

TABLE II

DECOMPOSITION OF L-(+)-2-METHYL-3-PHENYL-2-BUTYL HYPOCHLORITE (0.075 *M*) IN CARBON TETRACHLORIDE AT 80°

$a = 3.492$ g.	= amt. of α -phenylethyl chloride added prior to decomn. of hypochlorite
$x = +7.21^\circ$	= opt. rotation of the added chloride, a
b	= total amt. of α -phenylethyl chloride formed from the hypochlorite
y	= opt. rotation of the chloride, b
$c = 2.041$ g.	= amt. of <i>dl</i> -chloride added to aliquot of final soln.
$f = 237/107$	= ratio of total volume of final soln. to volume of aliquot to which c was added
θ	= fract. retention of activity of α -phenylethyl chloride under the exptl. conditions
$\alpha_1 = +4.55^\circ$	= opt. rotation of chloride isolate from aliquot containing chloride a and b
$\alpha_2 = +2.58^\circ$	= opt. rotation of chloride isolated from aliquot containing chloride a , b and c
$\alpha_3 = +0.90^\circ$	= opt. rotation of chloride isolated from an expt. in which hypochlorite was decomposed in the absence of any carrier chloride

ethyl chloride. Subjection of a 0.75-g. sample of α -phenylethyl chloride, $\alpha^{27.5D} + 8.69^\circ$ (*l* 1 dm., neat), $[\alpha]^{27D} + 7.86^\circ$ (*l* 1 dm., 7.4% in carbon tetrachloride) to the same chromatographic procedure afforded 0.52 g. of recovered α -phenylethyl chloride, $n^{20D} 1.5214$, $[\alpha]^{28D} + 7.24^\circ$ (*l* 1 dm., 7.9% in carbon tetrachloride).

Effect of Hypochlorite Concentration on Optical Activity of α -Phenylethyl Chloride.—A sample of the hypochlorite in carbon tetrachloride (0.6 *M*), prepared from the same sample of optically active alcohol employed above, was decomposed and the α -phenylethyl chloride isolated as before, $\alpha^{31.4D} + 1.00^\circ$ (*l* 1 dm., neat).

Calculations.—The data used in the calculations of rotation of alkyl chloride produced from hypochlorite, extent of racemization of alkyl chloride under the experimental conditions and yield are summarized in Table II.

$$\alpha_1 = (a \times \theta + by\theta)/(a + b) \quad (7)^{15}$$

$$\alpha_2 = (a \times \theta + by\theta)/(a + b + fc) \quad (8)^{15}$$

$$\alpha_3 = y\theta \quad (9)$$

Solution of equations 7 and 8 for b gives a value of 2.425 g. for this quantity. Solution for θ then gives 0.983, implying that within the limits of experimental error there is no racemization of active α -phenylethyl chloride under the experimental conditions. Solution for y , the rotation of α -phenylethyl chloride produced from the optically active hypochlorite, gives $+0.915^\circ$. The lower limit to y , ascertained by solution of equations 7 and 8 with θ of unity, is $+0.726^\circ$. The best value for optically pure α -phenylethyl chloride is 126° .¹⁶ Correcting for the degree of optical purity (53%) of the hypochlorite, the α -phenylethyl chloride produced therefrom was 1.1–1.3% retention of optical activity and is of retained configuration.

Effect of Oxygen on Rate of Consumption of Hypochlorite.—One-ml. portions of a solution of the hypochlorite in carbon tetrachloride (initial concentration, 0.035 *M*), prepared by the method described above, were sealed in Pyrex tubes (free space, 4 cc.), heated at 80° for the requisite time intervals, and analyzed for hypochlorite by iodometric analysis (addition of sample to oxygen-free acetic acid containing 1 ml. of saturated potassium iodide solution and titration of the liberated iodine with thiosulfate solution). Half of the tubes were sealed under atmospheric pressure and half were degassed (two cycles of freezing, evacuating, thawing and shaking) and sealed at a final pressure of 0.1 mm. The data are reported in Table I.

NOTE ADDED IN PROOF.—The isolation of α -phenylethyl chloride (99% *DL*-1% *L*) from the decomposition of L-2-methyl-3-phenyl-2-butyl hypochlorite also has been reported recently by D. B. Denney and W. F. Beach, *J. Org. Chem.*, **24**, 108 (1959).

(15) These equations are rigorously correct only for a situation in which both a and b are present at the start and not for a case, such as the one here, in which b is slowly generated as the reaction proceeds. However, the closeness of θ to unity and the relative smallness of the term by compared to ax is sufficient justification for the use of equations 7 and 8 in this case.

