The Peroxide-induced Polymerization of Epoxides

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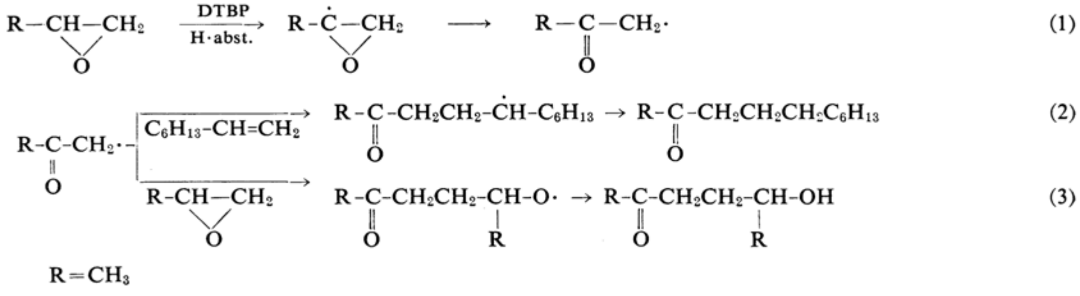
Free radical reactions of epoxides have been studied by some workers and classified into two types, one involving the abstraction of a hydrogen atom at the ring carbon and the other involving ring-opening by a radical attack. The observation by Gritter and



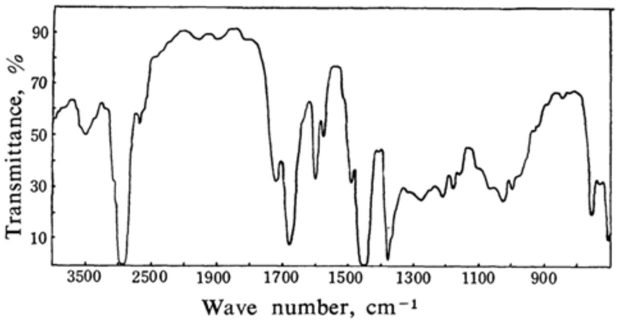


Fig. 1. Infrared spectrum of the SO polymer (Nujol).

Wallace[1] that 5-oxy-2-hexanone and 2-undecanone were formed by two competing reactions, Eqs. 2 and 3, in the di-*t*-butyl peroxide-induced addition of propylene oxide to 1-octene, has been of great interest to us.

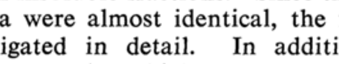
If reaction 3 occurs successively to any appreciable extent, the formation of a polyether having acyl and hydroxyl end groups is to be expected. Indeed, Gritter and Wallace recently pointed out a slight formation of telomers when propylene oxide was treated with peroxides,[2] but no additional information on the polymer was given. Conant and Peterson[3] also observed that, in the presence of a benzoyl peroxide catalyst, cyclohexene oxide was polymerized to a viscous liquid with difficulty, even under severe conditions. On the contrary, Hopff and Zahner[4] reported that styrene oxide could not be polymerized using peroxides and an aliphatic azo compound as initiators.

In order to check the radical polymerization of epoxides and to characterize the resulting polymers, we have now examined the reaction of styrene oxide (SO) and phenyl glycidyl ether (PGE) with some radical initiators. To facilitate the isolation of the polymer, high boiling aromatic or aliphatic epoxides which might be expected to yield a solid polymer have been selected.

Results and Discussion

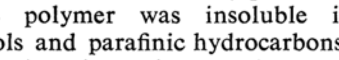
The Polymerization of SO with Di-*t*-butyl Peroxide (DTBP).—Some of the results are shown in Table I. Acetophenone was the only low molecular-weight product isolated. This clearly indicates the formation of phenacyl radical which corresponds to acetonyl radical in Eq. 1. By fractional precipitation, a polymeric residue was separated into two fractions, i. e., ethanol-insoluble and ligroin-insoluble fractions. Since their infrared spectra were almost identical, the former was investigated in detail. In addition, control experiments in which SO was heated alone, with *t*-butanol or acetone, gave no polymer.

