVSKIY, M. F.

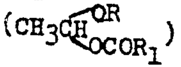
191T38

USSR/Chemistry - Vinyl Compounds Sep 51



"Conversions of Simple Vinyl Ethers. VI. Chemical Properties of Incomplete Acylals of the Type $CH_3CH\begin{smallmatrix}OR\\OCOR_1\end{smallmatrix}$," M. F. Shostakovskiy, N. A. Gershteyn, Lab Vinyl Compds, Inst Org Chem, Acad Sci USSR

"Zhur Obshch Khim" Vol XXI, No 9, pp 1602-1610



Investigation of interaction of incomplete acylals ($CH_3CH\begin{smallmatrix}OR\\OCOR_1\end{smallmatrix}$) with alcs ROH showed that products are esters (R_1COOR) and acetals ($CH_3CH(OR)_2$). Interaction of incomplete acylals

191T38

USSR/Chemistry - Vinyl Compounds (Contd) Sep 51

with org acids R_1COOH yielded esters and complete acylals ($CH_3CH(OCOR_1)_2$), which were hydrolyzed under specified conditions. Proposes reaction mechanisms.

191T38

SHOSTAKOVSKIY, M. F.

191T39

USSR/Chemistry - Chloro Derivatives of Ethers Sep 51

"Synthesis of α, β-Dichloroethylalkyl Ethers and Their Conversions. II. Synthesis of α, β-Dichloroethylmethyl, α, β-Dichlorodiethyl, and α, β-Dichloroethylisopropyl Ethers," M. F. Shostakovskiy, F. P. Sidel'kovskaya, Lab Vinyl Compds, Inst Org Chem, Acad Sci USSR

"Zhur Obshch Khim" Vol XXI, No 9, pp 1610-1617

Improved method for prepn of α, β-dichloroethylbutyl ether, described previously, with yield of 71% of theoretical. By addn of Cl to vinylmethyl, vinylethyl, vinylisopropyl ethers, prepd corresponding

191T39

USSR/Chemistry - Chloro Derivatives of Ethers (Contd) Sep 51

α, β-dichloroethylalkyl ethers. Further chlorination yielded α, β, β-trichloroethylalkyl ethers, which were isolated and characterized. All products are easily hydrolyzed. α, β-dichloro ethers can be detd by titration with $AgNO_3$ or NaOH.

191T39

SHOSTAKOVSKIY, M. F.

USSR/Chemistry - Vinyl Compounds

Oct 51

"Synthesis and Properties of Vinyl Methyl Ether," M. F. Shostakovskiy, P. V. Tyupaev, Lab of Vinyl Compds, Inst of Org Chem, Acad Sci USSR.

"Zhur Obshch Khim" Vol XXI, No 10, pp 1830-1836.

Optimum conditions for safe vinylation of MeOH using C_2H_2 not dissolved in inert gas was found to obtain in autoclave at 150° C. Pressure, depending on initial pressure of C_2H_2 and mostly on alc-ether ratio in reaction mixt, sometimes reached 55-60 atm. Established methods for purification of vinylmethyl ether, detd its consts, introducing corrections into literature data.

PA 194T31

SHOSTAKOVSKIY M. F.

FA 194T61

USSR/Chemistry - Chloroacetaldehyde Dec 51

"Synthesis of Acetals of Chloroacetaldehyde," M. F. Shostakovskiy, F. P. Sidel'kovskaya, Lab of Vinyl Compds, Inst of Org Chem, Acad Sci USSR

"Zhur Obshch Khim" Vol XXI, No 12, pp 2163-2170

Worked out synthesis of acetals of chloroacetaldehyde (useful in synthesis of physiologically active amino- and betainoaldehydes and other substances) by action of alcs or alcoholates on α, β-dichloroethylalkyl ethers. Yields run as high as 90% of theoretical. Addn of Cl to vinyl ethers in presence of analogous alcs yielded

194T61

USSR/Chemistry - Chloroacetaldehyde (Contd) Dec 51

corresponding acetals of chloroacetaldehyde. Addn of Cl to vinylethyl ether in presence of excess BuOH yielded dibutylchloroacetal (yield 50% of theoretical). Proposes reaction mechanisms.

194T61

[illegible], M. F.

183T37

USSR/Chemistry - Polymerization May 51

"Processes for the Conversion of the Nitrile of Acrylic Acid and α-Methyl-Styrene in the Presence of Hydrogen Peroxide," M. F. Shostakovskiy, A. V. Bogdanova, Lab Vinyl Compds, Inst Org Chem, Acad Sci USSR

"Zhur Prik Khim" Vol XXIV, No 5, pp 495-501

Examd processes of conversion of acryl-nitrile (I) and α-methyl-styrene (II) through addn of H_2O, alcs, phenols due to action of H_2O_2. I polymerized easily, did not interact with H_2O,

183T37

USSR/Chemistry - Polymerization (Contd) May 51

alcs, phenols; II was not polymerized or added to, but was oxidizable under these conditions. Copolymer of I and II was formed through action of H_2O_2, confirming concept of free radical mech.

183T37

CA

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The transformations of acrylonitrile and α-methylstyrene in the presence of hydrogen peroxide. M. F. Shostakovskii and A. V. Bogdanova. *J. Applied Chem. U.S.S.R.* 24, 541-8(1951)(Engl. translation).—See C.A. 46, 1961*f*.
B. R.

SHOSTAKOVSKIY, M.F.

PA 190T41

USSR/Chemistry - Plastics Oct 51

"The Viscosity Properties of Vinyl Alkyl Ether Polymers," M. F. Shostakovskiy, B. V. Deryagin, I. F. Bogdanov, N. N. Zakhavayeva, Inst Org Chem and Inst Phys Chem, Acad Sci USSR

"Zhur Prik Khim" Vol XXIV, No 10, pp 1063-1070

Polymers of vinyl alkyl ethers have very favorable temp viscosity curve (index of viscosity). A 2% soln of these polymers strongly reduces metal corrosion.

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190T41

SHOSTAKOVSKIY, M.F.

PHASE I TREASURE ISLAND BIBLIOGRAPHIC REPORT AID 174 - I

BOOK Call No.: QD341.E7S5
Author: SHOSTAKOVSKIY, M. F.
Full Title: VINYL ETHERS
Transliterated Title: Prostyye vinilovyye efiry
Publishing Data
Originating Agency: Academy of Sciences of the U.S.S.R. Institute of Organic Chemistry
Publishing House: Academy of Sciences, U.S.S.R.
Date: 1952 No. pp.: 280 No. of copies: 2,000
Editorial Staff
Editor: Kolesnikov, G. S. Tech. Ed.: None
Editor-in-Chief: Petrov, A. D., Cor. Member Acad. of Sciences, U.S.S.R. Appraiser: None
Others: Names of many Soviet scientists are mentioned in connection with the bibliographic documentation.
Text Data
Coverage: A survey of basic work done on the synthesis of vinyl ethers is given. The physical and chemical properties of the ethers, their reactions with alcohols, phenols, and acids are described. Hydrolysis, polymerization, and analysis of vinyl ethers are covered thoroughly. (Tables, charts)

Prostyye vinilovyye efiry AID 174 - I

The book might be of interest because of the importance of vinyl ethers to modern industry.

Purpose: The purpose of the author was to set forth the discovery of the reaction of vinylation, the application of this reaction in the chemical industry, and the contributions of Soviet scientists to the chemistry of vinyl ethers.

Facilities: None

No. of Russian and Slavic References: 270; Foreign: 275 (1856-1951)

Available: Library of Congress.

Rubber Abst.
Vol. 31
Dec. 1953
Synthetic Rubber
and Like Products

4987. Role of peroxides in processes of polymerization of vinyl compounds. M. F. SHOSTAKOVSKII, V. P. SHISHIKOV, and V. A. NETERMAN. Khim. i. Fiz Khim. Vysokomolekul. Soedinenii, Doklady 7-oi Konf. Vysokomolekul. Soedineniyam 1952, 28-34; Chem. Abs., 1953, 47, 7819. Three general classes of vinyl monomers are distinguished according to the mechansim of their polymerisation. The action of benzoyl peroxide is discussed, and the relation between activity of monomer, copolymer activity, and the polymerisation reaction described. Various experiments on the action of benzoyl peroxide were carried out. Examples relate to methacrylates, vinyl esters, vinyl chloride, and the like, in solution or emulsion. 3S12

5-21-54

SHOSTAKOVSKIY, M. F.

6

(4) chem

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

Synthesis and properties of 1-alkoxyethyl esters of unsaturated carboxylic acids (acylals). M. F. Shostakovskii, N. A. Gershtein, Ya. L. Raskin, and L. B. Ostroumova. *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.* 1952, 453-8 (Engl. translation).—See *C.A.* 47, 4850*a*. H. L. H.

SHOSTAKOVSKIY, M. F.

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

③

Synthesis of sulfur compounds based on vinyl ethers. V. Some new representatives of the series α,β- and β,β'-dialkoxydiethyl sulfides. E. N. Prilezhaeva, E. S. Shapiro, and M. F. Shostakovskii. *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.* 1952, 459–63(Engl. translation).—See *C.A.* 47, 4840g. H. L. H.

SHOSTAKOVSKIY, M. F.

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

5

③ Chem

Synthesis of the vinyl ethers of higher aliphatic alcohols. M. F. Shostakovskii, B. I. Mikhant'ev, and V. A. Neterman. *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.* 1952, 465-7(Engl. translation).—See *C.A.* 47, 3789*e*.
H. L. H.

SHOSTAKOVSKIY, M.F.

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

3 Chem.

Syntheses of acetals of ethylene glycol. M. F. Shostakovskii, N. A. Gershtein, and Z. S. Volkova. *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.* 1952, 617-25 (Engl. translation).—See *C.A.* 47, 10472*f*. H. L. H.

MF

SHOSTAKOVSKIY, M.F.

③ Chem

Synthesis and polymerization of vinylcaprolactam. M. F. Shostakovskii, N. A. Medzykhovskaya, and M. G. Zelenskaya. Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci. 1952, 627-32(Engl. translation). See C.A. 47, 10479i.
H. L. H.

MF

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

SHOSTAKOVSKIY, M.F.

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

Synthesis and transformations of vinylcaprolactam. I. Polymerization in the presence of hydrogen peroxide. M. F. Shostakovskii, F. P. Sidel'kovskaya, and M. Zelenskaya. *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.* 1952, 633-9 (Engl. translation). See *C.A.* 47, 9917g.
H. L. H.

