(210-212 (730 mm.),[13] n^{20}_{D} 1.5088-96 (n^{18}_{D} 1.5125[13]), Cl 20.7; mol. wt.[11] 168 (182), calcd. for *t*-butylchlorobenzene 21.03%, 168; infrared indicates mixture of *meta* and *para*, no *ortho*; (b) 17 g., b. p. 220-222; n^{20}_{D} 1.5084-1.5100, Cl 18.9%, mol. wt. 182 (168); calcd. for amylchlorobenzene 19.42%, 182. (c) 17 g., b.p. 251-254°, n^{20}_{D} 1.5190-1.5237, Cl 15.3%, calcd. for di-butyl 15.11%; for butylbutenyl[12] 15.24%.

Identification.—*t*-Butylbenzene, *m*- and *p*-*t*-butyltoluenes, and the various pentylbenzenes were identified by physical properties and by reference to available standards and infrared spectra. No attempt was made to identify the polyalkylated derivatives.

***t*-Butyl-*p*-xylene.**—This compound was prepared in 11% yield by alkylation of *p*-xylene (5 moles) with isobutylene (1 mole) in the presence of nitromethane–aluminum chloride (100 g./28 g.) complex at 25°. The product was worked up as in procedure 1,[3] and fractionated to separate the *t*-butyl derivative, b.p. 217°, n^{20}_{D} 1.5000, d^{20}_{4} 0.8738. (Burgoyne, *et al.*,[14] reported 213-217° (735 mm.), $n^{28.5}_{D}$ 1.5003, $d^{29.5}_{29.5}$ 0.8757, for this compound prepared in 5.2% yield *via* the reaction of *t*-butyl chloride with the Grignard reagent prepared from 2-bromo-*p*-xylene.) The infrared spectrum confirmed 1,2,4-trisubstitution and presence of a *t*-butyl side chain, and was identical to that for the C_{12}-aromatic obtained from *p*-xylene and 2-methyl-2-butene. These data do not eliminate the 1,3-dimethyl-4-*t*-butyl isomer which might form by isomerization of *p*- to *m*-xylene followed by alkylation. However, the formation of this isomer is not considered probable in view of the complete absence of (1) *m*-xylene in the recovered xylene, and of (2) the 1,3-dimethyl-5-*t*-butyl isomer in the product. Furthermore, dealkylation of this material over silica alumina[15] (Socony–Vacuum "Chrome Bead") at 375°, 1.8 vol. per vol. of catalyst per hour, yielded a liquid product consisting of 85% *p*-xylene, 4 ± 2% *m*-xylene, and only traces of *o*-xylene and toluene. The gas evolved contained 78% isobutylene and 14.4% isobutane. Under the same conditions with pure *p*-xylene as the feed, the product contained 90% *p*-, 4 ± 2% *m*-, no *o*-xylene and 6 ± 2% toluene.

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[11] Mass spectrograph parent mass main peaks (minor peaks) based on Cl^{35} isotope.

[12] This fraction rapidly discolors potassium permanganate solution, indicating olefinic bonds.

[13] For *p*-*t*-butylchlorobenzene; I. P. Tsukervanik, *J. Gen. Chem.*, (*U.S.S.R.*), **8**, 1512 (1938).

[14] E. E. Burgoyne, T. J. Klose and D. K. Watson, *J. Org. Chem.*, **20**, 1508 (1955).

[15] M. J. Schlatter, paper presented before the Division of Petroleum Chemistry of the American Chemical Society, Symposium on Petrochemicals in the Postwar Years, at the Chicago Meeting, September, 1953.

HARVEY, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Room Temperature Polymerization of Propylene Oxide

BY LEON E. ST. PIERRE[1a] AND CHARLES C. PRICE[1b]

RECEIVED DECEMBER 6, 1955

Polymerization of propylene oxide proceeds readily at room temperature in the presence of powdered potassium hydroxide. The polymer has a molecular weight of 3000–5000 and has a high proportion of unsaturated end-groups, apparently largely of an allyl ether type, with some propenyl type in the primary polymer. The polymerization appears to be a specific surface-catalyzed reaction and a chain-type reaction, not a slow stepwise build-up, since polymer formed at low conversion is substantially the same molecular weight as at higher conversion. Non-oxidative degradation of the polymer has been shown to be catalyzed by toluenesulfonic acid at 270°. The products are volatile, and the presence of propionaldehyde and dimethyldioxane was established. Degradation with evolution of hydrogen and other gases was observed by electron irradiation.