The polymer was insoluble in aliphatic alcohols and parafinic hydrocarbons, but it was soluble in other solvents. It was tensile when molten, but it was too brittle to be of practical use. Analytical data showed fairly good agreement with the calculated value of $(SO)_n$. The average molecular weight was found to be ca. 1500∼2000. An estimation of the epoxy value by the hydrochloric acid-dioxane method showed no evidence for the existence of an epoxide ring. The infrared spectrum exhibited a characteristic absorption at 3500 (hydroxyl), at 1720 and 1680 (carbonyl), and at 1030∼1100 cm⁻¹ (ether) (see Fig. 1). It seems that these data do not conflict with the tentative structures, I and/or II, for the polymer which are deduced from Eq. 3.



$$C_6H_5COCH_2\text{-}\left(\text{-}CH_2\text{-}\underset{\substack{|\\C_6H_5}}{CH}\text{-}O\text{-}\right)_n\text{-}H$$

(I)



$$C_6H_5COCH_2\text{-}\left(\text{-}\underset{\substack{|\\C_6H_5}}{CH}\text{-}CH_2\text{-}O\text{-}\right)_n\text{-}H$$

(II)

However, the following additional data indicate that the polymer structure should be represented in somewhat modiffed forms.

First, the hydroxyl number, as estimated by both acetic anhydride and phenyl isocyanate methods, was 1.8∼2.0 per molecule. This result seems to imply that a terminated polymer (initially formed)[5] is revived by hydrogen atom abstraction with any radical at the α-carbon of the phenyl or hydroxyl groups and that then a branching involving a repeated

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[1] R. J. Gritter and T. J. Wallace, *J. Org. Chem*, **26**, 282 (1961).

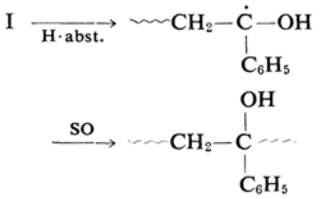
[2] T. J. Wallace and R. J. Gritter, *Tetrahedron*, **19**, 657 (1963).

[3] J. B. Conant and W. R. Peterson, *J. Am. Chem. Soc.*, **54**, 628 (1932).

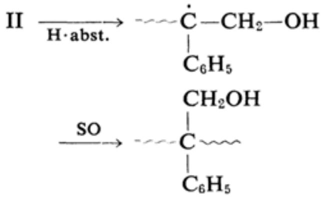
[4] H. Hopff and H. Zahner, *Angew. Chem.*, **72**, 117 (1960).

[5] The average degree of polymerization of this polymer is estimated to be nearly 6∼7 on the basis of both hydroxyl number and carbonyl number (see below).

attack on the epoxide occurs (see Eqs. 4-i, ii). Here, the facile abstraction of an α-hydrogen atom of alcohols and benzyl compounds is a well-known type of reaction.



$$\mathrm{I}\xrightarrow[\text{H}\cdot\text{abst.}]{}\sim CH_2-\underset{\underset{C_6H_5}{|}}{\dot{C}}-OH \xrightarrow{SO} \sim CH_2-\overset{\overset{OH}{|}}{\underset{\underset{C_6H_5}{|}}{C}}\sim \qquad (4\text{-i})$$

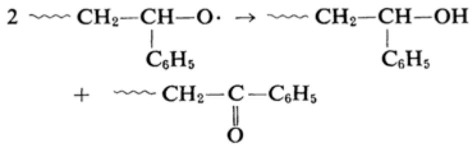


$$\mathrm{II}\xrightarrow[\text{H}\cdot\text{abst.}]{}\sim\underset{\underset{C_6H_5}{|}}{\dot{C}}-CH_2-OH \xrightarrow{SO} \sim\overset{\overset{CH_2OH}{|}}{\underset{\underset{C_6H_5}{|}}{C}}\sim \qquad (4\text{-ii})$$