SHOSTAKOVSKIY, M.F.; GERSHTEYN, N.A.; VOLKOVA, Z.S.

Synthesis of acetals of ethylene glycol. Izvest. Akad. Nauk S.S.S.R., Otdel.
Khim. Nauk '52, 671-81. (MLRA 5:9)
(CA 47 no.20:10472 '53)

SHOSTAKOVSKIY, M. F.

5

3 Chem

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

Indirect vinylation of aliphatic alcohols. M. F. Shostakovskii, B. I. Mikhant'ev, and N. N. Ovchinnikova. *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.* 1952, 959-62 (Engl. translation).—See *C.A.* 48, 1242c. H. L. H.

SHOSTAKOVSKIY, M. F.

Chemical Abst.
Vol. 48 No. 4
Feb. 25, 1954
Organic Chemistry

Acetylenic alcohols and glycols. II. Synthesis of mono- and diacetals of tetramethylbutynediol. M. F. Shostakovskii and A. V. Bogdanova. *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1952, 1094-8; cf. *C.A.* 43, 3785*i*; 48, 1241*e*.—Heating 35.5 g. $(Me_2C(OH)C{:})_2$ with 50 g. $CH_2{:}CHOBu$ in autoclave 9 hrs. at 96-110° gave 30 g. $Me_2C(OH)C{:}CCMe_2OCHMeOBu$ (I), b_7 121-2°, n_D^{20} 1.4440, d_{20} 0.9175, and 12 g. $(BuOCHMeOCMe_2C{:})_2$ (II), b_8 146-7°, n_D^{20} 1.4380, d_{20} 0.9150. The diol (35.5 g.) in 50 g. dioxane treated over 1 hr. with 50 g. $BuOCH{:}CH_2$ and 3 drops concd. HCl at 53-6°, then heated 3.5 hrs. at 65-70° and dist., gave 84.9% I and 2.4% II; if heating extends to 8 hrs. the yield of II rises to 66%. Similarly obtained (2nd procedure, above) was: from $C_8H_{17}OCH{:}CH_2$, 62% $Me_2C(OH)C{:}CCMe_2OCHMeOC_8H_{17}$, b_1 138-8.2°, n_D^{20} 1.4420, d_{20} 0.8713, and 30.3% $(C_8H_{17}OCHMeOCMe_2C{:})_2$, b_1 184-6°, n_D^{20} 1.4460, d_{20} 0.8905; from $EtOCH{:}CH_2$, 56% $(EtOCHMeOCMe_2C{:})_2$, b_2 103.5-5.0°, n_D^{20} 1.4320, d_{20} 0.9125.

G. M. Kosolapoff

Chem 3

(3)

MF

SHOSTAKOVSKIY, M. F.; CHEKULAYEVA, I.A.; GERSHTEYN, N. A.

Aminoethanols

Synthesis and transformations of vinyl ethers of aminoethanols. Part 1 Synthesis of aminoacetals M. F. Shostakovskiy, I. A. Chekulayeva, N. A. Gershteyn. Izv. AN SSSR. Otd. Khim. nauk No. 1, 1952.

Monthly List of Russian Accessions, Library of Congress, September, 1952. UNCLASSIFIED.

SHOSTAKOVSKII, M. F.

Chem abs. V48
1-25-54
Organic Chemistry

β-Aminoethyl isopropyl acetal. M. F. Shostakovskii, I. A. Chekulaeva, and N. A. Gershtein. *Akad. Nauk S.S.S.R., Inst. Org. Khim., Sintezy Org. Soedinenii, Sbornik* 2, 16-17(1952); cf. *C.A.* 43, 6159*c*.—Into a pre-cooled autoclave was charged 16.4 g. $MeCH(OCHMe_2)OCH_2CH_2Cl$ and 50 ml. liq. NH_3; the mixt. was heated 6 hrs. at 140-50° (110 atm. max. pressure) and filtered after cooling, release of NH_3 pressure and washing the app. with Et_2O. Distn. gave 47% $MeCH(OCHMe_2)OCH_2CH_2NH_2$, b_{19} 71-6°, b_{28} 75-6°, d_{20} 0.9123, n^{20}_D 1.4240. Similarly from $MeCH(OCH_2CHMe_2)OCH_2CH_2Cl$ were obtained: $MeCH(OCH_2CHMe_2)OCH_2CH_2NH_2$, b_8 83-4°, d_{20} 0.9000, n^{20}_D 1.4246; $[MeCH(OCH_2CHMe_2)OCH_2CH_2]_2NH$, b_{14} 160-5°, d_{20} 0.9210, n^{20}_D 1.4320; and $[MeCH(OCH_2CHMe_2)OCH_2CH_2]_3N$, b_4 210-20°, d_{20} 0.9322, n^{20}_D 1.4380. Among the by-products in prepn. of the iso-Pr deriv. there were found: $[MeCH(OCHMe_2)OCH_2CH_2]_2NH$, b_4 147-53°, d_{20} 0.9326, n^{20}_D 1.4300, and $[MeCH(OCHMe_2)OCH_2CH_2]_3N$, b_4 185-95°, d_{20} 0.9307, n^{20}_D 1.4340, in 29% and 8.5% yields, resp. Heating for 10 hrs. or longer increases the yield of the mono-NH_2 deriv. to over 45%, while lowering the proportion of NH_3 to 4 moles to 1 mole of chloro deriv. raises the yield of the secondary amine to 40%. G. M. Kosolapoff

Chem Abs v 48

1-25-54

Organic Chemistry

(2)

α-Butoxyethyl isobutyrate. N. A. Gershtein and M. F. Shostakovskii. Akad. Nauk S.S.S.R., Inst. Org. Khim., Sintezy Org. Soedinenii, Sbornik 2, 19-30(1952); cf. C.A. 43, 3785i.—Heating in autoclave [illegible] g. iso-PrCO$_2$H and BuOCH:CH$_2$ 5-6 hrs. at 140-50° gave 90.9% MeCH(OBu)O$_2$CCHMe$_2$, b$_{2.5}$ 52-3°, d$_{20}$ 0.8961, n$^{20}_{D}$ 1.4080; distn. is done in dry N atm. Similarly were prepd.: 80.1% MeCH(OBu)O$_2$CCH$_2$CHMe$_2$, b$_{3.5}$ 66.8-7.0°, d$_{20}$ 0.8874, n$^{20}_{D}$ 1.4140; 49.4% MeCH(OPh)OAc, b$_{2.5}$ 78.5-9.0°, n$^{20}_{D}$ 1.4905, d$_{20}$ 1.075; by-product in the latter prepn.: 23.6% MeCH(OPh)$_2$, b$_{1.5}$ 117.2-17.5°, n$^{20}_{D}$ 1.5568, d$_{20}$ 1.087. G. M. K.

7-13-59

SHOSTAKOVSKIY, M.F.

Chem abs v48
1-25-54
Organic Chemistry

✓ Butyl heptyl chloroacetal. M. F. Shostakovskiĭ and F.
P. Sidel'kovskaya. Akad. Nauk S.S.S.R., Inst. Org.
Khim., Sintezy Org. Soedinenii, Sbornik 2, 20-1(1952);
cf. C.A. 42, 4520a; 44, 7754h.—To 10 g. KOH and 20 g.
n-$C_7H_{15}OH$ was slowly added 30 g. $ClCH_2CHClOBu$; at
first the mixt. is cooled with H_2O, while in the last stages it
is warmed to 60-70° and kept thus for 4 hrs. After filtration
of KCl (washing with Et_2O), distn. of the org. portion gave
30% $ClCH_2CH(OBu)(OC_7H_{15})$, b_{15} 158-61°, b_{16} 159°, n_D^{20}
1.4367, d_{20} 0.9337, and 7 g. $ClCH_2CH(OC_7H_{15})_2$, b_{17} 188-
-8.5°, n_D^{20} 1.4420, d_{20} 0.9247, the latter being formed by
disproportionation of the 1st product. Similarly were ob-
tained: 90% $ClCH_2CH(OBu)_2$, b_{17} 115-15.7°, n_D^{20} 1.4330,
d_{20} 0.9682, and 77% $ClCH_2CH(OCH_2CH_2CHMe_2)_2$, b_{20}
128-30°, n_D^{20} 1.4300, d_{20} 0.9382.

G. M. Kosolapoff

MF
1-28-54

SHOSTAKOVSKIY, M. F.

Chem Abs V48
1-25-54
Organic Chemistry

7

5 Chem

α-Butoxyethyl methacrylate. M. F. Shostakovskii, N. A. Gershtein, Ya. L. Raskin, and L. F. Ostroumova. *Akad. Nauk S.S.S.R., Inst. Org. Khim., Sintez Org. Soedinenii, Sbornik* 2, 22-4(1952); cf. C.A. 43, 3785f.—Heating 25 g. BuOCH:CH$_2$ and 21.5 g. freshly distd. CH$_2$:CMeCO$_2$H in sealed tube 5-5.5 hrs. on a steam bath gave on distn. in N atm. 90% *MeCH(OBu)O$_2$CCMe:CH$_2$*, b$_5$ 99°, b$_7$ 86°, b$_{13}$ 89°, d$_{20}$ 0.9296, n_D^{20} 1.4256. Similarly were prepd.: 84.5% *MeCH(OEt)O$_2$CCMe:CH$_2$*, b$_7$ 65°, b$_{14}$ 73°, d$_{20}$ 0.9178, n_D^{20} 1.4200; 78.5% *MeCH(OCH$_2$Ph)O$_2$CCMe:CH$_2$*, b$_1$ 83.7-4.0°, d$_{20}$ 1.0367, n_D^{20} 1.5008; 77.8% *MeCH(OC$_6$H$_{11}$)O$_2$CCMe:CH$_2$*, b$_{14}$ 112-12.5°, d$_{20}$ 0.9776, n_D^{20} 1.4560; the necessary *vinyl cyclohexyl ether*, b$_{20}$ 52-4°, d$_{20}$ 0.888, n_D^{20} 1.4547.

G. M. Kosolapoff

AF
4-22-54

SHOSTAKOVSKIY, M.F.