The present work on the preparation of polypropylene oxide[2] through the polymerization of propylene oxide was undertaken with the hope that a polymer network based on high molecular weight material of this structure might have useful elastomeric properties. Earlier work, using bases at elevated temperatures (100–200°) and pressures,[3a,b] had been found to produce polymer of relatively low molecular weight, in the neighborhood of 1000 to 2000. Other work reported since the completion of this investigation,[4] however, discloses that the polymerization of propylene oxide by the use of ferric chloride or ferric hydroxide catalysis at 50–150° yields high molecular weight polymer, which is partially rubbery and partially solid. This claim was made earlier by Staudinger although he did not specify the polymerization procedure.

During the course of our work, it was accidentally discovered that propylene oxide could be polymerized readily by powdered potassium hydroxide at room temperature and atmospheric pressure, which led us to a study of catalysis and temperature effects on this polymerization. Propylene oxide was stirred at room temperature with about 10% by weight of a great variety of inorganic and organic bases. Of those studied, only powdered potassium hydroxide gave a reasonably fast polymerization under these conditions. In Table I are listed some of the catalysts used and their catalytic effects. In all cases where heterogeneity existed the catalysts were powdered and then continuously stirred during polymerization. The reactions were all carried out at room temperature and the presence of a non-volatile residue, after heating a portion of the liquid phase on a steam-bath, was taken to be a positive criterion of polymerization.

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[1] (a) General Tire and Rubber Co. Fellow, 1951–1953. Research Laboratories, General Electric Co., Schenectady, N. Y. (b) John Harrison Laboratory of Chemistry, University of Pennsylvania, Philadelphia 4, Pa. Presented at the 128th Meeting of the American Chemical Society, Minneapolis, Minn., September 12, 1955.

[2] First reported by P. A. Levene and A. Walti, *J. Biol. Chem.*, **75**, 325 (1927).

[3] (a) U. S. Patent 2,425,845, August 19, 1947, W. J. Toussaint and H. R. Fife (to Union Carbide and Carbon Corp.); (b) Makoto Okawara, *J. Chem. Soc. Japan, Ind. Chem. Sec.*, **55**, 335 (1952).

[4] U. S. Patents 2,706,181 and 2,706,182, April 12, 1955, M. E. Pruitt and J. M. Bagett (to Dow Chemical Co.).

[5] H. Staudinger, "Die hochmolekularen organischen Verbindungen," Berlin, J. Springer, 1932, p. 295.

TABLE I

ROOM TEMPERATURE POLYMERIZATION OF PROPYLENE OXIDE BY SOME INORGANIC BASES

Base	Time, hr.	Results
KOH	51	33% polymerized
$NaOCH_3$	72	No polymer
LiOH	72	No polymer
NaOH	54	No polymer
$NaNH_2$	92	1% of a low polymer

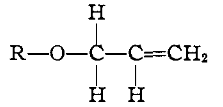
Such bases as Triton B and Triton B ethoxide also polymerized propylene oxide but in low yields and to low molecular weights. The polymers produced by the action of powdered potassium hydroxide on propylene oxide were found to be in a molecular weight range of 3000–5000 by cryoscopic and end group analysis.

The polymerization rate was shown to be sensitive to temperature, but since the monomer boils at 35° only a small range of temperature was open to investigation at atmospheric pressure. Runs were made at 33, 20, 0 and −78° using a mixture of powdered potassium hydroxide in dry propylene oxide. At 0 and −78° no polymerization could be noted after three days of stirring. The rates of polymerization at 20 and 33° are shown in Tables III, IV and V.

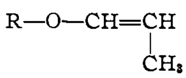
In connection with questions regarding possible mechanisms, measurements of the reduced viscosity of 4% solutions of the polymer in benzene were made. Tables III, IV and V also list the changes in viscosity with percentage conversion of monomer. The immediate attainment of a high molecular weight and the relatively small increase thereafter suggests a chain mechanism for the polymerization involving slow generation of active centers followed by rapid stepwise addition of monomer to form the product polyglycol chains. Indeed this very scheme was proposed by Staudinger[5] in 1932.