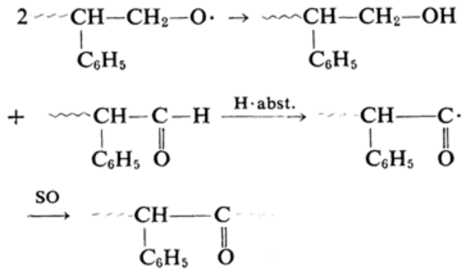
A clear demonstration of a hydroxyl group in the product indicates that, in the propagation step, a preferential attack occurs on the ring carbon atom rather than on the oxygen atom of epoxide. On the other hand, an attack on the ring oxygen would not lead to the appearance of a hydroxyl end group. It is noteworthy that propagation proceeds in a form different from that in the cationic polymerization of epoxides. In connection with the above radical polymerization, the formation of an alternating polymer⁶⁾ from ethylene oxide and perfluoropropene under photo- or radical-initiation is of interest; it seems to involve a somewhat similar propagation step ($C\cdot \rightarrow O\cdot \rightarrow C\cdot \rightarrow O\cdot \rightarrow \cdots$). It has also been reported that the copolymerization of trifluoronitrosomethane and perfluoroolefins⁷⁾ yielded alternating polymers by a similar mechanism.

There remains the problem of which α-carbon the attack of radicals occurs in. As has been described above, Gritter and Wallace¹⁾ observed a predominant formation of a secondary ketoalcohol in a similar reaction; however, a minor attack on the secondary ring carbon, which seems to be energetically favorable,⁸⁾ although sterically unfavorable, may also be considered (see below).

Second, the content of the carbonyl group as determined by the 2,4-dinitrophenylhydrazine method was, unexpectedly, 1.5~1.6 units per molecule. By this treatment, two carbonyl bands (1720 and 1680 cm^{-1}) which were found in the original polymer completely disappeared. One carbonyl group is clearly due to the phenacyl end group; and the other one would be produced by disproportionation between two alkoxy radicals (see Eqs. 5-i, ii). In the latter case, a revival of the initially-terminated polymer with an aldehyde end group by means of hydrogen transfer may also be considered.



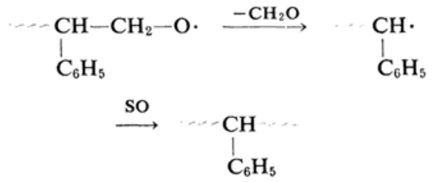
$$2\sim CH_2-\underset{\underset{C_6H_5}{|}}{CH}-O\cdot \rightarrow \sim CH_2-\underset{\underset{C_6H_5}{|}}{CH}-OH + \sim CH_2-\underset{\underset{O}{\|}}{C}-C_6H_5 \qquad (5\text{-i})$$



$$2\sim\underset{\underset{C_6H_5}{|}}{CH}-CH_2-O\cdot \rightarrow \sim\underset{\underset{C_6H_5}{|}}{CH}-CH_2-OH + \sim\underset{\underset{C_6H_5}{|}}{CH}-\underset{\underset{O}{\|}}{C}-H \xrightarrow{\text{H}\cdot\text{abst.}} \sim\underset{\underset{C_6H_5}{|}}{CH}-\underset{\underset{O}{\|}}{C}\cdot \xrightarrow{SO} \sim\underset{\underset{C_6H_5}{|}}{CH}-\underset{\underset{O}{\|}}{C}\sim \qquad (5\text{-ii})$$

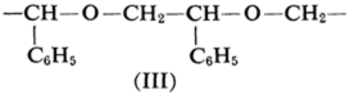
The 1680 cm^{-1} band may be assigned to the carbonyl absorption of phenacyl end groups (cf. Eq. 5-i), and the 1720 cm^{-1} band, to that of the aldehyde and/or the ketone in Eq. 5-ii. The possibility of the radical attack on the secondary ring carbon of the epoxide cannot be excluded because of the appearance of the latter (1720 cm^{-1}) band.