Chem Abs v48
1-25-54
Organic Chemistry

Butoxyethyl acetate. M. F. Shostakovskii, N. A. Gershtein, A. V. Bogdanova, and V. P. Shishkov. *Akad. Nauk S.S.S.R., Inst. Org. Khim., Sintezy Org. Soedinenii, Sbornik* 2, 25-8(1952); cf. *C.A.* 42, 4519*d*; 43, 3785*i*.—Three methods are described. To 100 g. BuOCH:CH_2 was added with stirring at room temp. 60 g. AcOH, after which the mixt. was kept 4-5 hrs. at 60° and allowed to stand overnight; distn. in dry N atm. gave 91% *MeCH(OBu)OAc*, (I), b_9 51.5-1.8°. To 11 g. AcOH was added dropwise 20 g. MeCHClOBu at below 20°, after which the mixt. was stirred 2 hrs. at 50-5° and allowed to stand overnight; distn. gave 23 g. crude product, b_{24} 67-70°, which was washed 3 times with 5% $NaHCO_3$ and dried; distn. gave 85% I, b_{20} 67-8°. To 43 g. AcOCH:CH_2 and 150 g. BuOH 0.21 g. Bz_2O_2 was added and the homogeneous soln. was kept in ampul 30 days at 20° (heating yields insol. resin). Distn. gave 46% I, b_{11} 52-3.5°, and 1 g. polyvinyl acetate. Pure I, b_9 51.5-1.8°, b_{20} 67-8°, d_{20} 0.9182, n_D^{20} 1.4040. Similarly were prepd.: 87% *EtOCHMeOAc* (from EtOCHBrMe and NaOAc in dioxane) or 35.6% from AcOCH:CH_2 and EtOH with Bz_2O_2; the product, b. 129°, b_{11} 48-50°, d_{20} 0.9442, n_D^{20} 1.3930; 28% *PrOCHMeOAc* (from AcOCH:CH_2 and PrOH with Bz_2O_2), b_{20} 55°, d_{20} 0.9246, n_D^{20} 1.3980; 47% *iso-AmOCHMeOAc* (from AcOCH:CH_2 and iso-AmOH with Bz_2O_2), b. 145°, d_{20} 0.9202, n_D^{20} 1.4212. G. M. Kosolapoff

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Chem

Chem Abs V48
1-25-54
Organic Chemistry

α-Butoxyethyl lactate. B. I. Mikhant'ev and M. F. Shostakovskii. Akad. Nauk S.S.S.R. Inst. Org. Khim., Sintesy Org. Soedinenii, Sbornik 2, 31-2(1952); cf. C.A. 43, 3785i.—To 90 g. $MeCH(OH)CO_2H$ was added over 2 hrs. 100 g. $BuOCH:CH_2$ and the mixt. was stirred 5-6 hrs. at 92-5°. Distn. gave 38% $MeCH(OBu)O_2CCH(OH)Me$, b. 188-9°, d_{20} 0.9700, n_D^{20} 1.4195. Similarly was prepd. 32% $MeCH(OEt)O_2CCH(OH)Me$, b. 152-4°, d_{20} 1.012, n_D^{20} 1.4100, after 5 hrs. at 34-6°. The reactants must be completely anhyd. G. M. Kosolapoff

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7-19-54

SHOSTAKOVSKIY, M. F.

Chem. 4

Chem Abs V48
1-25-54
Organic Chemistry

Vinyl 2-aminoethyl ether. M. F. Shostakovskii, I. A. Chekulaeva, and N. A. Gershtein. (Akad. Nauk S.S.S.R. Inst. Org. Khim., *Sintezy Org. Soedinenii, Sbornik* 2, 33-4 (1952); cf. *C.A.* 38, 330⁴.—To 72 g. $HOCH_2CH_2NH_2$ was slowly added 2.8 g. K and the product in 150 ml. C_6H_6 was placed into an autoclave; C_2H_2 was added to 14-16 atm. and the mixt. was heated to 120-40° 4-6 hrs.; after cooling to 20-30° the C_2H_2 pressure was again restored and heating repeated until the calcd. amt. is consumed. Distn. gave 85% $H_2NCH_2CH_2OCH:CH_2$ crude, b. 110-20°, which was treated with Na in the cold and redistd. yielding the *pure product*, 57 g., b_{755} 115-16°, n_D^{20} 1.4390, d_{20} 1.9018 (sic). The autoclave must not have any Cu parts in order that explosions be averted. G. M. Kosolapoff

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Chem Abs
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Organic Chem

Vinyl benzyl ether. M. F. Shostakovskiĭ and N. A. Gershteĭn. *Akad. Nauk S.S.S.R., Inst. Org. Khim., Sintezy Org. Soedinenii, Sbornik* 2, 35-6(1952); cf. *C.A.* 38, 330⁴.—Heating 80 g. $PhCH_2OH$ and 6.4 g. powd. KOH in autoclave under initial C_2H_2 pressure of 15–18 atm., to 140–50° 1 hr., followed by cooling, and renewing the C_2H_2 pressure repeatedly until absorption ceased, gave after diln. of the product with Et_2O, washing the soln. with H_2O and distn. 68% *$PhCH_2OCH:CH_2$*, b_{22} 81.5°, b_{15} 47.2–7.5°, d_{20} 0.9711, n^{20}_D 1.5185. Similarly can be obtained 68–70% *vinyl cyclohexyl ether*, b_{13} 52–4°, b_{17} 63°, b_{744} 148.5–8.7°, d_{20} 0.888, n^{20}_D 1.4547. The autoclave must not have any Cu parts, or Ag parts. G. M. Kosolapoff

MF
7-28-54

SHOSTAKOVSKIY, M.F.

Chem Abs

V.48 25 Jan 54

Organic Chem

✓ Vinyl guaiacyl ether. M. F. Shostakovskii, V. P. Shishkov, and M. G. Zelenskaya. *Akad. Nauk S.S.S.R., Inst. Org. Khim., Sintezy Org. Soedinenii, Sbornik* 2, 37–8 (1952); cf. *C.A.* 38, 330^4.—To an autoclave with 400 g. guaiacol, 40 g. KOH, and 40 ml. H_2O is added C_2H_2 to 16–18 atm., the vessel heated with agitation to 180–200° until C_2H_2 absorption ceases. C_2H_2 is again admitted and the process repeated until the reaction stops. After steam distn. the product is redistd. yielding 62% *o*-$MeOC_6H_4OCH:CH_2$, b_{10} 112–13°, d_{20} 1.0648, n_D^{20} 1.5350. If H_2O is omitted, the yield drops and tars are formed. The app. must not contain Cu or Ag parts in contact with C_2H_2.

G. M. Kosolapoff

MF 7-14-54

Chem

Chem Abs 175
1-25-54
Organic Chemistry

Vinylation of ethylene glycol. Ethylene glycol mono-, divinyl ethers. Ethylene glycol cyclic acetal. M. F. Shostakovskii and P. V. Tyupaev. *Akad. Nauk S.S.S.R., Inst. Org. Khim., Sintezy Org. Soedinenii, Sbornik* 2, 39–43(1952); cf. *C.A.* 38, 330^4.—An autoclave is charged with 15 g. KOH and 300 g. $(CH_2OH)_2$ and C_2H_2 added to 8–16 atm. It is carefully heated with agitation to 140° for 0.5 hr., cooled to 30–40°, C_2H_2 again added and reheated. After uptake of 0.8 mole C_2H_2 per mole glycol the app. is cooled and the products distd. yielding: 40% $HOCH_2CH_2OCH{:}CH_2$ (I), 80 g. $(CH_2OCH{:}CH_2)_2$ (II), and 15 g. $Me\overline{CH.O.CH_2.CH_2.O}$ (III). II is predominantly formed if the heating cycle is increased to 1–2 hrs. especially near the end of the reaction with pressure reaching 28 atm. In this case the yields are: 70% II and 14% III. If the reaction is run at 190° until complete satn. with C_2H_2 takes place and the mixt. is kept at this temp. 3 hrs. after each addn. of C_2H_2, III is the main product (68%) with 8% II. II and III are best purified by treatment with Na in the cold. In distn. of II it is best to pass a slow stream of air through the app. for agitation. I is best distd. from a small piece of K_2CO_3, for prevention of isomerization to III or more complex products. I b_{753} 140°, d_{20} 0.9821, n_D^{20} 1.4360; II b_{748} 126.8°, d_{20} 0.9220, n_D^{20} 1.4350; III b_{748} 81–2°, d_{20} 0.9795, n_D^{20} 1.3972.

G. M. Kosolapoff

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4-19-54

Chem

Chem Abs v48
1-25-54
Organic Chemistry

N-Vinyl-ε-caprolactam. M. F. Shostakovskii, N. A. Medzykhovskaya, and M. G. Zelenskaya. *Akad. Nauk S.S.S.R., Inst. Org. Khim., Sintezy Org. Soedinenii, Sbornik* 2, 44–5(1952); cf. *C.A.* 38, 330⁴.—ε-Caprolactam (28 g.) is allowed to react with 9.7 g. K at 60–80° in 150 ml. MePh. The mixt. is charged into an autoclave with 198 g. caprolactam and 200 ml. MePh and the app. is charged with C_2H_2. With agitation the autoclave is heated to about 100° (max. temp. 125°) until reaction ceases, after which a fresh portion of C_2H_2 is admitted. The process is repeated until absorption ceases. Distn. gave 71% *N-vinyl-ε-caprolactam*, m. 34–5°, b_4 95°, b_{22} 131–2°. The K in the prepn. can be replaced by Na. No Cu or Ag parts of the app. must come in contact with C_2H_2.
G. M. Kosolapoff

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7-19-54

SHOSTAKOVSKIY, M.F.

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Chem Abs v48
1-25-54
Organic Chemistry

Vinyl lactate. M. F. Shostakovskii and B. I. Mikhant'ev. *Akad. Nauk S.S.S.R., Inst. Org. Khim., Sintezy Org. Soedinenii, Sbornik* 2, 40-7(1952); cf. Reppe, *Acetylene Chemistry* 1949, p. 57 (*C.A.* 43, 9078*d*).—An autoclave is charged with 90 g. anhyd. $MeCH(OH)CO_2H$ and 10-12 g. Zn or Cd lactate, and C_2H_2 added to 15-16 atm. Heating with agitation at 90-100° for 4-5 hrs. until absorption ceases followed by distn. of the products, gave 32% $MeCH(OH)CO_2CH:CH_2$, b. 153° (crude, b. 140-52°), d_{20} 1.0774, n_D^{20} 1.4088. No Cu or Ag parts must come into contact with C_2H_2. G. M. K.