End group analysis of these low-temperature polymers indicated a much higher double bond to hydroxyl ratio than was found in polymers obtained commercially. The latter, presumably prepared at higher temperatures and pressures,[6] exhibit a double bond to hydroxyl ratio of less than 0.02/1, while for those prepared at room temperature this ratio is 0.67/1.

Evidence that the unsaturation was formed during the polymerization and not during the isolation may be deduced from the infrared spectra of polymer isolated by different procedures. The infrared spectra suggest the unsaturation to be present in two forms prior to treatment with acid during isolation. One such form would be the allyl ether A (6.06 μ band) and the other the propenyl ether B (6.27 μ band).


$R{-}O{-}CH_2{-}CH{=}CH_2$

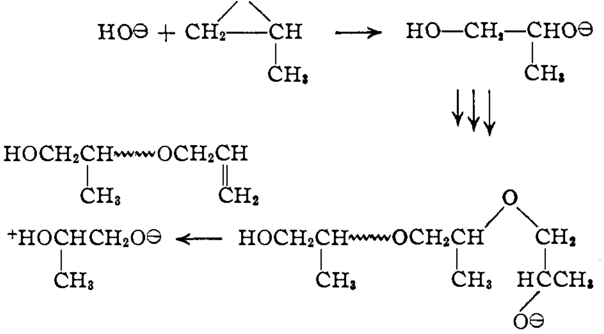
A


$R{-}O{-}CH{=}CH{-}CH_3$

B

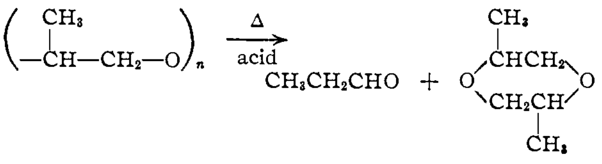
The complete elimination of the absorption at 6.27 μ in the acid-treated products is taken as evidence that there was complete hydrolysis of the propenyl ether with only the allylic ether remaining in the final product. Attempts to estimate the relative quantities of these two unsaturated end-groups failed to yield reliable data. The presence of a double-bonded end-group was further shown by the behavior of the polymer toward 1,5-naphthalene diisocyanate, before and after oxidation with hydrogen peroxide in formic acid. The untreated polymer increased in viscosity slightly but did not gel when treated with diisocyanate equivalent to the hydroxyl groups. After oxidation, designed to convert the end-group double bond to a glycol, thereby converting a monohydric polymer to trihydric, the polymer formed an insoluble gel with an amount of diisocyanate equivalent to the hydroxyl groups.

A likely course for the polymerization process might be outlined



The abstraction by the negative oxygen in a growing chain of a hydrogen six atoms away could terminate a growing chain, producing either the allyl ether end-group, as indicated, or the propenyl ether end-group, by attack at the methylene rather than the methyl group. Presumably the specificity of solid potassium hydroxide for this polymerization is due to the fact that its geometry provides a positive potassium geometrically arranged so as to be close to each successive negative oxygen atom.

Polypropylene oxide in a nitrogen atmosphere was found to be unstable at 270°, especially in the presence of toluenesulfonic acid, which decomposed it largely to volatile products. Propionaldehyde and dimethyldioxane were identified in the decomposition products.



This degradation was markedly reduced in the presence of base and thermal decomposition was more extensive in the presence of air than under nitrogen.

Experimental[7]

A. Analytical Techniques. 1. Hydroxyl Content by Phthalation.—The method used in this type of determina-

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[6] U. S. Patent 2,448,664, May 30, 1944, H. R. Fife and F. H. Roberts (to Union Carbide and Carbon Corporation).

[7] Micro-analyses by Micro-Tech Laboratories, Skokie, Ill. All melting points are uncorrected. Infrared analyses were run by Mr. A. Verbiscar on a Baird spectrophotometer, model AB-1-178.

