Acetylenic Ethers

Polymerization of Ethyl Ethynyl and Butyl Ethynyl Ethers

THOMAS L. JACOBS and NORMAN JUSTER
Department of Chemistry, University of California, Los Angeles, Calif., 90024,
and Pasadena City College, Pasadena, Calif., 91106

Both ethyl ethynyl ether and butyl ethynyl ether undergo a complex reaction at 25° C. or above with formation of a series of products of progressively higher viscosity and finally of a black glass with the approximate composition $(C_2H)_n$. With the ethyl ether, the first product is the dimer, 2,4-diethoxy-1-buten-3-yne, which is in equilibrium with the monomer. The next product is $C_8H_6O_2(OC_2H_5)_2$, which appears to be formed from 4 molecules of monomer or 2 of dimer. Further polymerization gives complex mixtures. Rates of polymerization were measured.

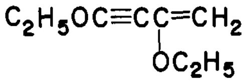
ACETYLENIC ETHERS in which the oxygen is directly attached to an acetylenic carbon are known to polymerize readily (*8-10*). The polymerization of ethynyl phenyl ether is a complicated process which has not been completely elucidated; in part formation of a linear polyene chain is apparently involved; this rapidly undergoes crosslinking in a second stage, possibly by a Diels-Alder reaction (*9*). The qualitative observation that ethyl ethynyl ether and butyl ethynyl ether polymerize somewhat more slowly has been reported (*8*), but further work has not been published because the process has proved to be even more complicated than that observed with ethynyl phenyl ether. The following incomplete account of work (*12*) on the polymerization of alkyl ethynyl ethers is presented now because others are becoming interested in the problem and the study is not being actively pursued in the authors' laboratory.

Several recent references (*3, 5, 15*) mention polybutoxyacetylene but give no information on its synthesis. The polymerization of alkoxyacetylenes with a Ziegler-type catalyst to yield a polyconjugated system was described in a recent patent (*13*). The formation of a dimer of ethyl ethynyl ether has been encountered in a reaction of this compound with sodamide in liquid ammonia (*1*) but the structure of the product has not been determined. Substituted alkyl ethynyl ethers, $RC{\equiv}COC_2H_5$, have also been observed (*7, 14*) to undergo a reaction in which 2 molecules of the acetylenic ether combine to form 2,4-dialkyl-3-ethoxy-2-cyclobuten-1-ones (*14*) with loss of ethylene. Alkynyl methyl ethers, which cannot eliminate an alkene in this way, do not give cyclobutenone derivatives, but polymerize at elevated temperatures; the polymers have not been studied (*14*).

Ethyl ethynyl ether and butyl ethynyl ether are stable at −18° C. and below in the absence of air and moisture. At 40° C., under a nitrogen atmosphere, or in tubes sealed under reduced pressure, these compounds become increasingly yellow and after about 4 days yield an amber, oily mixture which acts like a drying oil on standing in air. After 10 to 15 days this oil becomes a brown viscous jelly and, after a month, a brown-black tar. At 60° C. these same changes occur more rapidly and at 25° C. more slowly. Lengthy treatment at 40° to 60° C. or heating at 90° C. for 7 days yields an insoluble black glass. Except for a dimer found after about 2 hours of polymerization and also as a component of later polymer mixtures, the polymeric products obtained had empirical compositions that were not in agreement with those of monomer. Thus, except for dimer formation, true addition polymerization did not occur.

With ethyl ethynyl ether the dimer was the only polymeric material detectable after 2 hours at 40° C.; its concentration increased up to about 4 hours, remained constant for around 100 hours, and thereafter slowly decreased until after 30 days it could no longer be detected.

The dimer of ethyl ethynyl ether is a colorless, evil-smelling, sirupy liquid which slowly turns yellow on standing. The structure 2,4-diethoxy-1-buten-3-yne,

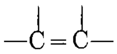


$$C_2H_5OC{\equiv}C\underset{\displaystyle OC_2H_5}{C}{=}CH_2$$

was established by spectral and chemical means. When the pure dimer was dissolved in carbon disulfide and examined spectroscopically, a typical acetylenic hydrogen stretching band developed rapidly at 3290 cm.$^{-1}$ and reached a constant value after 3 hours. This probably resulted from equilibration to form monomer. Pure dimer gave no precipitate of cuprous or silver derivative, but the equilibrated solution gave a precipitate. It is unlikely that the presence of acetylenic hydrogen can be accounted for by loss of ethanol to form 1-ethoxy-1,3-butadiyne because the broad infrared band at 3300 cm.$^{-1}$ shown by ethanol in carbon disulfide is absent. If the monosubstituted acetylenic material is ethyl ethynyl ether, the equilibrium mixture contains about 37% of dimer at 40° C. in 10% solution.