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7-19-54

SHOSTAKOVSKIY, M. F.

Chem Abs

V.48 25 Jan 54

Organic Chem

Vinyl phenyl ether. M. F. Shostakovskii and M. S. Burmistrova. *Akad. Nauk S.S.S.R., Inst. Org. Khim., Sintezy Org. Soedinenii, Sbornik* 2, 48-50(1952); cf. *C.A.* 37, 2336^a; 46, 10124*b*.—An autoclave with 200 g. PhOH and 30 ml. H_2O is charged with 20 g. KOH and C_2H_2 added (not less than '0 atm.). Heating with agitation to 175° until the pressure drops to 1-1.5 atm., C_2H_2 again added and the cycle repeated until reaction ceases (usually over theoretical amt. of C_2H_2 is consumed), gave after washing with H_2O and distn. 70% *PhOCH:CH$_2$*, b.155-6°, d_{20} 0.9771, n_D^{20} 1.5224. Similarly prepd.: 60% *o-MeC$_6$H$_4$OCH:CH$_2$*, b.167-8.5°, d_{20} 0.9545, n_D^{20} 1.5160; 55% *m-analog*, b.173-4.5°, d_{20} 0.9605, n_D^{20} 1.5186; *p-analog*, b. 175-5.5°, d_{20} 0.9687, n_D^{20} 1.5170. Cu and Ag must not come in contact with C_2H_2 in the app. Residual pressure in app. is best released before each cycle. G. M. K.

SHOSTAKOVSKIY, M. F.

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Chem Abs V48
1-25-54
Organic Chemistry

Vinyl ethyl ether of ethylene glycol. M. F. Shostakovskii and P. V. Tyupaev. *Akad. Nauk S.S.S.R., Inst. Org. Khim., Sintezy Org. Soedinenii, Sbornik* 2, 51–3(1952); cf. *C.A.* 38, 330^4; U.S. 1,959,927, *C.A.* 28, 4431^6.—An autoclave is charged with 18 g. KOH and 360 g. $EtOCH_2CH_2OH$, C_2H_2 is added from a cylinder and the vessel heated with agitation to 150° 0.5 hr. After cooling to 30–40° the C_2H_2 pressure is restored and the heating repeated until the reaction ceases (the last charges of C_2H_2 require 1–2 hrs. for consumption). The final pressure is about 29 atm. After washing with H_2O, the product gave on distn. 84% $EtOCH_2CH_2OCH:CH_2$, b_{754} 123.7–3.9°, d_{20} 0.8760, n_D^{20} 1.4125. Before final distn. the product is treated with Na in the cold. No Ag or Cu parts of app. must come in contact with C_2H_2.

G. M. Kosolapoff

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Chem Abs V 48
1-25-54
Organic Chemistry

Vinyl ethyl sulfide. E. N. Prilezhaeva and M. F. Shostakovskii. Akad. Nauk S.S.S.R., Inst. Org. Khim., Sintezy Org. Soedinenii, Sbornik 2, 54-6(1952); cf. C.A. 38, 330⁴.—An autoclave is charged with 1.5-2 g. powd. KOH and 35 g. EtSH and C_2H_2 is added to 18-20 atm. (for 1 l. app. this represents a 50% excess). Heating with agitation to 120-5°, initially, then to 135-45° 1-1.5 hrs. (max. pressure 30 atm.) gave after diln. with Et_2O and removal of tar some 65% *$EtSCH:CH_2$*, b. 89-92°. Steam distn. of the residue gave some 7.7% *$(EtSCH_2)_2$*, $b_{4.4}$ 69.5-70°. Redistn. gave pure *$EtSCH:CH_2$*, b. 91.9-2.2°, n_D^{20} 1.4756, d_{20} 0.8756. It forms a salt with $HgCl_2$, m. 32-4°.

G. M. Kosolapoff

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SHOSTAKOVSKIY, M. F.

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Chem abs V 48
1-25-54
Organic Chemistry

α,β-Dibromomethyl methyl ether. M. F. Shostakovskiĭ and P. V. Tyupaev. Akad. Nauk S.S.S.R., *Inst. Org. Khim., Sintezy Org. Soedinenii, Sbornik* 2, 81-4(1952); cf. *C.A.* 38, 330⁴.—In a flask provided with a Hg-sealed stirrer passing through a reflux condenser, and a dropping funnel with a cooling jacket and a pressure equalizing tube is charged some CCl_4 (enough to activate the thermometer inserted into the flask). The flask is then charged with 200 g. dry Br while the cooled dropping funnel is charged with 73 g. $MeOCH:CH_2$. After cooling the Br soln. to −7° a slow addn. of the ether is begun with good stirring at −3 to −5°. After completion of addn. the product is distd. yielding 82.8% pure $BrCH_2CHBrOMe$, b_4 52°, b_{18} 56°, b. about 160° (decompn.), d_{20} 1.9701, n_D^{20} 1.5300. G. M. K.

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chem

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Chem Abs V48
1-25-54
Organic Chemistry

Divinyl ether of 1,4-butylene glycol. M. F. Shostakovskii and P. V. Tyupaev. *Akad. Nauk S.S.S.R., Inst. Org. Khim., Sintezy Org. Soedinenii, Sbornik* 2, 85-7 (1952).—Into an autoclave is charged 25 g. KOH in 500 g. (CH$_2$CH$_2$OH)$_2$ and C$_2$H$_2$ from the cylinder to 18 atm. (no contact between Ag or Cu parts is permitted). With agitation the app. is heated to 140° 0.5 hr.; when the pressure declines appreciably, the vessel is cooled to 30-40° and again C$_2$H$_2$ is added; this cycle is repeated until reaction ceases. After washing the product 2-3 times with H$_2$O it is distd. after drying over K$_2$CO$_3$, yielding 70% (*CH$_2$CH$_2$OCH:CH$_2$*)$_2$, b$_{15}$ 73-7° (crude). Pure product, b$_{11}$ 75°, b$_{755}$ 167-8°, d$_{20}$ 0.8985, n_D^{20} 1.4398. The product is subject to thermopolymerization. For complete removal of HO contg. impurities it is best treated in the cold with Na, and distd. from it. G. M. Kosolapoff

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7-19-54

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Chem

Chem Abs V48
1-25-54
Organic Chemistry

Dimethyl chloroacetal. M. F. Shostakovskii and F. P. Sidel'kovskaya. *Akad. Nauk S.S.S.R., Inst. Org. Khim., Sintesy Org. Soedinenii, Sbornik* 2, 90–1(1952).—To 26 g. $ClCH_2CHClOMe$ is added with stirring 9.5 g. MeOH and the mixt. is kept overnight after which most of the HCl is removed with stream of dry air. Distn. yields 90% $ClCH_2CH(OMe)_2$, b_{752} 133–4°, n_D^{20} 1.4157, d_{20} 1.1080. Similarly are prepd.; 79.6% $ClCH_2CH(OEt)_2$, b_{35} 71–2°, n_D^{20} 1.4175, d_{20} 1.0172; 70% $ClCH_2CH(OCHMe_2)_2$, b_{14} 57°, n_D^{20} 1.4283, d_{20} 0.9809; 91% $ClCH_2CH(OBu)_2$, b_{17} 115–15.7°, n_D^{20} 1.4330, d_{20} 0.9082. The prepn. in the presence of KOH gives the same yield.

G. M. Kosolapoff

4-19-54

SHOSTAKOVSKIY, M. F.

Chem
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Chem Abs V 48
1-25-54
Organic Chemistry

✓Trimer of thioacetaldehyde (β-form) (β-1,3,5-trimethyl-2,4,6-trithiane). M. F. Shostakovskii, E. N. Prilezhaeva, and E. S. Shapiro. *Akad. Nauk S.S.S.R., Inst. Org. Khim., Sintezy Org. Soedinenii, Sbornik* 2, 126-8(1952).—BuOCH:CH_2 (15 g.) cooled to −10° is satd. over 1 hr. with dry HCl to form MeCHClOBu, and the product is directly treated at −10 to −15° with H_2S (thoroughly dry) for 1 hr., after which H_2S is passed in at room temp. until no more absorption takes place. The product is washed with H_2O on a glass filter, yielding 83-8% *Me-CH.S.CHMe.S.CHMe.S*, m. 125-6° (from EtOH). Other alkyl vinyl ethers can be used similarly. G. M. K.

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7-28-54

SHOSTAKOVSKIY, M.F.

Chem Abs V48
1-25-54
Organic Chemistry

2-Chlorovinyl butyl ether. M. F. Shostakovskiĭ and F. P. Sidel'kovskaya. Akad. *Nauk S.S.S.R., Inst. Org. Khim., Sintezy Org. Soedinenii, Sbornik* 2, 144-5(1952); cf. *C.A.* 44, 7754*h*.—Heating 100 g. $ClCH_2CHClOBu$ and 130 g. Et_2NPh at 70-80° 35 hrs. with stirring, followed by filtration of the amine-HCl (85 g.), washing the ppt. with Et_2O, and distn. of the combined filtrates gave 66% *ClCH:-CHOBu*, b_{15} 48-50°, d_{20} 0.9883, n^{20}_D 1.4428. Similarly are obtained: 35% *ClCH:CHOEt*, b_{17} 47.5-8.5°, d_{20} 1.0386, n^{20}_D 1.4385; and 25% *ClCH:CHOCHMe*$_2$, b_{10} 44.5-5.7°, n^{20}_D 1.4390, d_{20} 1.0240. As by-products in these prepns. there are formed acetals: $ClCH_2CH(OR)_2$. G. M. K.