TABLE II

ROOM TEMPERATURE POLYMERIZATION OF PROPYLENE OXIDE WITH POWDERED POTASSIUM HYDROXIDE

Expt.	Monomer, g.	KOH, g.	Time, hr.	Yield, g.	OH, eq./g. $\times 10^4$	C=C, eq./g. $\times 10^4$	η_{sp}/c[a]	n^{20}D
2a	200	40	42	160[b]	3.82	...	...	...
2b	150	20	64	36.5[c]	2.96	...	0.141	...
2c	150	10	48	...	4.88	...	.138	...
2d	420	10	141	250[c]	...	1.35	.154[d]	1.4509
2e	406	30	42	209[c]	3.61	...	.136	1.4509
2f	800	60	220	360[c]	6.02	1.37	.161	...

[a] 4% solution in benzene; c = g. of polymer in 100 g. of solution. [b] Isolated by washing product in ether with hydrochloric acid and evaporating to 150° at 3 mm. [c] Isolated by shaking an ether solution with Amberlite IR-120(H) to remove base, followed by vacuum evaporation. [d] Cryoscopic molecular weight (benzene), 3440.

tion is that outlined by Siggia.[8] The sample, weighed into a small ampoule open at one end, was refluxed for two hours in 10 ml. of 0.688 M phthalic anhydride in pyridine. About 10 ml. of carbon dioxide-free water was then added and the solution was titrated to a phenolphthalein end-point using 0.05 to 0.01 N standard sodium hydroxide. The difference in titer between a blank and the sample gave a measure of the amount of anhydride taken up by the alcohol present. Phthalation was found to be more sensitive and more reproducible than acetylation on the propylene oxide polymers.

2. **Determination of Unsaturation.**—Several methods were investigated in seeking to establish a satisfactory analytical technique. A reliable and reproducible technique was finally arrived at and used in the latter stages of the work. A weighed amount of polymer was dissolved in 10 ml. of chloroform and 10 ml. of glacial acetic acid. After cooling in an ice-bath, 10 ml. of bromine in glacial acetic acid was pipetted in. After standing for exactly 2 minutes, 25 ml. of 10% aqueous potassium iodide was added and the solution was immediately titrated with standard sodium thiosulfate using starch indicator. A blank was run at the same time and the unsaturation determined by difference.

3. **Viscosimetry.**—The viscosity runs were made in an Ostwald viscosimeter using a 5-ml. sample. The particular instrument used had a flow time for pure benzene of 76.0 seconds at 20°.

B. **Polymerization Procedures.** 1. **Polymerizations at elevated temperatures and pressures,** as described in the patent literature, were carried out at temperatures up to 140° and pressures up to 320 p.s.i. using sodium methoxide and sodium hydroxide as catalysts. The products were oils with cryoscopic molecular weights of 900–1300, and with hydroxyl contents of 1 to 1.3 $\times 10^{-3}$ equivalent of hydroxyl per gram.

Polymer 1025, a polypropylene oxide purchased from the Union Carbide and Carbon Corp., was a water-white oil. An infrared analysis was obtained; η_{sp}/c 0.0406, n^{20}D 1.4493.

2. **Room Temperature Polymerization.**—One or two samples of propylene oxide, being dried at room temperature over potassium hydroxide, were observed to have undergone polymerization to a polymer of appreciably greater molecular weight (*ca.* 3000) than the samples from the elevated temperatures experiments. Qualitative experiments indicated that this low temperature polymerization was not effectively catalyzed by lithium, sodium or barium hydroxides, sodium methoxide, potassium carbonate, sodamide or trimethylbenzylammonium hydroxide or ethoxide (see Table I).

A number of samples of polymer were prepared by the low temperature procedure and are described in Table II. In all cases, propylene oxide which had been dried over pellet potassium hydroxide and redistilled was used. The potassium hydroxide for polymerization was finely powdered immediately before use.

3. **Isolation of Volatile Fractions from Potassium Hydroxide Catalyzed Polymerization.**—Dried propylene oxide (150 g., 2.58 moles) was stirred at room temperature with powdered potassium hydroxide for 68.7 hours. A portion of the liquid phase, weighing 132 g., was poured off and distilled. A total of 88.2 g. of volatile material was collected in a Dry Ice-acetone-bath up to a pot temperature of 185° at 0.5 mm. pressure. On redistillation, all of this material distilled over at a temperature of 34°, indicating the presence of nothing but recovered propylene oxide in this volatile fraction.