The course of the complex polymerization of ethyl ethynyl ether remains obscure and the many experiments (*12*) carried out to examine it are described only briefly. For the first 100 hours at 40° C. kinetic experiments gave a fairly constant specific rate and during this time a single compound, $C_8H_6O_2(OC_2H_5)_2$, I, appeared to be almost the only nonvolatile product formed. The molecular formula of I corresponds to combination of 4 molecules of ethyl ethynyl ether (or 2 of dimer) with loss of 2 molecules of ethylene. However, no more than traces of ethylene could be detected and approximately 2 moles of ethanol were produced for each mole of I. Ethanol and I were produced even when very careful attempts were made to exclude moisture during the polymerization and workup, but the ratio was reduced to 1.3 to 1 and the yield of I dropped from 8 to 12% to 6%; somewhat more ethylene was formed, but still very little. These results suggest that I is not a primary product of the polymerization but is formed by hydrolysis of such a product which reacts very rapidly with water. A vacuum train technique with very dry ethyl ethynyl ether would probably be required to study this.

The nature of the polymerization and the character of the polymers appeared to undergo a marked change after approximately 100 hours. At this point the polymerized mixture became tarry and its color darkened to reddish brown. Ethylene was always detected as a cleavage product following this time and ethanol did not increase in amount. The residues that remained after monomer and other volatile components were removed were shown by chromatography and other separation processes to be complex mixtures containing many components. Although many of these were not of very high molecular weight, it did not prove possible to isolate pure components for investigation. The empirical compositions of the residues varied with time and the cryoscopic molecular weights increased irregularly.

An attempt was made to examine the structures of the unseparated polymerization mixtures from longer experiments by hydrolysis with hydrogen chloride in wet, peroxide-free ether under mild conditions. The remaining ethoxyl content was thus removed as ethanol, suggesting that the ethoxyl groups were still present in  $-\overset{|}{C}=\overset{|}{C}-O-C_2H_5$ or $-C\equiv C-O-C_2H_5$ units. Treatment of the hydrolysis residues with hot aqueous potassium hydroxide did not lead to the production of acetic acid; the hydrolyzate contained organic acids but was partly polymeric and no pure compounds were isolated.

Ethyl ethynyl ether was also studied at 60° C. and the transformations appeared to parallel those at 40° C. A few experiments were carried out at 25° C.

The black glass which was the final product of the polymerization had the composition $(C_2H)_n$ (see Table II). It was insoluble in common solvents, acids, and bases. A similar substance was formed rapidly when earlier tarry polymers were heated above 100° C. under nitrogen. The glass was hard and brittle. A finely powdered sample sintered slightly at 300° C. but did not char or change further up to 800° C.; charring occurred in a Bunsen flame. The thin film formed between two glass plates clamped together and heated to ~300° C. was translucent and dark brown with black specks and some bubbles; the plates were cemented together but the bond was weak.

The black glass was attacked only slowly by hot, basic potassium permanganate in a procedure that has been used for degradation of coal (*11*) and reaction was incomplete after 5 days. Carbon dioxide and a small amount of acetic acid were the only products identified. Most of the glass appeared to be unchanged. The residue from this experiment was slowly attacked by hot nitric acid and completely dissolved after 600 hours, but carbon dioxide was the only product identified.

Butyl ethynyl ether was studied similarly, but less extensively, at both 40° and 60° C. Its transformations were slightly slower than those of the ethyl ether, but appeared to be very similar. A dimer was isolated, but not in sufficient quantity for detailed examination.

During the early part of the polymerization, rate data fitted equally well first- or second-order kinetics and no others. First-order fit is better very early in the polymerization and as it worsens with time, second-order fit improves. After around 100 hours at 40° C. or 75 hours at 60° C. the rate curves deviate from any simple order in an anomalous fashion; these times correspond to less than a single half life in each instance. The rate constants are approximately one tenth of those computed for ethynyl phenyl ether at 40° C.