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1-25-54
Organic Chemistry

Ethyl butyl acetal. M. F. Shostakovskii and N. A. Gershtein. *Akad. Nauk S.S.S.R., Inst. Org. Khim., Sintezy Org. Soedinenii, Sbornik* 2, 154-61(1952); cf. *C.A.* 41, 1909c; 43, 3785i.—To 100 g. $BuOCH{:}CH_2$ is added with stirring 46 g. abs. EtOH containing 1 drop concd. HCl (temp. rises to 99°) and the mixt. is stirred until the temp. drops to room level. After allowing the mixt. to stand overnight, it is neutralized with K_2CO_3 and distd. yielding 16% $MeCH(OEt)_2$, b. 103-4°, 45% $MeCH(OEt)OBu$, b. 148-9°, and 20% $MeCH(OBu)_2$, b. 183.5-5.0°. In another procedure 200 g. $BuOCH{:}CH_2$ and 92 g. abs. EtOH are heated in a rotating autoclave 8-10 hrs. at 100-20°; distn. yields 24% $MeCH(OEt)_2$, 45.7% $MeCH(OEt)OBu$ and 19.2% $MeCH(OBu)_2$, along with BuOH and AcH. Pure $MeCH(OBu)OEt$, b_{760} 148-9°, d_{20} 0.8312, n_D^{20} 1.3991. The following acetals can be readily prepd. by this procedure and the following cases are listed (% yield, acetal, b.p., d_{20}, and n_D^{20} given): 92.8, $MeCH(OEt)_2$, 103-4°, 0.8254, 1.3820; 68.7, $MeCH(OCHMe_2)_2$, 125-8°, 0.8142, 1.3882; 81.5, $MeCH(OBu)_2$, 184-6°, 0.8267, 1.4090; 60, $MeCH(OMe)OEt$, 84.5-5.5°, 0.8264, 1.3765; 68.2, $MeCH(OEt)OCHMe_2$, 116-18°, 0.8144, 1.386; 65.6, $MeCH(OEt)OCH_2CHMe_2$, 155-8°, 0.8216, 1.3840; 50, $MeCH(OBu)OMe$, 130-1.5°, 0.8370, 1.3890; 57.3, $MeCH(OBu)OPr$, 160-5°, 0.8292, 1.4038; 74.5, $MeCH(OBu)OCHMe_2$, 151-6.5°, 0.8233, 1.3998; 91.2, $MeCH(OBu)OCH_2CHMe_2$, b_{14} 74-6°, 0.8235, 1.4062; 60.9, $MeCH(OBu)OCMe_3$, b_{14} 64-5°, 0.8250, 1.4068; 44.5, $MeCH(OBu)OCH_2CH_2CHMe_2$, b_{113} 135-8°, 0.8313, 1.4120; 25.5, $MeCH(OBu)OC_7H_{15}$, b_{16} 130-30.5°, 0.8397, 1.4210; 43.5, $MeCH(OBu)OC_8H_{17}$, b_{16} 158-60°, 0.8264, 1.4235; 44, $MeCH(OBu)OC_9H_{19}$, b_{13} 162-4°, 0.8288, 1.4260; 37, $MeCH(OBu)OC_6H_{11}$, b_{16} 123-5°, 0.8957, 1.4415; 81.6, $MeCH(OBu)OPh$, b_9 107-7.5°, 0.9588, 1.4830; 90.3, $MeCH(OBu)OC_{10}H_7$-2, b_5 163-5°, b_{14} 187-7.5°, 1.0543, 1.5548; 83.5, $MeCH(OBu)OCH_2CH{:}CH_2$, b. 162-5°, 0.8456, 1.4140; 89.3, $MeCH(OBu)OCMe_2C{:}CH$, 181-2°, 0.8579, 1.4190; 88.8, $MeCH(OMe)OCMe_2C{:}CCH{:}CH_2$, $b_{1.5}$ 43-5°, b_7 36.7-7.2°, 0.8924, 1.4530; 90.6, $MeCH(OEt)OCMe_2C{:}CCH{:}CH_2$, b_6 51.2-1.5°, 0.8865, 1.4520; 73, $MeCH(OBu)OCMe_2C{:}CCH{:}CH_2$, b_{10} 103-5.5°, 0.8727, 1.444; 86.3, $MeCH(OCH_2CHMe_2)OCMe_2C{:}CCH{:}CH_2$, $b_{5.5}$ 78.6-9.2°, 0.8678, 1.4475; 56, $MeCH(OBu)OC_{10}H_{17}$, b_{20} 146-58°, 0.8679, 1.4498.

G. M. K.

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SHOSTAKOVSKIY, M. F.

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Chem Abs V48
1-25-54
Organic Chemistry

Ethyl phenyl acetal. M. F. Shostakovskil and A. V. Bogdanova. Akad. Nauk S.S.S.R., Inst. Org. Khim., Sintezy Org. Soedinenil, Sbornik 2, 166–7(1952); cf. C.A. 45, 1501b.—To 8.5 g. KOH in 75 ml. abs. EtOH is added at 5–7° slowly 23.6 g. MeCHClOPh. After stirring 2 hrs. longer and allowing the mixt. to stand overnight, it was filtered and the filtrate distd. yielding 87% $MeCH(OEt)OPh$, b_4 70–1°, d_{20} 0.9940, n_D^{20} 1.4936. G. M. Kosolapoff

MF
1-28-54

SHOSTAKOVSKIY, M. F.

Chem abs V47
1-25-54
Organic Chemistry

✓ **Ethyl 2-chloroethyl acetal.** M. F. Shostakovskii and N. A. Gershtein. (Akad. Nauk S.S.S.R., Inst. Org. Khim., *Sintezy Org. Soedinenii, Sbornik* 2, 168–70(1952); cf. *C.A.* 43, 6159*c*.—To 161 g. $HOCH_2CH_2Cl$ was added in 2 hrs. 144 g. $EtOCH:CH_2$ (temp. rises to 30°); after 10–12 hrs. the mixt. was distd. in N yielding 46.5% *MeCH(OEt)-OCH₂CH₂Cl*, b_{25} 71.8–2.0°, b_3 23.2–3.8°, d_{20} 1.0101, n_D^{20} 1.4210. $MeCH(OEt)_2$ and $MeCH(OCH_2CH_2Cl)_2$, b_{20} 122–2.5°, are the by-products also formed. Similarly are prepd.: 60.8% $MeCH(OBu)OCH_2CH_2Cl$, b_8 70–1°, b_3 55–6°, d_{20} 0.9838, n_D^{20} 1.4280, along with 12.7% $MeCH(OCH_2CH_2Cl)_2$.
G. M. Kosolapoff

4-20-54

SHOSTAKOVSKII, M. F.

Chem Abs V 48
25-54
Organic Chemistry

1-Ethoxy-1-acetylmercaptoethane. E. N. Prilezhaeva, M. F. Shostakovskii, and E. S. Shapiro. *Akad. Nauk S.S.S.R., Inst. Org. Khim., Sintezy Org. Soedinenii, Sbornik* 2, 171-3(1952); cf. *C.A.* 46, 883*f*.—To 8.5 g. MeCH(SH)OEt in 20 g. dry pyridine was added at −5° 9 g. AcCl keeping the temp. under 5°. After stirring 0.5 hr. and allowing the mixt. to stand overnight, it was dild. with Et_2O and H_2O, the aq. layer was extd. with Et_2O, the combined org. layers were washed with H_2O, dried over Na_2SO_4 and distd. yielding 64% *MeCH(OEt)SAc*, b_{11} 60-3.5°. Pure product, b_{11} 62-2.5°, d_{20} 1.004, n_D^{20} 1.4556. Similarly are prepd.: 73% *MeCH(OBu)SAc*, b_7 78-8.5°, n_D^{20} 1.4560, d_{20} 0.9664; 55-6% *MeCH(OEt)SBz*, b_4 120-20.5°, n_D^{20} 1.5472, d_{20} 1.0891; 36-40% *MeCH(OBu)SBz*, b_4 139-40°, n_D^{20} 1.5346, d_{20} 1.0492.

G. M. Kosolapoff

SHOSTAKOVSKIY,M. F.

Chem Abs V 48
1-25-54
Organic Chemistry

Chem 4
④

1-Ethoxyethyl mercaptan and bis(1-ethoxyethyl) sulfide. M. F. Shostakovskii, E. N. Prilezhaeva, and E. S. Shapiro. *Akad. Nauk S.S.S.R., Inst. Org. Khim., Sintezy Org. Soedinenii, Sbornik* 2, 174–8(1952); cf. *C.A.* 46, 883*f*.—$EtOCH{:}CH_2$ (20 g.) in an ampul is flushed with a stream of dry H_2S, then chilled with liquid N for condensation of 28–8.5 g. H_2S in the ampul. The latter is rapidly sealed and placed into an autoclave for 20–4 hrs. under a pressure of 15–16 atm. of N or H (good quality of ampuls is strongly advised). The ampul is opened after chilling in liquid N and the contents are distd. yielding 47% *MeCH(OEt)SH*, b_{11} 38–9°, and 46.9% $S(CHMeOEt)_2$, b_4 58.2–8.6°. Some $MeCH(OEt)_2$ is also formed. The proportions of the products are varied by variation of the proportion of the reagents. Similarly can be prepd.: 28–9% *MeCH(OBu)SH*, $b_{20.5}$ 52.2–3.0°, and 65–6% $S(CHMeOBu)_2$, $b_{3.5}$ 96.5–6.7°, from 1 mole $BuOCH{:}CH_2$ and 1.3 moles H_2S. Higher proportion of H_2S yields more mercaptan and less sulfide.

G. M. Kosolapoff

SHOSTAKOVSKIY, M.F.

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Chem Abs V48
1-25-54
Organic Chemistry

α-**Ethoxyethyl formate.** N. A. Gershtein and M. F. Shostakovskii. *Akad. Nauk S.S.S.R., Inst. Org. Khim. Org. Soedinenii, Sbornik* 2, 179-80(1952); cf. *C.A.* 43, 3785i; Voronkov, *C.A.* 43, 6576d.—To 72 g. $EtOCH:CH_2$ was added with stirring at cooling below −5° (max. temp. must be under 11° at the end of addn.) 46 g. HCO_2H (b. 100-1°). After stirring 2-3 hrs. the mixt. was left overnight, when distn. *in vacuo* under N gave 92% $MeCH(OEt)O_2CH$, b_{14} 38-9°, d_{20} 0.9751, n_D^{20} 1.3874. Similarly is prepd. 85.7% $MeCH(OBu)O_2CH$, b_{14} 72.2-2.5°, d_{20} 0.9272, n_D^{20} 1.4020. G. M. Kosolapoff

SHOSTAKOVSKIY, M. F., GERSHTEYN, N. A.,

Acylals

Synthesis and properties of unsaturated-alkoxyethylidene esters of carboxylic acids (acylals). Izv.AN SSSR Otd. khim. nauk No. 3, 1952.

Monthly List of Russian Accessions, Library of Congress, November, 1952. UNCLASSIFIED.

SHOSTAKOVSKIY, M. F.