C. **Studies on Rate, Temperature, Degree of Polymerization and Yield in Potassium Hydroxide Catalyzed Polymerizations.** 1. **Room Temperature Polymerization of Propylene Oxide.**—Dried propylene oxide (900 g., 15.5 moles) and 60 g. (1.07 moles) of finely powdered technical grade potassium hydroxide were stirred at room temperature. Samples were removed at intervals and isolated by dissolving the polymer in ether, shaking with acidic ion exchange resin and, after filtering, evaporating to 140° at 0.5 mm. The polymer product was weighed and analyzed viscosimetrically (see Table III).

TABLE III

THE RATE OF POTASSIUM HYDROXIDE CATALYZED POLYMERIZATION OF PROPYLENE OXIDE AT ROOM TEMPERATURE

Time, hr.	Yield, %	η_{sp}/c	n^{20}D
12	0	0	
35	15	0.111	1.4508
40	15		1.4496
48	17	0.121	1.4505
71.5	19		1.4510
132	40	0.123	1.4495

2. **Polymerization of Propylene Oxide at 33°.**—To dried propylene oxide (250 g., 4.3 moles) was added 16.7 g. (0.298 mole) of dry, finely powdered potassium hydroxide, and stirring was commenced. Samples were removed, dissolved in ether, neutralized by shaking with acid ion exchange resin, and then filtered and solvent removed. The yield of polymer and its viscosity were determined (see Table IV).

TABLE IV

THE RATE OF POTASSIUM HYDROXIDE CATALYZED POLYMERIZATION OF PROPYLENE OXIDE AT 33°

Time, hr.	Yield, %	η_{sp}/c	n^{20}D
21	46	0.151	1.4509
25	54.2	.162	1.4510
27	70.6	.157	1.4510
33.5	81.2	.161	1.4510
57.5	88.4	.167	1.4510

In addition to these measurements, the sample isolated at 57.5 hours, designated C2a, was found to have a hydroxyl content by phthalation of 2.93 $\times 10^{-4}$ equiv./g. and 1.98 $\times 10^{-4}$ equiv. C=C/g. was found by analysis using bromine in acetic acid. The infrared spectrum exhibited a double bond absorption at 6.06 μ.

In addition to the isolation of C2a, two other crude fractions of the 57.5-hour reaction mixture were removed and the polymer isolated in a different manner.

One fraction, designated C2b, was dissolved in ether and washed with aqueous 1 N sulfuric acid. The ether layer was subsequently washed with dilute aqueous sodium bicarbonate solution and then twice with distilled water. The ether layer was then dried to 170° at a pressure of 0.8 mm. This polymer was almost water-white in appearance

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[8] S. Siggia, "Quantitative Organic Analysis *via* Functional Groups," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 100.

as compared to a light brown color for C2a. Hydroxyl and unsaturation analyses were run in the same manner as on C2a and were found to be 3.04×10^{-4} equiv. OH/g. and 1.93×10^{-4} equiv. C=C/g. An infrared analysis was also carried out and the spectrum proved to be identical to that of polymer C2a.

The third fraction, designated C2c, was isolated by dissolving in ether and filtering to remove catalyst. The filtrate was then dried to 170° at 0.9 mm. The product was darker brown than C2a and was subjected to the same analyses as the other two fractions. The unsaturation was found to be 2.19×10^{-4} equiv. C=C/g. and the hydroxyl content 3.27×10^{-4} equiv. OH/g. This latter figure is a corrected value as the polymer was found to contain 2.11×10^{-5} equiv. KOH/g. The infrared spectrum exhibited two peaks in the double bond region, one at 6.06 μ and a stronger one at 6.27 μ.

3. **Polymerization of Propylene Oxide at 20°.**—Dried propylene oxide (140 g., 2.42 moles) and 9.4 g. (0.167 mole) of dry powdered potassium hydroxide were allowed to react at 20° with stirring in exactly the same manner as outlined above for polymerization at 33°.