The elimination of formaldehyde, which is a well-known reaction of primary alkoxy radicals,⁸⁾ may also be considered (see Eq. 6). However, this was not confirmed experimentally.



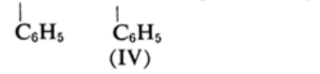
$$\sim\underset{\underset{C_6H_5}{|}}{CH}-CH_2-O\cdot \xrightarrow{-CH_2O} \sim\underset{\underset{C_6H_5}{|}}{CH}\cdot \xrightarrow{SO} \sim\underset{\underset{C_6H_5}{|}}{CH}\sim \qquad (6)$$

In addition, the absorption in the 1030~1100 cm^{-1} region, corresponding to ether, exhibited a medium but broad band with two peaks, although ether absorption is known to be considerably strong. Perhaps this is to be ascribed to the separate contributions of two different ether units, III and IV, in which the latter is produced by a competitive attack on another ring carbon of the epoxide during the propagation.



$$-\underset{\underset{C_6H_5}{|}}{CH}-O-CH_2-\underset{\underset{C_6H_5}{|}}{CH}-O-CH_2-$$

(III)



$$-\underset{\underset{C_6H_5}{|}}{CH}-O-\underset{\underset{C_6H_5}{|}}{CH}-CH_2-O-CH_2-$$

(IV)

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6) M. Hauptshein and J. M. Lesser, *J. Am. Chem. Soc.*, **78**, 676 (1956).

7) G. H. Crawford, D. E. Rice and B. F. Landrum, *J. Polymer Sci.*, **A-1**, 565 (1963).

8) P. Gray and A. Williams, *Chem. Revs.*, **59**, 239 (1959).

The Polymerization of PGE with DTBP.— The results are presented in Table II. In this reaction, no appreciable amount of the ketone derived from phenoxyacetonyl radical, $C_6H_5OCH_2COCH_2\cdot$, could be isolated. The polymer obtained from PGE was soluble in ethanol, but it could be fractionally precipitated with isobutanol. Its elementary analysis was in good agreement with the expected value, and the average molecular weight was 1200. The polymer had strong absorption bands at 3500 (hydroxyl), 1720 (carbonyl) and 1030~1100 cm^{-1} (ether). Besides, the hydroxyl and carbonyl groups in the polymer were both

Table I. Reaction of SO with DTBP

Run	SO g. (mol.)	DTBP g. (mol.)	Reaction temp. & time a) °C, hr.	SO recovered %	Acetophenone % b)	Polymer g. (%) c)	Remarks on ethanol-insol. fraction					
							g.	M. p. °C	M.w. d)	[η] e)	OH group units/molecule	CO group h) units/molecule
1	60 (0.50)	7.3 (0.05)	120~130; 10(6)	95		3.5 (5.8)	0.5	100~105				
2	90 (0.75)	14.5 (0.10)	130~135; 7(3)	90	8.8	5.8 (6.5)	1.5	135~140	1300			
3	60 (0.50)	29 (0.20)	140~145; 6(3)	75	5.0	12.5 (21)	9.0	160~165	2000	0.07	1.8 f); 2.0 g)	1.5
4	240 (2.00)	29 (0.20)	135~143; 5(0)	90		23 (9.6)	6.5	145~150	1800	0.05	2.0 f); 2.0 g)	1.6

a) Figures in parentheses represent the time required for the addition of the peroxide. b) Based on DTBP. (Determined by 2, 4-D method). c) Total yield of ligroin-insol. and ethanol-insol. fractions. Based on SO. d) By cryoscopic method in benzene. e) In benzene, at 25°C. f) By acetic anhydride method. g) By phenyl isocyanate method. h) By 2, 4-D method.