USSR/Chemistry - Organic Sulfur Compounds May/Jun 52

"Synthesis of Sulfur Compounds on the Basis of Simple Vinyl Ethers. Part 5. Some New Representatives of the α,β- and β,β-Dialkoxydiethylsulfides," Ye. N. Prilezhayeva, E. S. Shapiro, M. F. Shostakovskiy, Inst of Org Chem, Acad Sci USSR

"Iz Ak Nauk, Otdel Khim Nauk" No 3, pp 478-483

Addn of H_2S to vinyl isobutyl and vinyl isoamyl ethers in presence of HCl in dioxane forms mixts of α,β- and β,β-dialkoxyethylsulfides. Some chem conversions of new homologues of the dialkoxydiethylsulfide and of the β,β-dialkoxydiethylmercaptal series were studied.

PA 220T11

SHOSTAKOVSKIY, M. F.

USSR/Chemistry - Vinyl Ethers May/Jun 52

"Synthesis of Vinyl Ethers of Higher Fatty Alcohols," M.F. Shostakovskiy, B.I. Mikhant'yev, V.A. Neterman, Inst of Org Chem, Acad Sci USSR

"Iz Ak Nauk, Otdel Khim Nauk" No 3, pp 484-488

Studied vinylization of fatty alcs C_6 to C_{10}. Obtained vinyl ethers C_8 to C_{12} in yields of 80.4 to 89.2% of the theoretical yield. Gives the phys characteristics of the synthesized vinyl ethers.

220T12

SHOSTAKOVSKIY, M. F.

USSR/Chemistry - High-Molecular Compounds Jul/Aug 52

"Synthesis and Polymerization of Vinylcaprolactam," M. F. Shostakovskiy, N. A. Medzykhovskiy, M. G. Zelenskaya, Inst of Org Chem, Acad Sci USSR

"Iz Ak Nauk SSSR, Otdel Khim Nauk" No 4, pp 682-689

Parallel to investigations on vinylpyrollidone, authors carried out work on vinylcaprolactam (I) and its polymers, because this product is made from industrial raw material that is more easily accessible in the USSR. Found conditions under

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which I is obtained with a yield of ~70%. In the vinylation of ε-caprolactam (II) with acetylene, used as a catalyst "K salt of II, i. e., product of the interaction of potassium metal with II. Upon synthesis, I crystallizes readily. Hydrolysis of I leads to acetaldehyde, II, and salt of ε-aminocaproic acid. Polymerization of I proceeds well in the presence of hydrogen peroxide after heating to 140-150°. Isolated cryst product of reaction of I with O_2. This product may serve as peroxidic initiator of polymerization of I. Polymerization of I under the action of heat does not take place.

229T17

SHOSTAKOVSKIY, M. F.

USSR/Chemistry - High-Molecular Compounds Jul/Aug 52

"Synthesis and Transformations of Vinylcaprolactam. I. Polymerization in the Presence of Hydrogen Peroxide," M. F. Shostakovskiy, F. P. Sidel'kovskaya, M.G. Zelenskaya, Inst of Org Chem, Acad Sci USSR

"Iz Ak Nauk SSSR, Otdel Khim Nauk" No 4, pp 690-695

Using undild acetylene (authors state that this is the procedure customary in the USSR as distinguished from foreign practice), the authors vinylated caprolactam. They found that the Na salt

229T18

of caprolactam (product of interaction of Na metal with caprolactam) is a suitable catalyst for the vinylation. They state that it is safer to use Na salt than K salt. They investigated polymerization of vinylcaprolactam in the presence of H_2O_2 at temps in the range 100-150° and found that with higher temps the rate of polymerization increases, while the quantity of catalyst that is needed drops.

229T18

1. SHOSTAKOVSKIY, M. F.; MIKHANT'YEV, B. I.; OVCHINNIKOVA, N. N.

2. USSR (600)

4. Vinylation

7. Indirect vinylation of aliphatic alchols. Izv. AN SSSR. Otd. khim. nauk. No. 6, 1952.

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

1. SHOSTAKOVSKIY, M. F., BOGDANOVA, A. V.

2. USSR (600)

4. Acetals

7. Investigation of acetylenic alcohols and glycols. Part 2. Synthesis of mono- and diacetals of tetramethylbutynediol. Izv. AN SSSR Otd. khim. nauk no.6 1952

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

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CP

Synthesis of vinyl ether of guaiacol and a study of its properties. M. F. Shostakovskii, V. P. Shishkov, and M. G. Zelenskaya. *Zhur. Priklad. Khim.* (J. Applied Chem.) 24, 1166-72(1952).—Heating guaiacol in an autoclave with acetylene and 50% aq. KOH under 15 atm. H 36 hrs. to 180-200° gave after steam distn. 62% *vinyl ether of guaiacol* (I), b_{760} 200.5-2.0°, b_{10} 112-13°, d_4^{20} 1.0648, n_D^{20} 1.5398. Heating 450 g. guaiacol with 450 g. $(CH_2Cl)_2$ and 75 g. KOH 10 hrs. at 140-50° gave 29% *o-$MeOC_6H_4OCH_2CH_2Cl$*, b_8 140-1°, b. 250-1°, m. 44°, which, treated with alc. KOH 4 hrs. at 80°, gave 52% I, identical with the above. Hydrolysis of I in 10% H_2SO_4 at 60° is rather slow and in 6 hrs. 46% remains unreacted; addn. of dioxane as a mutual solvent hastens the hydrolysis to some extent; at 100° the hydrolysis is 60% complete in 5 hrs. without and 89% complete with dioxane. I polymerizes slowly with a $FeCl_3$ catalyst at room temp. but at 80° it forms a blue viscous mass within 3 hrs.

G. M. Kosolapoff

CA

Organic Chemistry 10

Synthesis and properties of the polymer of vinyl ethyl ether. M. F. Shostakovskii, F. P. Sidel'kovskaya, and V. A. Gladyshevskaya. *Zhur. Priklad. Khim.* (J. Applied Chem.) 25, 102-4(1952).—The polymer of highest mol. wt. is obtainable only from a very pure monomer, which is best purified by distn., 5 aq. washes, drying with K_2CO_3, then with Na, and redistn. Freshly distd. pure $EtOCH:CH_2$, b. 35.5°, n_D^{20} 1.3778, d_4^{20} 0.7585, should not have any C_2H_2 or peroxides. To the monomer is added dropwise 5% $FeCl_3.6H_2O$ in EtOH or BuOH, which leads to a delayed vigorous reaction and thickening of the material, which is placed in a bath at 45-50°, more catalyst soln. added until the desired 0.03 mole/100 ml. ether is attained, the process continued 3-4 hrs. at 45° (sufficient for a 200-g. batch), and the low-boiling matter removed *in vacuo*, leaving the polymer, n_D^{20} 1.4250-1.4540, η 1.13-1.20 poises (mol. wt. 4000). The product is nearly solid, insol. in H_2O, sol. in org. solvents, including EtOH. Its viscosity drops rapidly at 70-80°, apparently via oxidative destruction; however, even at 200-60° the material loss is but 0.3% in 3 hrs., although an AcH odor is pronounced. The polymer is stable to H_2O at room temp.

G. M. Kosolapoff

SHOSTAKOVSKIY, M.F.; ZELENSKAYA, M.G.

Properties and transformations of vinyl guaiacyl ether. Zhur. Priklad. Khim. 25, 1221-5 '52. (MLRA 5:11)
(CA 47 no.17:8678 '53)

SHOSTAKOVSKIY, M. F.

Ethylvinyl Ether; Polymers and Polymerization

Polymer of ethylvinyl ether, synthesis and properties.
Zhur. prikl. khim. 25, No. 1, 1952
Laboratoriya Vinilovykh Sovidineniy Instituta Organicheskoy
Shimii AN SSSR

SO: *Monthly List of Russian Accessions*, Library of Congress, August 1952 1953, Uncl.

USSR/Chemistry - Vinyl Ethers, Catalysts Aug 52

"The Catalytic Hydrogenation of Vinyl Ethers,"
D. V. Sokol'sky, M. F. Shostakovsky, B. I. Mikhant'ev,
F. G. Golodov, Inst of Org Chem, Acad Sci USSR and
Kazakh SSR

"Zhur Prik Khim" Vol 25, No 8, pp 867-875

Vinyl ethyl, vinyl isopropyl and vinyl butyl ethers can be hydrogenated quantitatively by using a low temp and aq solns, and in the presence of nickel and Pd/$CaCO_3$ catalysts. Hydrogenation at temps close to zero requires little time. With the 2d

228T11

batch of vinyl ether, the activity of the catalyst increases, and the rate of hydrogenation is shortened from 3 hrs to 20-30 min. For H-volumetric analysis of vinyl butyl ether, the best catalyst is Ni, and for vinyl isopropyl ether the best catalyst is Pd/$CaCO_3$. Both catalysts are suitable for the hydrogenation of vinyl ethyl ether. The emf at the catalyst was measured during the course of the reaction and a special jacketed vessel made of Mo glass used.

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SHOSTAKOVSKIY, M. F.

SHOSTAKOVSKY, M. F.

SHOSTAKOVSKIY, M.F.; BANKVITSER, A.L., redaktor.

[Academician Aleksei Evgrafovich Favorskii] Akademik Aleksei Evgrafovich Favorskii. Moskva, Gos. nauchno-tekhn. izd-vo khim. lit-ry, 1953. 157 p. (MLRA 7:4)
(Favorskii, Aleksei Evgrafovich, 1860-1945)

SHOSTAKOVSKIY, M. F.

Transformations of vinyl ethers. VIII. Transformations of acetals of ethylene glycol. M. F. Shostakovskii, N. A. Gershtein, and Z. S. Volkova. *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.* 1953, 89-95(Engl. translation).—See *C.A.* 48, 3249*f*.
H. L. H.

SHOSTAKOVSKIY, M.F.

✓ **Activation of vinylcaprolactam in the presence of hydrogen peroxide.** M. F. Shostakovskii and E. P. Sidel'kovskaya. *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.* 1953, 97-9 (Engl. translation).—See *C.A.* 48, 3264*f*. H. L. H.

SHOSTAKOVSKIY, M.F.