TABLE V

THE RATE OF POTASSIUM HYDROXIDE CATALYZED POLYMERIZATION OF PROPYLENE OXIDE AT 20°

Time, hr.	Yield, %	η_{sp}/c	$n^{20}D$
8.5	0		
23	3.7		
51.5	32.9		1.4514
57.2	48.9	0.149	1.4513
72.5	66.2	.154	1.4514
105.5	71.2	.157	1.4515

4. **Attempted polymerization** of propylene oxide at 0° gave a negligible amount of polymer after 62 hours. At −78°, no evidence for polymer could be detected after 89 hours.

D. Polymer Degradation. 1. **Determination of Thermal Stability.**—Polypropylene oxide 2b (1.2 g.) was placed in a small flask which was connected to a mercury manometer. The system was flushed with nitrogen and made gas tight. The flask was then placed in a bath and heated to 250°. After two hours at this temperature, a pressure difference of 0.20 cm. was observable in the manometer. Heating was continued and the bath temperature raised to 300°, whereupon the pressure differential was 1.4 cm. At this point the system was opened and on closing the pressure very quickly rose to 1.4 cm. once again. The system was once more opened and upon blowing nitrogen gas through, vapor could be observed emerging from the outlet tube.

2. **Investigation of Decomposition at 270°.**—Samples of polypropylene oxide 2b were weighed into four flasks, designated a, b, c and d, and heated to 270° for four hours. The results are summarized in Table VI.

TABLE VI

DEGRADATION OF POLYPROPYLENE OXIDE AFTER FOUR HOURS AT 270°

Sample	Wt., g., polymer	Under	Wt. loss, %	η_{sp}/c
a	2.4745 + 0.0133 toluenesulfonic acid	N_2	92	[a]
b	0.3434 + 0.0061 KOH	N_2	3.4	0.089
c	1.3203	N_2	37.3	.051
d	2.1052	Air	23.7	.018

[a] Insufficient polymer left for viscosity determination; all residues were deep brown or black liquids. For the starting polymer 2b, η_{sp}/c 0.141

3. **Determination of Products from Acid-catalyzed Decomposition.**—Polypropylene oxide 2c (10 g.) was placed in a distilling flask and 0.05 g. of *p*-toluenesulfonic acid was added. To the outlet arm of this flask a series of three collecting tubes was connected, the first tube being cooled in an ice-bath, the second in an acetone–Dry Ice-bath and the third in a liquid nitrogen bath. The system was flushed out with dry nitrogen and the decomposition flask placed in an oil-bath. After heating for 2.5 hours at 270°, the residue in the decomposition flask weighed 1.5 g. and the yellow distillate in the ice-bath weighed 7.5 g.

Distillation of the latter gave two reasonably constant boiling fractions: one, b.p. 117–118°, 2.5 g., had a refractive index, $n^{20}D$ 1.4082. The physical constants of this fraction were similar to those of dimethyl-1,4-dioxane, which was reported to have a boiling point of 114–117°.[1]

Anal. Calcd. for $C_6H_{12}O_2$: C, 62.07; H, 10.34. Found: C, 61.34; H, 10.28.

A second fraction, 0.5 g. distilling at 139–141°, exhibited two peaks in the carbonyl region, one at 5.85 μ and the other at 5.95 μ. Another peak was found in the double bond region at 6.08 μ. This fraction probably contained acrylic acid, boiling point 141.9°, and possibly some propionic acid, boiling point 141°.

The material boiling below 117° was converted to derivatives of propionaldehyde. A dimedone derivative was prepared by the method of Shriner and Fuson, and, after being recrystallized, melted at 154–156°. The dimedone derivative of propionaldehyde melts at 155°.[9] The 2,4-dinitrophenylhydrazone was prepared by the method of Shriner and Fuson and, after two recrystallizations, melted at 145°, while the same derivative of propionaldehyde melted at 154°.

4. **Oxidative Decomposition of Polypropylene Oxide.**—Oxygen was slowly bubbled through polypropylene oxide 2e (14 g.) heated in a boiling water-bath. Samples were removed from the decomposition flask at intervals and analyzed for peroxide content,[8] acidity and reduced viscosity. The acidity was determined by titrating with standard base and ethanolic solution of the polymer. Results are summarized in Table VII.