(16) R. L. Burwell, Jr., A. D. Shields and H. Hart, *THIS JOURNAL*, **76**, 908 (1954).

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[CONTRIBUTION FROM THE SHELL DEVELOPMENT Co.]

Intramolecular Radical Reactions. Decomposition of Pure Bis-(2-methyl-2-hexyl) Peroxide in the Liquid Phase

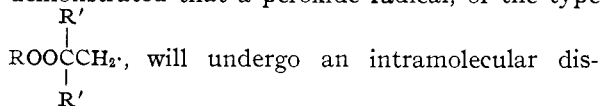
BY H. E. DE LA MARE AND F. F. RUST

RECEIVED DECEMBER 11, 1958

The liquid phase, thermal decomposition of neat bis-(2-methyl-2-hexyl) peroxide gives among other products 2,2,5-trimethyltetrahydrofuran as well as 3- and 4-membered cyclic ethers. A mechanism involving intramolecular radical displacements at the peroxide bond is proposed to account for ring closure.

Introduction

Earlier studies¹ on the thermal and photochemical decomposition of liquid di-*t*-butyl peroxide demonstrated that a peroxide radical, of the type



will undergo an intramolecular displacement reaction to give an olefin oxide—in the case of di-*t*-butyl peroxide, isobutylene oxide. Subsequently, such a transformation was proposed

(1) E. R. Bell, F. F. Rust and W. E. Vaughan, *THIS JOURNAL*, **72**, 337 (1950).

as an important step in the formation of olefin oxides during olefin oxidation,² an idea which has recently received additional support.³

That larger ring cyclic ethers such as tetrahydrofurans also can be products of hydrocarbon oxidation has been shown by oxidation studies of pentane⁴ and hexane⁵ in the cool flame region. Not only tetrahydrofurans but also trimethylene oxides have been isolated as products of the higher

(2) G. H. Twigg, *Chem. Eng. Sci. Suppl.*, **3**, 55 (1954).

(3) F. R. Mayo, *THIS JOURNAL*, **80**, 2499 (1958).

(4) A. R. Ubbelohde, *Proc. Roy. Soc. (London)*, **A152**, 378 (1935).

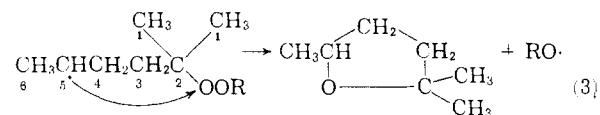
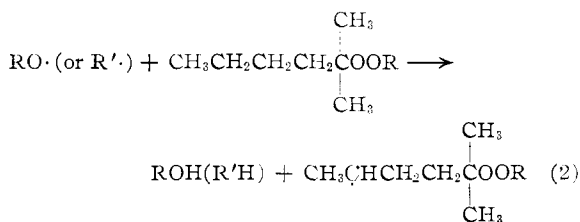
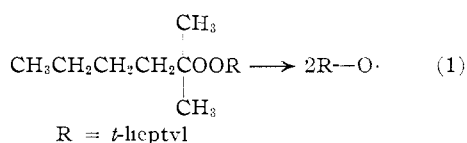
(5) H. C. Bailey and R. G. W. Norrish, *ibid.*, **A212**, 311 (1952).

temperature (450°) vapor phase oxidation of 2,2,4-trimethylpentane, "isooctane," and a mechanism of intramolecular hydrogen abstraction followed by a radical displacement at the peroxide group was proposed for the cyclic ether formation.⁶

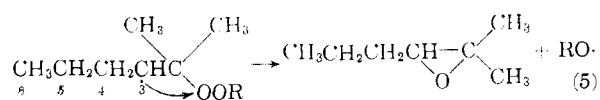
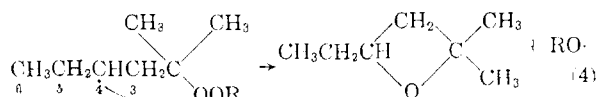
The study of the decomposition of pure bis-(2-methyl-2-hexyl) peroxide ("di-*t*-heptyl peroxide") experimentally demonstrates that intramolecular radical displacement reactions such as those proposed above will in fact give rise to trimethylene oxide and tetrahydrofuran rings.