Chemical Abst.
Vol. 48 No. 6
Mar. 25, 1954
Organic Chemistry

Activation of vinylcaprolactam in the presence of hydrogen peroxide. M. F. Shostakovskii and F. P. Sidel'kovskaya. *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1 53, 108-11.—The reaction of *N*-vinylcaprolactam (I) with H_2O in the presence of H_2O_2 is a 2-fold event, involving hydrolysis to caprolactam and AcH, and polymerization at the vinyl group. The latter reaction acquires greater and greater predominance as temp. is increased and the diln. of I is decreased. The reaction was followed by detn. of the AcH and isolation of the polymer (a resinous solid). A 1:10 molar mixt. of I and H_2O in 4 hrs. at 98-9° gave 10.5% polymer and 64% caprolactam; with a 1:15 molar ratio this became 15.8 and 75%, resp., while with a 1:135 ratio 7.5 and 84.5%, resp. Only a trace of reaction occurs at 79-80°. Without H_2O_2 no reaction occurs at 100°. In the above expts. 0.5 g. 28% H_2O_2 was used per 15.9 g. I.

G. M. Kosolapoff

SHOSTAKOVSKIY, M.F.

✓ Comparative evaluation of the action of metal chlorides in processes of polymerization. I. Catalytic polymerization of styrene under the influence of ferric chloride and stannic chloride. M. F. Shostakovskii and V. A. Gladyshevskaya. *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.* 1953, 319-23 (Engl. translation).—See *C.A.* 47, 10372a. H. L. H.

SHOSTAKOVSKIY, M. F.

Synthesis of [illegible] compounds on the basis of vinyl ethers and acetylene. VI. Reaction of mercaptans with vinyl ethers. M. F. Shostakovskii, E. N. Prilezhaeva, and E. S. Shapiro. *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1953, 357-67; cf. *C.A.* 47, 4810g.—Into 3.9 g. EtSH and 7.2 g. $EtOCH{:}CH_2$ at −20° was briefly passed a current of SO_2, the mixt. stirred 2 hrs. at room temp., and left overnight; distn. gave 81.7% *MeCH(OEt)SEt*, b_{760} 67.5-8.5°, b_{11} 53-4°, n_D^{20} 1.4428, d_{20} 0.900; alc. $HgCl_2$ gives a quant. ppt. of EtSHgCl. Similarly EtSH and $BuOCH{:}CH_2$ in the presence of little SO_2 after 20 hrs. in a sealed tube at room temp. gave 86.5% *MeCH(OBu)SEt*, b_5 56-7°, n_D^{20} 1.4461, d_{20} 0.8855. At room temp. the reaction of EtSH with $EtOCH{:}CH_2$ catalyzed by O is not complete even in 2 months; heating some 60 hrs. at 60-5° gave 95% *$EtSCH_2CH_2OEt$* (I), b_{25} 78-8.5°, n_D^{20} 1.4507, d_{20} 0.9126; the catalytic amts. of dissolved O were merely the traces left in the starting materials after vacuum distns. With alc. $HgCl_2$ the product forms a viscous unknown mass. Oxidation of I with H_2O_2 in AcOH gave 50.7% *sulfoxide* ($C_6H_{14}O_2S$), b_6 112.2-13.5°, n_D^{20} 1.4696, d_{20} 1.0354. Similar reaction of $BuOCH{:}CH_2$ with EtSH was even slower and gave the max. yield (96.8%) of *$BuOCH_2CH_2SEt$*, b_5 65-6°, n_D^{20} 1.4520, d_{20} 0.8979, after 35 hrs. at 60°. With H_2O_2 in AcOH it gave the *sulfoxide*, b_{15} 112-12.5°, b_3 117.2-17.4°, n_D^{20} 1.4664, d_{20} 0.9955. $BuOCH{:}CH_2$ and $BuOCH_2CH_2SH$ under similar reaction conditions heated 50 hrs. to 60-5° in a period of 7 days gave 93.9% *$(BuOCH_2CH_2)_2S$*, $b_{4.5}$ 130-1.0°, n_D^{20} 1.4560, d_{20} not cited. $EtOCH{:}CH_2$ and EtSH react more rapidly in ordinary closed flask in contact with atm. O and in 6 days give 94.6% addn. product. If the vinyl ether contains some peroxide the reaction is retarded. Completely peroxide-free starting material gave a mixt. of reaction products contg. some 97.5% $EtSCH_2CH_2OEt$ and only 2.5% MeCH(OEt)SEt; if the ether contains peroxides from air contact, the reaction product is mainly (65.5%) the latter product, and only 34.5% of the former product is formed. Under conditions of free air access, $EtOCH{:}CH_2$ and MeCH(OEt)SH yield only *$MeCH(SCH_2CH_2OEt)OEt$*, $b_{2.5}$ 65-8°, n_D^{20} 1.4505. $BuOCH{:}CH_2$ adds quite less rapidly than the Et analog and after 8 hrs. at 50° or 12 hrs. at 100° yields 87-9% addn. products with EtSH. At room temp. the product is mainly $BuOCH_2CH_2SEt$ with some 13% MeCH(OBu)SEt. At elevated temp. the main product (59-62%) is the latter substance, while the former substance is the lesser constituent (37-40%). Pure *MeCH(OBu)SEt*, b_4 56.1-6.2°, n_D^{20} 1.4476, d_{20} 0.8897; pure *$BuOCH_2CH_2SEt$*, $b_{3.5}$ 67.8-8.2°, n_D^{20} 1.4521, d_{20} 0.8981. Keeping $BuOCH{:}CH_2$ with $BuOCH_2CH_2SH$ 20 days at room temp. gave 85.7% mixed *$(BuOCH_2CH_2)_2S$* and *$MeCH(OBu)SCH_2CH_2OBu$*, b_2 118-24°, contg. 34.5% of the latter. Similarly $BuOCH{:}CH_2$ and MeCH(OBu)SH after 7 days gave 60% mixed $MeCH(OBu)SCH_2CH_2OBu$ and $[MeCH(OBu)]_2S$, b_1 102-6°, contg. 90.4% of the former. A mixt. of 30 g. $BuOCH{:}CH_2$ and 9.3 g. AcSH after 2 days gave 90.7% *$AcSCH_2CH_2OBu$*, $b_{3.1}$ 84-4.1°, n_D^{20} 1.4605, d_{20} 0.9805. G. M. Kosolapoff

SHOSTAKOVSKIY, M.F.

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Synthesis and transformations of vinyl ethers of ethanolamines. III. The character of the double bond of vinyl ethers of ethanolamines. M. F. Shostakovskii and I. A. Chekulaeva. *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1953, 368-73; cf. *C.A.* 47, 1595e, 9911g.—Passage of ethylene oxide into 75 g. Et_2NH in 250 ml. H_2O over 4.5 hrs. at 5-10° gave, after addn. of 60-70 g., 60% $Et_2NCH_2CH_2OH$, b. 159-61°, n_D^{20} 1.4412, d_{20} 0.8838. This with 10% ROK in C_4H_8 was heated in an autoclave under 15 atm. C_2H_2 initial pressure to 140-50°, yielding 95-8% $Et_2NCH_2CH_2OCH:CH_2$ (I), b. 155-7°, n_D^{20} 1.4328, d_{20} 0.8396. Without C_4H_8 the yield drops to 83-5%, while KOH as catalyst gave a 0% yield, and much tar. Hydrogenation of the product over Raney Ni gave $Et_2NCH_2CH_2$-

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$C_4H_{10}O_4N_2Ag.2NH_3$. At 20°, mono-Ag aspartate (II) absorbs more than 3 NH_3, but no definite compd. could be isolated; at 0° and −18° it forms the *tetra-NH_3 complex*, $C_4H_6O_4NAg.4NH_3$. To prep. it successfully, II must be very finely divided (by adding its alc. soln.), for the granular ppt. formed by digestion of $H_2NCH(CO_2Ag)CH_2CO_2Ag$ (III) in hot aq. aspartic acid gives variable and uncertain results. At 20° and 0°, III forms $C_4H_5O_4NAg_2.3NH_3$ and, at −18°, $C_4H_5O_4NAg_2.4NH_3$ (cf. Bruni and Levi, no source cited). At 20°, Ag glutamate absorbs more than $3NH_3$, but no definite compd. could be isolated; at −18° the *tetra-NH_3 complex*, $C_5H_8O_4NAg.4NH_3$, is formed. At 20°, mono-Ag glutathionate absorbs more than $3NH_3$, but no definite compd. was isolated; at 0° and −18° the *tetra-NH_3 complex*, $C_{10}H_{16}O_6N_3SAg.4NH_3$, is formed. At 20°, di-Ag glutathionate forms the *tetra-NH_3 complex*, $C_{10}H_{15}O_6N_3SAg_2.4NH_3$, and at 0° and −18° the *hexa-NH_3 complex*, $C_{10}H_{15}O_6N_3SAg_2.6NH_3$. At 20°, D-$Me_2CHCH(NH_2)CO_2Ag$ absorbs more than $2NH_3$, but does not give a definite complex; at 0° and −18°, it forms the *tri-NH_3 complex*, $C_5H_{10}O_2NAg.3NH_3$. At 20°, 0°, and −18°, the Ag deriv. of saccharin forms the *tri-NH_3 complex*, $C_7H_4O_3SNAg.3NH_3$. These results parallel those obtained by Ley for Cu complexes [*Z. Elektrochem.* 10, 954(1904); *C.A.* 3, 1015]. In conjunction with the earlier work of B.-M., the expts. lead to certain general conclusions. For the NH_3 group to be co- [illegible]

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Indirect vinylation of monocarboxylic acids and hydroxy acids. M. F. Shostakovskii, B. I. Mikhant'ev, and N. N. Ovchinnikova. *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1953, 556–61.—Transesterification of vinyl ethers with acids yields vinyl esters in moderate recoveries. Thus, stirring 23.2 g. $AmCO_2H$, 100 g. $BuOCH{:}CH_2$, and 0.1 g. P_2O_5 led to a spontaneous reaction (temp. rise up to 105°) despite external cooling; after some 35–40 min. the mixt. was neutralized with K_2CO_3 and yielded 72.5 g. $BuOCH{:}CH_2$, some AcH, and 47% *$AmCO_2CH{:}CH_2$*, b. 168–70°, n^{20}_D 1.4160, d_{20} 0.8995; (hydrogenation gave the satd. analog); small amts. of $MeCH(OBu)_2$ were also recovered from the original reaction mixt., along with traces of $AmCO_2Bu$ and 28% *$MeCH(OBu)O_2CAm$*, b_4 88–90°, n^{20}_D 1.4140. Similarly 18 g. $MeCH(OH)CO_2H$ and 100 g. $BuOCH{:}CH_2$ with 0.1 g. P_2O_5 gave 85.1% unreacted $BuOCH{:}CH_2$, 15% *$MeCH(OH)CO_2CH{:}CH_2$*, b. 151–3°, d_{20} 1.064, n^{20}_D 1.4088, 3.4 g. $MeCH(OBu)_2$, 13.4% *$MeCH(OBu)O_2CCH(OH)Me$*, b. 188–9°, n^{20}_D 1.4195, d_{20} 0.9683. $MeCH(OH)CH_2CO_2H$ (10.4 g.) and 50 g. $BuOCH{:}CH_2$ with 0.1 g. P_2O_5 gave 86% unreacted $BuOCH{:}CH_2$, 18% *$MeCH(OH)CH_2CO_2CH{:}CH_2$*, b. 170–3°, d_{20} 1.0713, n^{20}_D 1.4136, and 3.8 g. $MeCH(OBu)_2$. G. M. Kosolapoff

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USSR.