No induction period was detectable with either ethyl or butyl ethynyl ether. The polymerizations of both monomers were relatively unaffected by free radical sources or inhibitors but were catalyzed by acids. Qualitative tests with 5 to 30 mole % of antimony trihalides, stannous chloride, stannic chloride, hydrochloric acid, and glacial acetic acid produced flashes of color (blue, magenta, red) and then vigorous polymerization to brown tars. Sulfuric acid and *p*-toluenesulfonic acid were highly catalytic and the cadmium halides somewhat less effective (iodide > bromide; chloride almost inactive). The experiments with acids would be expected to be complicated by formation of ethyl acetate (*2, 6*). The polymer mixtures resulting from cadmium halide catalysis were different in appearance, solubilities, sinter points, and other physical properties from the uncatalyzed polymers. Analysis of the material obtained by cadmium iodide catalysis disclosed the presence of more than 0.5 mole of cadmium per mole of monomer in the polymer and no detectable iodine. The polymer mixtures from sulfuric acid–catalyzed polymerizations contained the acid sulfate group in an amount nearly identical with the loss of alkoxyl content. The rate constants for polymerizations with and without catalysts are given in Table I; physical and analytical data for representative polymers are detailed in Table II.

EXPERIMENTAL

Infrared spectra were determined on a Perkin-Elmer Model 21 instrument except for a few early determinations made with a Beckman Model IR2; sodium chloride cells were used. Ultraviolet spectra were determined on a Cary recording spectrograph Model 11 PMS or a Beckman Model DU. Mass spectra were obtained on a Westinghouse Type LV instrument. Nuclear magnetic resonance spectra were obtained with a Varian Associates analytical NMR spectrometer Model A-60 (neat with tetramethylsilane as internal standard). Melting points were corrected.

Monomers were synthesized by two methods (*6, 8*). The yield of ethyl ethynyl ether from the reaction of chloroacetal with sodamide in liquid ammonia (*6*) was raised to 84% by use of pure chloroacetal and care to prevent manipulative loss of product. An additional 6% was isolated from various

Table I. Rate Constants for Polymerization[a]

Catalyst[b]	40° C. $k_1 \times 10^7$ sec.$^{-1}$	40° C. $k_2 \times 10^7$ liter mole^{-1} sec.$^{-1}$	60° C. $k_1 \times 10^7$ sec.$^{-1}$	60° C. $k_2 \times 10^7$ liter mole^{-1} sec.$^{-1}$
	Ethyl Ethynyl Ether			
None[c]	2.84	0.27	21.5	2.46
BP	2.84	0.27	25.0	3.38
BCBP	2.88	0.28	25.6	3.51
TAB	2.87	0.28	21.6	2.57
HDQ	3.28	0.32	24.5	3.22
PBNA	2.81	0.27	21.9	2.81
PTSA	43.2	9.54	80.7	14.6
3FSA	47.2	14.7	136.0	40.3
CdI_2	11.5	1.30	46.6	6.24
$CdBr_2$	4.85	0.48	31.4	3.74
$CdCl_2$	3.47	0.34	27.1	3.11
	Butyl Ethynyl Ether			
None[c]	2.60	0.33	19.7	3.05
BP	2.76	0.36	25.3	4.64
BCBP	2.82	0.37	26.2	4.87
TAB	2.52	0.33	23.6	4.24
HDQ	2.83	0.37	28.8	5.56
PBNA	2.67	0.35	23.1	4.09
PTSA	30.5	5.46	94.1	25.8
3FSA	36.2	6.97	163.0	40.2
CdI_2	9.67	1.33	43.4	7.69
$CdBr_2$	3.80	0.50	29.6	4.67
$CdCl_2$	2.84	0.36	22.1	3.30

[a] Rate constants calculated only for early part of polymerization when kinetic behavior was consistent. This corresponds to about 100 hours at 40° C. or 75 hours at 60° C. and in each instance is less than a single half life. [b] Catalysts added to a concentration of 0.5 mole %. BP, benzoyl peroxide. BCBP, bis-β-chlorobutyl peroxide. TAB, trityl azobenzene. HDQ, hydroquinone. PBNA, phenyl-2-naphthylamine. PTSA, *p*-toluenesulfonic acid. FSA, 3*F* sulfuric acid. [c] For comparison with data for phenyl ethynyl ether (*9*) where rate constant at 40° C. is $k_1 \times 10^6 = 2.2$ sec.$^{-1}$ and $k_2 \times 10^6 = 2.6$ weight fraction^{-1} sec.$^{-1}$, the values for ethyl and butyl ethynyl ethers at 40° C. are $k_2 \times 10^5 = 2.95$ weight fraction^{-1} sec.$^{-1}$ and 7.00 weight fraction^{-1} sec.$^{-1}$, respectively.