Results and Discussion

When di-*t*-heptyl peroxide was decomposed by heating the neat liquid at 116–123° (30 mm.) there was obtained a complicated mixture of products. The more volatile products⁷ (~15 components) were resolved quantitatively by gas-liquid partition chromatography on a column of oxydipionitrile supported on crushed firebrick. The distribution of the more volatile products is shown in Table I, where attention is directed particularly to the cyclic ether components. Their formation is considered to occur as



Alternatively, when RO· radicals from the initial scission remove hydrogen atoms from positions 4 or 3, trimethylene oxide or olefin oxide will be formed.



Although the preponderance of trimethyltetrahydrofuran is probably due in part to the facility with which 5-membered rings can be closed, it is felt that an important consideration must be the steric hindrance to hydrogen abstraction at the 4- and 3-positions imposed by the substituents on the 2-carbon atom.

(6) F. F. Rust and D. O. Collamer, *THIS JOURNAL*, **76**, 1055 (1954).

(7) Arbitrarily defined as those distilling below ~50° (1 mm.) which is the boiling point of di-*t*-heptyl peroxide.

Inspection of the other products listed in Table I indicates that they originate from well recognized degradation processes.

TABLE I
VOLATILE^a PRODUCTS FROM DECOMPOSITION OF DI-*t*-HEPTYL PEROXIDE

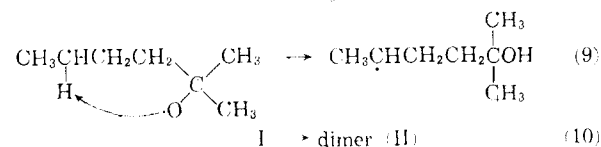
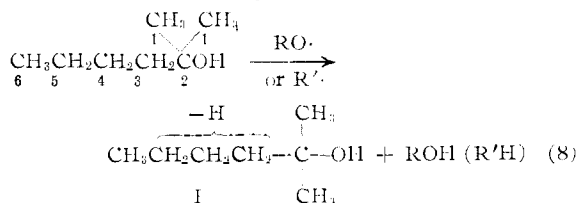
Peroxide charged, 0.295 mole; peroxide recovered, ~0.017 mole; time 37.5 hr. at 116 ± 1° and 15.5 hr. at 123 ± 1° bath temperatures

Peak no.	Emerg. time, min.	Product	~% wt. ^b	Moles/100 moles of peroxide reacted
1	0.1		0.1	...
2	.2	Methane, butane, ^c butenes, other hydrocarbons	.1	42 ^e
3	.3		.3	...
4	.6		.3	...
5	.9		.2	...
6	1.7	<i>n</i> -Octane	.5	0.7
7	7.5	2,2,5-Trimethyltetrahydrofuran	19.0	23
8	12.7	2-Methyl-2,4-epoxyhexane	4.4	5.3
9	14.2	Acetone	17.4	43
10	17.7	Unidentified	0.7	~0.7
11	22.5	2-Methyl-2,3-epoxyhexane	4.4	5.3
12	30.5	Unidentified	1.6	~2
13	35	Unidentified	1.7	~2
14	50	2-Methyl-2-hexanol ^d	48.2	61
15	60(?)	Di- <i>t</i> -heptyl peroxide	1.3	...
16	^e	Water

^a See footnote 7. ^b By GLC on oxydipionitrile; uncalibrated values (see Experimental). ^c Total butane (+ butene) production estimated by: moles acetone - 2 (moles octane) = 0.116. ^d Contains traces of 2-hexanone. ^e Not off column in observation time; functional group analysis did show 1.49% w. water in the original crude. In addition, 0.138 mole of total hydroxyl, 0.145 mole of total carbonyl and 0.024 mole of α-epoxide were found by functional group analysis.

Cleavage of the "*t*-heptyloxy" radical will give acetone and the *n*-butyl radical, which in turn is the source of butane, butylenes and octane via conventional hydrogen abstraction, disproportionation and association reactions. Similarly hydrogen atom abstraction by "*t*-heptyloxy" gives 2-methyl-2-hexanol.

The higher boiling fractions (higher than "di-*t*-heptyl" peroxide) were not completely identified although elemental and spectral analyses indicate that the material is largely of the formula (C₇H₁₄-OH)_n which would strongly suggest mixed dehydrodimers of 2-methyl-2-hexanol. Such products are believed to arise by two different paths



Higher multiples of I will result from further radical attack on II. Two points should be noted. Although it is reasonable from the previous facts to assume predominant attack at the C₅-hydrogens, this is not established. Further, one cannot assess the magnitude of the intramolecular reaction⁸ because 2-methyl-2-hexanol (b.p. 82° (75 mm.)) accumulates to some extent in the reaction kettle during the decomposition and is expected to serve as a good hydrogen donor.