TABLE VII

REACTION OF POLYPROPYLENE OXIDE WITH OXYGEN AT 100°

Time, hours	$n^{20}D$	Equiv. acid/g. $\times 10^5$	Peroxide, %	η_{sp}/c
0	1.4509	1.99	0.23	0.136
0.5	1.4509	3.94	.31	.142
2	1.4513	3.21	.98	.128
5	1.4508	13.7	2.34	.069
9	1.4489	36.5	4.04	.038

5. **Determination of Gaseous Products upon β-Ray Irradiation of Liquid Polypropylene Oxide.**—Polypropylene oxide 2e was placed in a Pyrex cell equipped with a window 5×10^{-5} inch in thickness. The liquid was carefully degassed on a vacuum line and the container sealed. Irradiation was thereupon carried out for a period of 20 minutes using 1.5-million volt electrons at a current of 0.4 micro-amp., after which time the gases present were collected for analysis. The liquid material was analyzed by infrared and also viscosimetrically. The reduced viscosity in benzene was found to be η_{sp}/c 0.122. Unirradiated 2e had η_{sp}/c 0.136.

The gases were analyzed on the mass spectrometer and the following molar percentages obtained:

H_2	63.0	H_2O	4.8
CH_4	2.4	C_3H_6	4.9

E. Attempted Hydroxylation of the Double Bonds.—Hydroxylation of the double bonds was attempted by the method used by Wittcoff, Roach and Miller[10] in the oxidation of allyl ether to diglycerol. Polypropylene oxide 2f (50 g.), containing 6.02×10^{-4} equiv./g. of hydroxyl and 1.37×10^{-4} equiv./g. of C=C, η_{sp}/c 0.161, was dissolved in 300 g. (6.53 moles) of formic acid. With stirring, 90 g. of 30% hydrogen peroxide (0.88 mole) was run in slowly. After a short time the temperature rose to 45° and, with slight cooling, remained at that point for three hours. The mixture was

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(9) E. C. Horning and M. G. Horning, *J. Org. Chem.*, **11**, 96 (1946).

(10) H. Wittcoff, J. R. Roach and S. E. Miller, THIS JOURNAL, **71**, 2666 (1949).

TABLE VIII

MAJOR INFRARED ABSORPTION PEAKS FOR SOME SAMPLES OF POLYPROPYLENE OXIDE AND RELATED COMPOUNDS

Propylene oxide		Polypropylene oxide 2f[a]		Polypropylene oxide 1025[b]		Dimethyldioxane	
ν, cm.$^{-1}$	% tr.	ν, cm.$^{-1}$	% tr.	ν, cm.$^{-1}$	% tr.	ν, cm.$^{-1}$	% tr.
3000	5	3480	77	3400	76	2960	61
1500	21	3360	79	2880	47	2850	63
1450	11	2900	17			1715	88
1405	6	1450	40	1450	72	1465	79
1375	21	1375	19	1370	58	1405	83
1270	9	1345	40	1340	72	1385	73
1147	21	1300	42	1295	76	1350	82
1135	23	1260	56	1260	79	1275	87
						1155	57
1105	15	1080–1120	5	1098	21	1125	58
1023	7	1050	42	1050	75	1085	59
						1035	64
948	7	910	45	910	79	950	73
895	25	867	70			933	72
820–40	7					845	83
747	14						

[a] The sample of polypropylene oxide hydroxylated by treatment with hydrogen peroxide was virtually identical except for stronger absorption at 3450 cm.$^{-1}$ (65% transmission).

[b] Note that the relative intensity of the hydroxyl band (3400 cm.$^{-1}$) is greater in this material, in agreement with analytical titration data. The spectrum was unchanged after γ-ray irradiation.

then placed in the refrigerator overnight after which time the excess peroxide was decomposed using aqueous sodium metabisulfite. The polymer was then taken up in ether and neutralized with 20% sodium hydroxide. An excess of 40 ml. of 20% sodium hydroxide was added and the solution was refluxed for two hours to saponify any formate esters present. The organic portion was again taken up in 300 ml. of ether and shaken with ion exchange resin to neutralize any base carried over. The ether solution was evaporated to a low volume and then taken up in dry benzene and filtered in an effort to break the emulsion which had been formed. The benzene solution was then evaporated to a temperature of 165° at a pressure of 0.7 mm., yielding 27.5 g. (55% of starting weight) of polymeric material. Bromine analysis indicated the complete absence of unsaturation and the hydroxyl equivalent per gram of polymer was found by phthalation to have risen to 1.02×10^{-3}. The reduced viscosity had fallen, however, to 0.0805.