Table II. Physical and Analytical Data for Representative Polymers

Catalysts[a]	Time, Hr., Temp., ° C.	Sinter Point,[b] ° C.	Melting Point, ° C.	Decomp. Point,[c] ° C.	Appearance	Av. Chain Length[d]	Microanalysis		
							% C	% H	% EtO
				Ethoxyacetylene					
None	Late polymer[e]	Over 400	. . .	Over 400	Shiny black glass	. . .	95.78	4.10	<0.2
None	335 60	Over 300	. . .	. . .	Brown tar	28	57.58	8.80	31.26
None	100 40	135–140	−29.1 to −27.4	140–150	Amber liquid	8.7	64.29	7.30	39.73
None	48 40	80–90	−70 to −50	. . .	Pale orange liquid	5.6	59.35	8.60	63.95
None	30 40	. . .	−40 to −25	. . .	Yellow liquid	4.9	67.01	8.44	63.89
None	2½ 40	. . .	18	. . .	Colorless liquid	4.1	68.40	8.71	64.01
BP	100 40	140–148	−25 to 18	130–140	Dark orange liquid	8.9	60.22	7.99	. . .
PTSA	100 40	260–270	. . .	. . .	Brown solid	48.8	. . .	. . .	. . .
CdI_2	100 40	Over 360	. . .	. . .	Pale yellow solid	. . .	34.95	2.91	57.37
$CdCl_2$	100 40	146–151	. . .	. . .	Amber oil	. . .	. . .	. . .	. . .
$SbCl_3$	100 40	. . .	. . .	. . .	Gray solid	. . .	. . .	. . .	. . .
TCA	100 40	130–140	. . .	. . .	Amber oil	8.3	. . .	. . .	. . .
				Butoxyacetylene					
None	500 40	155–162	. . .	162–170	Light tan solid	30.3	. . .	. . .	. . .
None	80 40	110–115	−29 to −22	155–165	Orange liquid	6.0	. . .	. . .	. . .
None	80 60	122–130	−25 to −20	159–166	Red-orange oil	8.3	. . .	. . .	. . .
BP	80 40	113–122	About −20	158–167	Red-brown oil	6.5	. . .	. . .	. . .
PTSA	80 40	248 to ?	. . .	. . .	Brown solid	39.6	. . .	. . .	. . .
CdI_2	80 40	Over 300	. . .	Over 300	Creamy solid	. . .	Contained Cd^{2+} ion		
$CdCl_2$	80 40	122–132	−27 to −21	158–161	Orange oil	. . .	. . .	. . .	. . .
$SbCl_3$	80 40	Over 300	. . .	Over 300	Gray solid	. . .	. . .	. . .	. . .
$SnCl_4$	80 40	. . .	. . .	. . .	Gray solid	. . .	. . .	. . .	. . .
TCA	80 40	113–118	. . .	155–170	Amber liquid	7.0	. . .	. . .	. . .

[a] See Table I for abbreviations of names of catalysts. [b] Temperature at which polymer shrinks and sets. [c] The tars and solids generally blacken; oils and liquids explode to a black glass powder or froth and set to a spongy black glass. [d] Recorded as average number of carbon atoms making up "backbone" chain of polymer; assumed equal to difference between total carbon content of "average molecule" and total carbon content of alkoxyl portion of this molecule, where available (estimated, where not accurately known). [e] Late polymers obtained after 700 hours at 40° C., 610 hours at 60° C., 45 hours at 90° C., and 150 hours at 100° C. Analytical results: % C ±0.30; % H ±0.12. Calcd. for $(C_2H)_n$: C, 95.96; H, 4.04.

residues and the by-products were β-chlorovinyl ethyl ether (4%) and acetamide (3%). A small amount of brown tar accounted for the rest of the starting material (figures from a 1.1-mole run).