Conclusions

It is concluded that intramolecular radical displacements on the O-O bond will give 3-, 4- and 5-membered cyclic ethers. The demonstration that such displacements are possible lends support to the proposal that a similar mechanism is involved in cyclic ether formation during vapor phase hydrocarbon oxidations.

Experimental

Preparation of Di-*t*-heptyl Peroxide.—The subject peroxide was made by a conventional procedure utilizing 115.6 g. of 2-methyl-2-hexanol (~1.0 mole), ~500 ml. of 65% sulfuric acid and 56.6 g. of 30% hydrogen peroxide (0.5 mole). The alcohol and then the peroxide were added to the acid at 0.5°. After stirring for ~5 hr. at 0.5°, the reaction mixture was allowed to warm gradually to ~15° at the end of 16 hr. The top phase was separated, washed with water and bicarbonate solution, dried over magnesium sulfate and distilled, b.p. 40.5–45° (1 to 2 mm.), yield 31%. The redistilled product gave b.p. 34° (~0.1 mm.), *n*²⁰_D 1.4238. *Anal.* Calcd. for C₁₄H₃₀O₂: C, 73.0; H, 13.1. Found: C, 73.1; H, 13.2. The infrared spectrum showed a strong band at 11.37 characteristic of dialkyl peroxides, and only a trace of carbonyl impurity was detectable.

Preparation of 2,2,5-Trimethyltetrahydrofuran.—An authentic sample of 2,2,5-trimethyltetrahydrofuran was made by steam distillation from a mixture of crude 2-methyl-2,5-hexanediol (γ-valerolactone + 2 MeMgI), water and *p*-toluenesulfonic acid. Redistillation gave a fraction having b.p. 102–103°, *n*²⁰_D 1.4039 (lit.⁹ b.p. 102–103°). *Anal.* Calcd. for C₇H₁₄O: C, 73.6; H, 12.4. Found: C, 73.7; H, 12.4.

Preparation of 2-Methyl-2-hexanol.—2-Methyl-2-hexanol was prepared by a conventional Grignard synthesis (*n*-Bu-MgBr + acetone). Redistillation in the Piroso-Glover column gave a heart cut, b.p. 80° (70 mm.), *n*²⁰_D 1.4177 (lit.¹⁰ b.p. 142° (730 mm.), 60° (25 mm.); *n*²⁰_D 1.4186, 1.4176).

General Procedure.—Di-*t*-heptyl peroxide was decomposed in the pure liquid phase by heating *in vacuo* (30 mm.) for 37.5 hr. at 116 ± 1° (kettle = 110–115°) and 15.5 hr. at 123 ± 1° (kettle = 113–118°). The reaction flask was attached to a 30-in. vacuum-jacketed silvered column (unpacked). The column in turn was equipped with an auto-

matic head which permitted constant removal of volatile products. The total material taken overhead was collected at –78° and then brought to 25° and allowed to de-gas. The volatile material was shown by mass spectrometry to be butane. A total "crude volatile" fraction of 39.9 g. was subjected to analysis by GLC (Gas Liquid Chromatography).

The high boiling products remaining in the kettle were distilled through a short modified Claisen head.

An indication of the essentially quantitative recovery of product is shown in Table II.

Chromatographic Resolution of "Volatile Fraction."—Preliminary scanning was made on small GLC columns (0.8 cm. X 3 m.) containing TEG (triethylene glycol), DC-710 (silicone oil) and DIDP (diisodecyl phthalate) and the initial separation was made on TEG (30% w. on crushed firebrick).

The best separation was effected on a TEG column (120 ml./min. of He, 100°)

Peak no.	~Emergence time, min.	Remarks ^a
0	0.5	Air
1	0.8	Probably butane
2	1.4
3	1.7
4	2.8	<i>n</i> -Octane
5	5.5
6	12.0	Acetone + 2,5,5-tetramethyltetrahydrofuran
7	14.3
8	19.0
9	27.0
10	~34.5	{ 2-Hexanone Di- <i>t</i> -heptyl peroxide (?)
11	83	2-Me-2-hexanol

^a Indicated structure by correlation with emergence times of authentic samples.