Table II. Reaction of PGE with DTBP

PGE g. (mol.)	DTBP g. (mol.)	Reaction temp. & time a) °C, hr.	PGE recovered %	Polymeric residue g. (%) i)	Remarks on isobutanol-insol. fraction				
					g.	M. p. °C	M.w. d)	OH group g) units/molecule	CO group units/molecule
194 (1.30)	19 (0.13)	145~155; 4(0)	93	15 (7.7)	3	105~110	1200	1.8	1.0

a), d), g) See footnote in Table I. i) Based on PGE.

Table III. Reaction of SO with BPO

SO g. (mol.)	BPO g. (mol.)	Reaction temp. & time a) °C, hr.	SO recovered %	Acetophenone % j)	Polymeric residue g. (%) k)	Remarks on ethanol-insol. fraction				
						g.	M. p. °C	M.w. d)	OH group f) units/molecule	CO group units/molecule
180 (1.50)	36.5 (0.15)	80~81; 5.5(1.0)	69	13	38 (21)	4.6	115~120	1300	1.0	0.85

a), d), f) See footnote in Table I. j) Based on BPO. (Determined by 2, 4-D method). k) Based on SO.

Table IV. Reaction of SO with BA

SO g. (mol.)	BA g. (mol.)	Reaction temp. & time °C, hr.	Products		
			1 : 1 Adduct l) g.	2 : 1 Adduct m) g.	Residue n) g.
30 (0.25)	6.1 (0.05)	80~81; 4.5	7.5	6.0	trace
30 (0.25)	1.2 (0.01)	80~81; 4.5	0.9	0.7	trace

l) Anal. Found: C, 74.41; H, 6.04. Calcd. for $C_{15}H_{14}O_3$: C, 74.36; H, 5.83%. m) Anal. Found: C, 76.20; H, 6.29. Calcd. for $C_{23}H_{22}O_4$: C, 76.22; H, 6.12%. n) Easily soluble in ethanol or ligroin.

estimated to be 1.8 units per molecule.[9] These data seem to predict the contribution of abnormal structures as in the case of the SO polymer.

A comparison of the polymerizing ability of SO and PGE seems to reflect the difference in their reactivities in radical ring-opening. As to the concentration of initiator radicals (acylmethyl radicals), the phenacyl radical would be superior to the phenoxyacetonyl radical. In fact, Wallace and Gritter[2] have recently found that SO was much more reactive than propylene oxide in a hydrogen atom abstraction by *t*-butoxyl radical, and that in the addition of the resulting keto radical to 1-octene, the yield of adduct from SO was higher than that from propylene oxide. If the ring-opening of SO and of PGE is equally facile, it may then be expected that SO will yield a polymer with a lower degree of polymerization but in a higher yield than in the case of PGE. However, the observed degree of polymerization of SO was about twice as large as that of PGE (see Footnotes 5 and 9), and the yield of SO polymer and PGE polymer in similar conditions were 9.6% and 7.7% respectively. Therefore, it may safely be deduced that the polymerizing ability of epoxides is largely dependent upon the ease of their ring-opening.

The Polymerization of SO with Benzoyl Peroxide (BPO).—Initially, a control experiment was conducted with SO and benzoic acid in order to ascertain the possibility of cationic polymerization with the acid (probably present in the reaction mixture). There was, however, no formation of a polyether, and considerable amounts of 1 : 1 and 2 : 1 adducts were isolated (see Experimental). Hence, it is obvious that the polymer from SO using a BPO catalyst would be formed by a radical mechanism. The results are presented in Table III. The ethanol-insoluble fraction of the polymer showed good analytical data. Its average molecular weight was found to be ca. 1300. This value nearly corresponds with that from the hydroxyl number in the DTBP-induced polymer. Its infrared spectrum showed a characteristic absorptin at 3500 (hydroxyl), 1720 and 1680 (carbonyl), and 1030~1100 cm^{-1} (ether). In this polymerization, the ring-opening of SO by an attack of benzoyloxy radical (formed by the decomposition of BPO) as well as by that of phenacyl radical may be expected. In fact, when the polymer was treated with aqueous sodium hydroxide in dioxane, a marked disappearance of the 1720 cm^{-1} band and an increase in the intensity of the hydroxyl band were observed. The determination of hydroxyl and carbonyl groups in the original polymer gave values of 1.0 and 0.75 units per molecule respectively. These results clearly indicate that both benzoyloxy and phenacyl radicals are used to initiate the polymerization and that the polymer has the normal polyether structure, in contrast with the DTBP-induced polymer. The low molecular weight and straight-chain structure of this polymer may result from the low reaction temperature.