Distillation of ethyl ethynyl ether through a 30-cm. column (tantalum spiral packing, careful neutralization of all interior surfaces) gave material boiling at 51.2–52° C./745 mm., 26.6–27.8° C./290 mm., n_D^{25} 1.3795 in good agreement with values in the literature (*6*, *8*, *16*). However, the product obtained from chloroacetal appears to contain a small amount (<0.5%) of a nitrogenous impurity. This was detected when a nitrogen-containing material was sublimed from polymer mixtures obtained by bulk polymerization. This impurity was never detected in polymerizations with monomer prepared by dehydrobromination of β-bromovinyl ethyl ether with powdered potassium hydroxide (*8*). Three careful fractionations of ethyl ethynyl ether failed to remove the impurity.

The sublimate (m.p. 78–79° C.) consisted of long white needles which quickly became yellow and wet when exposed to air. All attempts to crystallize this material gave brown oils.

Anal. Calcd. for $C_6H_{11}N_2O_2(OC_2H_5)$: C, 51.05; H, 8.75; N, 14.88; ethoxyl, 23.93; molecular weight 188.2. Found: C, 50.55; H, 8.51; N, 15.08; ethoxyl, 24.62; molecular weight (cryoscopic in dioxane), 192.

The material sublimed smoothly at 25° C. and 8 mm. It gave an acetyl derivative (m.p. 52–53° C.) and absorbed 1.8 moles of hydrogen over Adams' catalyst. The structure proof was not completed.

In our more recent work ethyl ethynyl ether obtained from the Pfister Chemical Works was used (*16*).

Butyl ethynyl ether was synthesized as described earlier (*8*). The yield of dibutyl bromoacetal was 97% [b.p. 131–32° C./21 mm. (94% after refractionation, b.p. 100.2–100.8° C./3.1 mm.)] from a 6-mole run. This gave dibutyl dibromoacetal (b.p. 110–11° C./2 mm.) in 39% yield. Reaction with zinc gave β-bromovinyl butyl ether (b.p. 57.4–58.2° C./8 mm.) in 76% yield. Dehydrobromination over powdered potassium hydroxide under nitrogen gave butyl ethynyl ether (b.p. 49.5–50.2° C./110 mm.) in 62% yield. The over-all yield from vinyl acetate was 17%.

Bulk polymerization was carried out in thick-walled borosilicate glass tubes, whose inner surfaces were neutralized and degassed. Freshly prepared monomer was transferred under dry, oxygen-free nitrogen; the tubes were cooled in liquid nitrogen and sealed under 2-mm. pressure. Polymerization was carried out in constant temperature baths. The tubes were shielded from light in all cases. They were opened at liquid nitrogen temperature and allowed to warm slowly while attached to a suitable liquid nitrogen trap for collection of any gaseous products. The liquid contents were then transferred under nitrogen to a vacuum train (neutralized inner surfaces). Unpolymerized monomer and other low-boiling components were separated from higher polymers at room temperature and pressures down to 2 mm.

Polymerization Products. Gaseous products were observed only from longer polymerizations. The principal such product from ethyl ethynyl ether was ethylene, which was identified by its infrared spectrum, mass spectral cracking pattern, and chemical reactions. Small amounts of acetylene and carbon dioxide were found. Very small amounts of other low molecular weight unsaturated hydrocarbons may also have been present. Rough quantitative determinations of the amount of ethylene produced per mole of monomer taken gave the following results: 175 hours at 40° C., 0.05 mole; 335 hours at 40° C. or 200 hours at 60° C., 0.06 mole; 335 hours and 525 hours at 60° C., 0.08 mole.

2,4-Diethoxy-1-buten-3-yne, the dimer of ethyl ethynyl ether, was purified by fractional distillation under reduced pressure (b.p. 21–25° C./10 mm., m.p. 18° C.).

Anal. Calcd. for $C_4H_2(OC_2H_5)_2$: C, 68.57; H, 8.57; OC_2H_5, 64.29; molecular weight, 140. Found: C, 68.40; H, 8.71; OC_2H_5, 64.01; molecular weight (cryoscopic in cyclohexane), 144, 146.

INFRARED SPECTRUM. 2205(m), 1790(w), 1605(s), 1424(s), 1262(s), 885(s) cm.$^{-1}$; the acetylenic hydrogen band at 3300 cm.$^{-1}$ (*4*) was absent.