Treatment of this hydroxylated polymer with 1,5-naphthalene diisocyanate produced an insoluble gel, in contrast to the original polymer, which increased in viscosity but did not become insoluble.

PHILADELPHIA, PENNA.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF MARYLAND]

Methyl-1,3,5-hexatrienes

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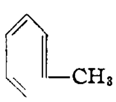
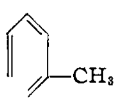
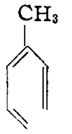
Methods of synthesis of 1-, 2- and 3-methyl-1,3,5-hexatrienes have been studied. The 1-, 2- and 3-methylhexatrienes give Diels–Alder adducts with maleic anhydride. The trienes undergo cyclization to methylcyclohexadienes by what is probably an internal Diels–Alder reaction. The methylcyclohexadienes were partially differentiated from the isomeric trienes by (1) reaction with maleic anhydride and (2) by aromatization.

The study of the conjugated trienes by this Laboratory has now been extended[1] from 1,3,5-hexatriene, the simplest of the conjugated trienes, to the monosubstituted hexatrienes, 1-, 2- and 3-methylhexatrienes, the particular isomers of which (I, II and III) are considered as the open chain analogs of toluene.


I


II


III

I, or one of its isomers, was readily prepared by the following reaction sequence: (1) addition of the methyl Grignard reagent to 2,4-hexadienal to give 2,4-heptadien-6-ol; (2) catalytic dehydration of the alcohol in the vapor phase with alumina. 1-Methylhexatriene[2] is a low melting solid (m.p. 22°) which undergoes polymerization rapidly in the solid state. It is, however, surprisingly stable in the liquid state, showing no marked deterioration upon standing for a period of several years in the absence of special precautions. A second isomeric substance is present in the catalytic dehydration product of the dienol. We first believed this substance was another geometrical isomer of 1-methyl-1,3,5-hexatriene but it was subsequently shown to be a methylcyclohexadiene (IV). The proportion of the methylcyclohexadiene increases with increasing temperature of dehydration. Further, passing 1-methyl-1,3,5-hexatriene over alumina at elevated temperatures converted it to methylcyclohexadiene.

These two substances were distinguished from each other by ultraviolet absorption spectra (Table I), hydrogenation experiments and the Diels–Alder adducts with maleic anhydride. The latter reaction with 1-methyl-1,3,5-hexatriene was interesting, for the addition of the anhydride apparently occurred across the triene at both the 1,4- and 3,6-positions. This fact was established by dehydrogenation of the adduct, and oxidation with permanganate to yield the tricarboxylic acid IX and tetracarboxylic acid X, Fig. 1. The tricarboxylic acid was isolated by extraction with ether (the tetra-

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[1] G. F. Woods and L. H. Schwartzman, THIS JOURNAL, **70**, 3394 (1948); **71**, 1396 (1949); G. F. Woods and S. C. Temin, *ibid.*, **72**, 139 (1950); G. F. Woods, N. C. Bolgiano and D. E. Duggan, *ibid.*, **77**, 1800 (1955).

[2] C. J. Enklar (*C.A.*, **7**, 1169, 1704 (1913)) reported on the dehydration of 2,6-heptadien-4-ol with potassium hydrogen sulfate. He obtained a low melting (−14.5°) hydrocarbon (no other data were given), which he states is possibly 1,3,5-heptatriene. K. H. Ou (*Ann. Chim.*, **13**, 175 (1940)) dehydrated 1,5-heptadien-4-ol at 170° with sodium hydrogen sulfate deposited on pumice. A hydrocarbon was obtained described as "possibly 1,3,5-heptatriene." He reports a boiling point of 100–102° and n^{22}_{D} 1.4798.