The Reaction of SO with α, α'-Azo-bis-isobutyronitrile (AIBN).—An attempt to polymerize SO using an AIBN catalyst was unsuccessful. The reaction resulted in a complete recovery of SO and the quantitative isolation of tetramethylsuccinonitrile derived from AIBN, without any formation of acetophenone or any polymeric product. This would seem to arise from the poor ability of AIBN in hydrogen atom abstraction.

Conclusion

From these results, it can be concluded that the preparation of high molecular weight polyethers from epoxides by peroxide-induced polymerization is practically impossible. The reasons for this may be summed up as follows. The chain propagation reaction involving the ring-opening seems to be energetically somewhat unfavorable, as compared to the initiation reaction containing an α-hydrogen abstraction from epoxide and successive rearrangement to acylmethyl radical. In addition, the facile hydrogen abstraction and disproportionation reactions of the growing alkoxy radical, especially at high temperatures, promote the short-chain termination and cause the branching.

Experimental

The DTBP-induced Polymerization of SO.—In a four-neck flask flushed with purified nitrogen, 240 g. (2.0 mol.) of SO and 29 g. (0.20 mol.) of DTBP were mixed. Under a nitrogen stream, the mixture was gradually heated and refluxed while being stirred at 135~143°C for 5 hr. All volatile fractions (up to 230°C/2 mmHg), such as acetone, *t*-butanol, acetophenone and unreacted SO etc., were removed, and 23 g. of a resinous polymeric residue was obtained. This was fractionated by precipitation from benzene with ethanol or ligroin into two fractions. Anal. of the ethanol-insoluble fraction. Found: C, 81.65; H, 6.71. Calcd. for $(C_8H_8O)_n$: C, 79.97; H, 6.56%.

The Determination of Hydroxyl and Carbonyl Groups.—The determination of hydroxyl and carbonyl contents in the polymer was carried out according to the following well-known methods.

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[9] On the basis of these data, the average degree of polymerization (i. e., that of propagation) is estimated to be about 3.

To obtain reliable data in these estimations, both original and reacted polymers were submitted to treatment in pulverized form.

Acetic Anhydride Method.[10)]—The polymer (1.0 g.) was acetylated with a mixture of acetic anhydride (1.0 ml.) and pyridine (3.0 ml.) at 75°C for 2 hr. In the estimation of unreacted anhydride, it was necessary to wash thoroughly with water the polymer which separated from the reaction mixture upon the addition of water.

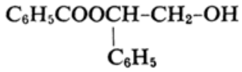
Phenyl Isocyanate Method.—The polymer (0.5 g.) was treated with phenyl isocyanate (0.3 g.) in the presence of pyridine (0.2 g.) in benzene (7 ml.) at 80°C for 2 hr. After the evaporation of low-boiling fractions, the residue was extracted with benzene several times to remove benzene-insoluble by-products (diphenylurea and isocyanate dimer). The dissolved polymer was precipitated with ethanol, and the hydroxyl number was calculated from its nitrogen content.

2, 4-Dinitrophenylhydrazine (2, 4-D) Method.[11)]—The polymer (0.5 g.) was added to a dioxane solution (15 ml.) of 2, 4-D (0.4 g.) containing concd. hydrochloric acid (1.0 g.); the mixture was refluxed for 1 hr. (when tetrahydrofuran was used as a solvent, the heating was continued for 2 hr.). After evaporation to dryness, the benzene-soluble portion in the residue was collected and repeatedly washed with a mixture of ethanol and hydrochloric acid. Then the polymer was redissolved in benzene and reprecipitated with aqueous ethanol containing hydrochloric acid.