By oversight the ultraviolet spectrum of the pure dimer was not determined. Less pure material in ethanol gave rather broad absorption with λ_{max} 211 mμ, ϵ 5500, but decreasing rather gradually to a shoulder at 251 mμ, ϵ 4400, and again gradually from 272 mμ, ϵ 3000 to 323 mμ, ϵ 1800, where another shoulder occurred; the absorption dropped nearly to zero at 340 mμ.

The dimer (0.04 mole) was hydrolyzed by refluxing with hydrochloric acid in peroxide-free ether to yield 0.039 mole of acetone and 0.075 mole of ethanol. Hydrogenation of the dimer over Adams' catalyst (room temperature in methanol) was incomplete; 2.6 moles of hydrogen were absorbed per mole of dimer and no definite product could be isolated.

Compound I, $C_8H_6O_2(OC_2H_5)_2$, was an orange liquid isolated in 8 to 12% yield by removing all volatile material at reduced pressure from ethyl ethynyl ether polymerized for 100 hours at 40° C. It reacted rapidly with oxygen and was handled under dry nitrogen. It could not be separated into components by chromatography on paper or alumina. It froze to a yellow glass at –20° to –30° C. and remelted at –29° to –27° C.; n_D^{25} 1.5012; d_4^{25} 1.08.

Anal. Calcd. for $C_8H_6O_2(OC_2H_5)_2$: C, 64.27; H, 7.19; OC_2H_5, 40.19; molecular weight 224.25. Found: C, 64.29; H, 7.30; OC_2H_5, 39.73; molecular weight (cryoscopic in cyclohexane), 224 ± 2.

ULTRAVIOLET SPECTRA. Absorptions are shown in the following table; sharply rising absorption below 216 mμ (ϵ > 10000 at 205 mμ); weak band (in ethanol) λ_{max} 460mμ, ϵ 840 (attributed to an impurity).

Solvent	$\lambda_{max.}$, Mμ	$\epsilon_{max.}$	Inflections: λ (Mμ) with [ϵ]
Cyclohexane	228	9350	275 [5770]; 282 [5560]; 298 [4860]
Methanol	232	9350	No inflections found in spectrum
Ethanol	236	9650	278 [6250]; 284 [6100]; 292 [5800]

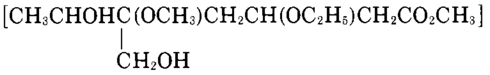
INFRARED SPECTRUM. 2270(s), 2170(w), 1895(w), 1777(w), 1740(s), 1712(s), 1657(s), 1640(s), 1622(s), 1481(s), 1448(s), 1389(s), 1328(s), 1200–1000(s), 921(s), 830(s), 810(s), and 708(s) cm.$^{-1}$

NMR SPECTRUM. 3.3 τ (s, 1H); overlying quadruplets centering at 5.74 τ and 5.81 τ (4H); 6.93–7.8 τ (m, slightly > 3H); 8.5–8.85 τ (slightly > 8H) containing 8.61 τ (d), 8.74 (irregular t); 8.84 τ (unresolved).

Zerewitinoff Determination, 0.9 to 1.0 active hydrogens (*17*).

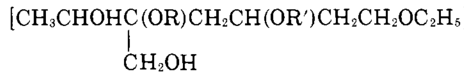
SOLUBILITY. Readily soluble in organic solvents, slightly in water to give a solution of pH 5 to 6; partially soluble in 5% aqueous sodium bicarbonate; soluble in 5% aqueous sodium hydroxide (red-brown solution which yielded only polymeric products).

I was unsaturated to bromine in carbon tetrachloride and dilute potassium permanganate; it gave iodoform with alkaline hypoiodite. Simple products were not isolated from these reactions. Hydrogenation was unsuccessful under neutral conditions, but a solution in methanol containing acetic acid was allowed to stand overnight and then absorbed 4 molecular equivalents of hydrogen over Adams' catalyst to yield two products assigned structures II,



$$[CH_3CHOH\underset{\substack{|\\ CH_2OH}}{C}(OCH_3)CH_2CH(OC_2H_5)CH_2CO_2CH_3]$$

and III



$$[CH_3CHOH\underset{\substack{|\\ CH_2OH}}{C}(OR)CH_2CH(OR')CH_2CH_2OC_2H_5],$$

R and R′ CH_3 and C_2H_5 or the reverse

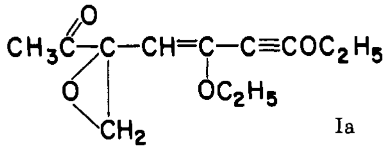
II, b.p. 121–23° C./2 mm., m.p. 19.5–20.5° C. Anal. Calcd. for $C_{12}H_{24}O_6$: C, 54.53; H, 9.15; alkoxyl, 3; active hydrogen, 2; molecular weight and sponification equivalent, 264.3. Found: C, 54.34; H, 9.20; alkoxyl, 2.96 (Zeisel); active hydrogen, 2.03 (Zerewitinoff); molecular weight (cryoscopic in cyclohexane), 267 ± 2; saponification equivalent, 273.