Transformations of vinyl ethers. Chemical properties of alkyl 2-chloroethyl acetals. M. F. Shostakovskii and N. A. Gershtein. *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.* 1953, 643-6(Engl. translation).—See *C.A.* 48, 13018*c*.

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Transformations of vinyl ethers. Chemical properties of alkyl 2-chloroethyl acetals. M. F. Shostakovskii and N. A. Gershtein (Inst. Org. Chem. Acad. Sci. U.S.S.R., Moscow). *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1953, 716–20; cf. *C.A.* 45, 2851*i*; 47, 1595*e*.—To 57 g. KOH in 480 g. abs. EtOH was added over 2.5 hrs. 77 g. MeCH(OEt)OCH_2CH_2Cl and the mixt. kept 8 hrs. at 80°, and filtered, yielding 11.7% *MeCH(OEt)*OCH_2CH_2OEt, b_4 40–40.5°, d_{20} 0.8955. Similarly was obtained 96.2% *MeCH(OBu)*OCH_2CH_2OEt, b_5 71–2.5°, d_{20} 0.8832, n^{20}_D 1.4090. Stirring 48 g. KOH, 414 g. abs. EtOH, and 47 g. $MeCH(OCH_2CH_2Cl)_2$ on a steam bath 15 hrs. gave 10 g. $MeCH(OCH_2CH_2OEt)_2$, b_{11} 109–10°, b_{10} 107–8°, n^{20}_D 1.4181, d_{20} 0.9379. Hydrolysis of the products readily gave AcH, the detn. of which was used as an analytical method.

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Ionic copolymerization of vinyl ethers. M. F. Shostakovskii, B. I. Mikhant'ev, and N. N. Ovchinnikova (Inst. Org. Chem. Acad. Sci. U.S.S.R., Moscow). *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1953, 721–5; cf. *C.A.* 48, 3243a.—To 72 g. $EtOCH:CH_2$ and 123 g. $CH_2:CHOC_6H_{13}$ was added at 35° 1–2 drops catalyst (5% $FeCl_3.6H_2O$ in BuOH); the reaction proceeded vigorously with heat evolution, and after 2 hrs., the mass was heated *in vacuo* to 100°, yielding a residue of 85% crude polymer. Extn. with EtOH and fractional pptn. with H_2O gave: polymer of $EtOCH:CH_2$, 2:1 copolymer of the Et and C_6H_{13} ethers, and a series of copolymers with reactant ratios ranging to 5:4. Similarly were isolated 1:1 copolymers of the following pairs (% yield, d_{20}; n^{20}_D, viscosity in centipoises of 0.1*M* soln. in C_6H_6 at 20°, and solubilities given): $EtOCH:CH_2$—$CH_2:CHOCHMe_2$, 52, 0.9270, 1.4510, 0.7867, sol. in EtOH higher alcs., Et_2O, C_6H_6, Me_2CO; $EtOCH:CH_2$—$CH_2:CHOBu$, 54, 0.9245, 1.4530, 0.7349, soly. as above; $EtOCH:CH_2$—$CH_2:CHOAm$-iso, 48, 0.9244, 1.4542, 0.6885, soly. as above; $EtOCH:CH_2$—$CH_2:CHOC_6H_{13}$, 43, 0.9233, 1.4558, 0.8054, soly. as above; iso-$PrOCH:CH_2$—$CH_2:CHOBu$, 75, 0.9230, 1.4545, 0.7330, soly. as above but not sol. in EtOH; $BuOCH:CH_2$—$CH_2:CHOC_7H_{15}$, 79, 0.9260, 1.4590, 0.8662, soly. as above but not sol. in EtOH and PrOH; $BuOCH:CH_2$—$CH_2:CHOC_8H_{17}$, 76, 0.9243, 1.4620, 0.9595, soly. as above; iso-hexyl vinyl ether—$CH_2:CHOC_{10}H_{21}$, 51, 0.9217, 1.4670, 0.8464, soly. as above but not sol. in alcs. below iso-AmOH; iso-$AmOCH:CH_2$—$CH_2:CHOC_8H_{17}$, 50, 0.9198, 1.4623, 0.8311, soly. as above; $C_6H_{13}OCH:CH_2$—$CH_2:CHOC_{10}H_{21}$, 59, 0.9231, 1.4657, 0.8807, soly. as above but not sol. in alcs. below hexyl; $BuOCH:CH_2$—$CH_2:CHOC_6H_{11}$, 62, 0.9316, 1.4800, 0.8818, sol. in BuOH, Et_2O, and C_6H_6; $BuOCH:CH_2$—$PhOCH:CH_2$, 49, 0.9620, 1.5070, 0.7312, soly. not shown.

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USSR.

✓ Synthesis and transformations of oxygen-containing organosilicon compounds. I. Synthesis of organosilicon acetals. M. F. Shostakovskii, I. A. Shikhiev, and D. A. Kochkin. *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.* 1953, 837-9(Engl. translation).—See *C.A.* 49, 1541*h*.

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SHOSTAKOVSKIY, M. F.

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Transformations of vinyl ethers. Synthesis of halo acetals on the basis of vinyl ethers. M. F. Shostakovskii and N. A. Gershtein. *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.* 1953, 927-9(Engl. translation).—See *C.A.* 49, 2307*d*. H. L. H.

SHOSTAKOVSKIY, M.F.

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Chemical transformation of unsaturated and high-molecular compounds. I. Copolymerization of methacrylic acid and vinyl alkyl ethers. M. F. Shostakovskii and A. M. Khomutov. *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.* 1953, 831-7(Engl. translation).—See *C.A.* 48, 6159c.

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SHOSTAKOVSKIY, M.F.

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✓Ionic polymerization of vinyl ethers. M. F. Shostakovskii, B. I. Mikhant'ev, and N. N. Ovchinnikova. *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.* 1953, 939-42 (Engl. translation).—See *C.A.* 49, 2290g. H. L. H.

SHOSTAKOVSKIY, M. F.

Synthesis and transformations of oxygen-containing organosilicon compounds. I. Synthesis of organosilicon acetals. M. F. Shostakovskii, I. A. Shikhiev, and D. A. Kochkin (Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1953, 941-4.—To 33 g. Et_3SiOH and 25 g. $BuOCH:CH_2$ was added 0.02 ml. 30% HCl and after 1 hr. the mixt. was heated 1 hr. at 80-93° and left overnight; after neutralization it yielded 55.17% *$MeCH(OBu)OSiEt_3$*, b_9 82-3°, d_{20} 0.8574, n^{20}_D 1.4271; this hydrolyzes slowly with 2% H_2SO_4 even at 60°; but reacts fairly well with 5% H_2SO_4 on a steam bath. Similarly Et_3SiOH and iso-$BuOCH:CH_2$ gave 51.7% *$MeCH(OCH_2CHMe_2)OSiEt_3$*, b_7 75-6°, d_{20} 0.8530, n^{20}_D 1.4252.

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✓**Transformations of vinyl ethers. Synthesis of halo acetals on the basis of vinyl ethers.** M. F. Shostakovskii and N. A. Gershtein (Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1950, 1043-7; cf. *C.A.* 43, 6159c.—Mixing alkyl vinyl ethers with $HOCH_2CH_2Cl$ readily gave the following acetals, $MeCH(OR)OCH_2CH_2Cl$, which were analyzed by hydrolysis with dil. H_2SO_4: (R, % yield, b.p./mm., d_{20}, and n_D^{20} given): Me, 61, 52-2.9°/16, 1.0541, 1.4211; *Pr*, 66.8, 65-7°/9, 0.9900, 1.4232; *Me₂CH*, 64.8, 42.5-4°/2, 0.9948, 1.4218; *iso-Bu*, 77.6, 68-9°/7, 0.9796, 1.4245; *iso-Am*, 93.2, 60-3°/1.5, 0.9672, 1.4212. Low yields (8-15%) of the corresponding sym. acetals were also formed in the reaction, as expected. The new products were: $MeCH(OCH_2CH_2Cl)_2$, $b_{11.5}$ 105.5-6.0°, d_{20} 1.1703, n_D^{20} 1.4529; and $MeCH(OCHMe_2)_2$, b_{760} 125.5-7.5°, d_{20} 0.8158, n_D^{20} 1.3900. G. M. Kosolapoff

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Chemical Abstracts
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Synthetic Resins
and Plastics

Chemical transformations of unsaturated and high-molecular compounds. I. Copolymerization of methacrylic acid and vinyl alkyl ethers. M. F. Shostakovskiĭ and A. M. Khomutov (Inst. Org. Chem., Acad. Sci. U.S.S.R., Moscow). *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1953, 1048–55.—Vinyl alkyl ethers and $CH_2:CMeCO_2H$ were copolymerized by heating in ampuls 72 hrs. at 60°. The copolymer of $EtOCH:CH_2$ was a hard solid when the components were used in 3:1 molar ratio (excess acid), but were viscous liquids when the ether was the predominant component. The copolymer from 3 moles $BuOCH:CH_2$ and 1 mole $CH_2:CMeCO_2H$ was a solid contg. 40.1% ether groups and was insol. in H_2O, forming a gel in MeOH; reversal of the proportions of monomers gave a solid product which was sol. in MeOH and which swelled and partly dissolved in H_2O. G. M. Kosolapoff