The DTBP-induced Polymerization of PGE.—The procedure was similar to that used in the case of SO. The polymer obtained was a colored viscous oil, and it was fractionated by precipitation from benzene with isobutanol. Anal. of the isobutanol-insoluble fraction. Found: C, 72.72; H, 5.89. Calcd. for $(C_9H_{10}O_2)_n$: C, 71.98; H, 6.71%.

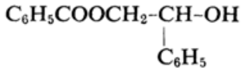
The BPO-induced Polymerization of SO.—To SO in a flask flushed with nitrogen, BPO was added in small portions, and the mixture was stirred at 80∼82°C. After dilution of the cooled reaction mixture with ether, the solution was washed four times each with aqueous sodium carbonate, with aqueous sodium thiosulfate and with water, and dried over anhydrous calcium chloride. By the removal of ether and of all volatile fractions (up to 230°C/2 mmHg), a resinous polymeric product was obtained; this was reprecipitated from ether with ethanol. Anal. of the ethanol-insoluble fraction. Found: C, 81.34; H, 6.14. Calcd. for $(C_8H_8O)_n$: C, 79.97; H, 6.71%.

The Reaction of SO with Benzoic Acid (BA).—As a control experiment for the BPO-induced polymerization, a mixture of SO and BA was heated under the same conditions. The distillation of the reaction mixture afforded considerable amounts of 1 : 1 and 2 : 1 (SO : BA) adducts (b. p. 167∼172°C/2.5 mmHg and 220∼225°C/3 mmHg respectively) and a trace of an ethanol-soluble residue, as Table IV shows. On referring to an authentic material of VI (m. p. 62°C) obtained by an independent method, it was ascertained that the former adduct was a mixture of two structural isomers, V and VI. In view of the facile rearrangement of V to VI, as in the case of the corresponding acetate,[12)] the determination of its composition was not carried out. A rough gas-chromatographic analysis of the latter adduct indicated that it was a 2 : 1 mixture of two isomers. Judging from the orientation of the ring-opening of the epoxide, these isomers would correspond to VII and VIII among the four possible isomers:



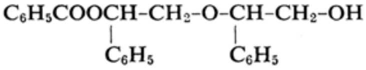
$C_6H_5COO\underset{C_6H_5}{CH}\text{-}CH_2\text{-}OH$

(V)



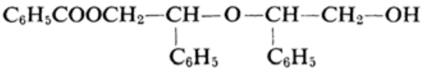
$C_6H_5COOCH_2\text{-}\underset{C_6H_5}{CH}\text{-}OH$

(VI)



$C_6H_5COO\underset{C_6H_5}{CH}\text{-}CH_2\text{-}O\text{-}\underset{C_6H_5}{CH}\text{-}CH_2\text{-}OH$

(VII)



$C_6H_5COOCH_2\text{—}\underset{C_6H_5}{CH}\text{—}O\text{—}\underset{C_6H_5}{CH}\text{—}CH_2\text{—}OH$

(VIII)

The Reaction of SO with AIBN.—To 120 g. (1.0 mol.) of SO in a flask flushed with nitrogen, 16.5 g. (0.1 mol.) of AIBN was added over a 1 hr. period at 79∼80°C and then stirred for 2 hr. each at 80 and at 90°C. In addition to the complete recovery of SO, a nearly quantitative amount of tetramethylsuccinonitrile and a trace of poly(α-methyl acrylonitrile) were isolated.

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10) C. L. Ogg, W. L. Porter and C. O. Willits, *Ind. Eng. Chem., Anal. Ed.*, **17**, 394 (1945).

11) H. A. Iddles and C. E. Jackson, ibid., **6**, 454 (1934).

12) T. Cohen, M. Dughi, V. A. Notaro and G. Pinkus, *J. Org. Chem.*, **27**, 814 (1962).