III, m.p. 255–56° C. Anal. Calcd. for $C_{13}H_{28}O_5$: C, 59.06; H, 10.68; alkoxyl, 3; active hydrogen, 2; molecular weight, 264.4. Found: C, 59.26; H, 10.86; alkoxyl, 3.012; active hydrogen, 2.04; molecular weight, 265 ± 2.

The infrared spectra for II and III were those expected for the structures shown.

I was hydrolyzed by hydrogen chloride in wet, peroxide-free ether (refluxing, nitrogen atmosphere) to yield a pale amber solid of saponification equivalent 108 ± 1. Oxidation of the solid with sodium hypochlorite gave chloroform and 2,4-dioxohexanedioic acid.

All of the reactions of I under acid conditions probably give rearranged products. Structure Ia explains a number of the reactions and was tentatively proposed at one time (*12*) for I. The NMR spectrum shows a vinyl proton and



Ia

two ethoxyl groups in slightly different environments. The methyl ketone group would be expected to absorb around 7.4 to 7.8 τ but the complex pattern would not be expected. Moreover it would be surprising to find the methylene group of the epoxide at 8.6 τ; the pattern in the 6.93- to 7.8-τ region is in fact very similar to that for the ring protons of propylene oxide. These considerations, and the difficulty of formulating a rational route from either monomer or dimer to Ia have convinced the authors that further work is needed to establish the structure of I.

The rates of polymerization and effects of catalysts were studied by cryoscopic (*9, 18*) and gravimetric methods. Samples of monomer were polymerized in thin-walled soft-glass bulbs (volume ~0.5 ml.) whose inner surfaces had been cleaned, neutralized, and dried. The bulbs were filled with nitrogen, catalysts or inhibitors were added if such were to be used, monomer was added under nitrogen, and the bulbs were sealed. The amounts of materials were determined by weight, and the samples were polymerized in constant temperature baths. Polymerization in vacuo gave the same results as under nitrogen. Freezing point depressions were determined in dioxane or cyclohexane in the usual Beckman apparatus. Corrections were made for the presence of acetone, alcohol, and dimer (amounts determined in larger runs after vacuum train separation); the average molecular weight of the polymer was taken into account in calculation of the amount of unreacted monomer from the observed freezing point depression. A standard cooling rate was used in each case.

Gravimetric determinations employed a thick-walled borosilicate glass tube which could be weighed accurately, in which the bulbs could be broken conveniently and which could be evacuated on a vacuum train. Volatile material was removed under reduced pressure at room temperature and collected for determination of by-products. Data from the two methods are summarized in Table I; agreement was ± 10%.

LITERATURE CITED

(1) Arens, J.F., private communication.
(2) Arens, J.F., Modderman, P., *Proc. Koninkl. Nederland. Akad. Wetenschap.* **53**, 1163 (1950).
(3) Belash, P.M., Smol'kov, N.A., Belov, V.F., Muratov, U.G., Nechushkin, A.M., Paushkin, Ya.M., Nizova, S.A., *Radiospektrosk. Tverd. Tela* **1967**, 411-14; *CA* **68**, 105625 (1968).
(4) Bellamy, L.J., "Infrared Spectra of Complex Molecules," 2nd ed., Wiley, New York, 1958.
(5) Belov, V.F., Oganesov, S.S., *Tr. Mosk. Inst. Neftekim. i. Gaz Prom.*, No. **58**, 136 (1965); *CA* **65**, 3988 (1966).
(6) Eglinton, G., Jones, E.R.H., Shaw, B.L., Whiting, M.C., *J. Chem. Soc.* **1954**, 1860; *Org. Syn.* **34**, 46 (1954).
(7) Ficini, J., *Bull. Soc. Chim. France* **21** [5], 1367 (1954).
(8) Jacobs, T.L., Cramer, R., Hanson, J.E., *J. Am. Chem. Soc.* **64**, 223 (1942).
(9) Jacobs, T.L., Tuttle, W.P., Jr., *Ibid.*, **71**, 1313 (1949).
(10) Jacobs, T.L., Whitcher, W.J., *Ibid.*, **64**, 2635 (1942).
(11) Juettner, B., Smith, R.C., Howard, H.C., *Ibid.*, **59**, 236 (1937).
(12) Juster, Norman, Ph.D. thesis, University of California, Los Angeles, Calif., 1956.
(13) Murahashi, S., Ketsuki, H. (to Mitsubishi Chemical Industries Co.), Japan. Patent **3713** (March 3, 1966); Appl. Sept. 17, 1963; *CA* **65**, 828 (1966).
(14) Nieuwenhuis, J., Arens, J.F., *Rec. Trav. Chim.* **77**, 761 (1958).
(15) Nizova, S.A., Patalakh, I.I., Paushkin, Ya.M., *Dokl. Akad. Nauk SSSR* **153**, 144 (1963).
(16) Pfister Chemical Works, Ridgefield, N.J., Tech. Bull.
(17) Pregl, F., "Quantitative Organic Microanalysis," revised and edited by J. Grant, 4th English ed., pp. 134-42, Blakiston, New York, 1946.
(18) Taylor, H.S., Vernon, A.A., *J. Am. Chem. Soc.* **53**, 2527 (1931).

RECEIVED for review August 1, 1967. Accepted September 21, 1968. Contribution 1812 from the Department of Chemistry, University of California, Los Angeles. Paper V on acetylenic ethers; for paper IV see Jacobs, T. L., Scott, W. R., *J. Am. Chem. Soc.* **75**, 5497 (1953).

Crystalline Propylene Glycol

WILLIAM L. HOWARD
The Dow Chemical Co., Basic Research, Freeport, Tex. 77541

Crystals of propylene glycol were induced in the *d*-isomer and used to seed the crystallization of the racemic mixture, m.p. −31.5° to −29.3° C. The *d*-isomer has two melting points, −35.5° to −33° C. and −31.6° to −29.6° C. Solubilities in acetone at −35°, −40°, and −78° C. are approximately 30, 10, and 2 grams per 100 ml., respectively. Suitable recrystallization solvents are acetone, *n*-propyl and *sec*-butyl alcohols, acetone and ethyl acetate or ethyl ether, and ethanol and ethyl ether; methanol and ethanol alone fail. Crystals can be induced at −78° C. in propylene glycol containing up to about 10% water.

PROPYLENE glycol has been known for over 100 years, but it has only now been obtained in the crystalline state. Crystallization was induced by ordinary scratching of a very pure sample of either the *d*- or the *l*-isomer. Seed crystals of either isomer would sometimes induce crystallization in the racemic mixture, but this was best done by crushing together crystals of the two isomers and using the mixture of crystals for seeds. Racemic crystals seeded either optical isomer. The glycol could be crystallized neat or from solution, but crystallization of only one isomer from the racemic mixture has not yet been achieved.

The melting point of racemic propylene glycol (The Dow Chemical Co., USP grade) was −31.5° to −29.3° C. Partial melting occurred in the *d*-isomer from −35.5° to about −33° C. where the mass completely solidified, to remelt from −31.6° to −29.6° C., suggesting the existence of at least two allotropic forms. The samples used for determination of the melting points contained about 0.02% water.

Unseeded supersaturated solutions of racemic propylene glycol of 50% and greater in acetone will exist indefinitely at Dry Ice temperature, but in the presence of crystals the solubility in acetone at −78° C. was 1.4 grams per 100 ml. At −40° and −35° C., the solubilities in acetone were 10 and 30 grams per 100 ml., respectively.

Acetone is the most convenient solvent found so far for the recrystallization of propylene glycol. Other suitable solvents are *n*-propyl and *sec*-butyl alcohols, mixtures of acetone with either *n*-propyl alcohol, ethyl acetate, or ethyl ether, and mixtures of ethanol with ethyl acetate or ethyl ether. Methanol and ethanol alone failed. Crystals could be induced at −78° C. in propylene glycol containing up to about 10% water.

RECEIVED for review June 6, 1968. Accepted September 19, 1968.