Large scale GLC columns (5 ml. charge; 3.2 cm. dia. X 3 m.) allowed the principal components to be isolated by trapping from the exit gas using liquid nitrogen traps. Several fractions were collected on a large scale TEG column (5.0 ml. charge)

Trap	Peak no. ^a	wt. ^b (g.)	<i>n</i> ²⁰ _D	Remarks
I	4	Insuff. to identify
II	6	1.207	1.3880	^c
III	7	0.1151	1.4012	^d
IV	8	.1335	1.4152	^e
V	9	.0645	1.4702 (20.5°)	Not identified
VI	10	.0349	1.4162
VII	11	1.840	1.4177 to 1.4197	Collected in 3 different traps

^a Number on small TEG column; see previous listing.

^b Samples were contaminated by trace amounts of water.

^c Infrared spectrum compatible with mixture of acetone and 2,2,5-trimethyltetrahydrofuran. Trapping experiments on DIDP gave clean separation of these two components; 0.520 g. of acetone, *n*²⁰_D 1.3592, and 0.782 g. of 2,2,5-trimethyltetrahydrofuran, *n*²⁰_D 1.4041, from ~5 ml. charged.

^d Principal component correlated with peak 8 on ODPN (oxydipropionitrile). ^e Principal component correlated with peak 11 on ODPN.

The final quantitative resolution was made on an ODPN (oxydipropionitrile) column (~20', 25%w. ODPN, 80°, 70 cc./min. flow of helium) which spaced the components evenly and gave excellent resolution in good time. These results are summarized in Table I. Trap materials III, IV and V collected on TEG were reanalyzed on ODPN and shown to contain 70–90% of one component in each fraction.

Identification of Products. Acetone, 2-methyl-2-hexanol and 2,2,5-trimethyltetrahydrofuran (which compose ~75% of the volatile products) were identified by correlation of the infrared spectra and emergence times (GLC) between known compounds and the isolated fractions. Since the crude volatile product was such a complicated mixture no attempt

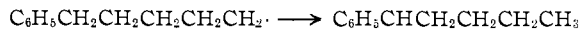
TABLE II
PRODUCT RECOVERY

Charged, g.	67.8 (<i>n</i> ²⁰ _D 1.4338)
Recovered, g.	39.9 (volatile ^a)
	21.2 (high boiling)
	~6.5 (estimate of <i>n</i> -butane ^b)
	67.6 g. (100%)

t-Heptyloxy radicals accounted for ~100%

^a Includes 0.6 g. of water. ^b From acetone production.

(8) See C. A. Grob and H. Kammüller, *Helv. Chim. Acta.*, **40**, 2139 (1957), for a similar intramolecular hydrogen abstraction



(9) F. Richter, Ed., "Beilstein's Handbuch der Organischen Chemie," 4th Ed., XVII (1st Supp.), Julius Springer, Berlin, 1956, p. 11.

(10) R. B. Wagner and H. D. Zook, "Synthetic Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 183.

TABLE III
DISTRIBUTION AND ANALYSIS OF HIGH BOILING PRODUCTS
Peroxide charged, 0.295 mole; peroxide undecomposed, ~ 0.017 mole

B.p., °C. (1 mm.)	n_{20}^D	Wt., g.	Mol. wt.	OH (equiv./100 g.)	Empirical formula	Infrared spectral analysis
23-51	1.4180	0.7	Included in Table I
50-52	1.4254	3.1	C _{7.0} H ₁₆ O _{0.98}	$\sim 77\%$ w. "di- <i>t</i> -heptyl" peroxide
50-54	1.4261	1.0		
54-87	1.4397	1.1	200	0.40	C _{7.0} H ₁₆ O _{0.95}	} $\sim 16\%$ w. "di- <i>t</i> -heptyl" peroxide; strong hydroxyl absorption
87-117	1.4573	4.0	236	0.78	C _{7.0} H ₁₆ O _{0.98}	
117-162	1.4651	1.9	~ 385	.69	C _{7.0} H ₁₆ O _{0.84}	} All show the same strong <i>t</i> -hydroxyl bands; equiv. (as C ₁₄ H ₃₀ O ₂) to 33 moles/100 moles of reacted peroxide
Bottoms (\sim m.p. 55-59°)		10.1	~ 450	.69	C _{7.0} H ₁₄ O _{0.92}	
Trap	1.4170	0.8	Included in Table I

was made to calibrate and correct the approximate %w. values shown in Table I. Functional group values and isolation experiments show the direction and magnitude of the error in GLC values. The acetone to 2,2,4-trimethyltetrahydrofuran ratio (~ 0.9 , Table I) appears to be somewhat high (isolation indicates ~ 0.6 to 0.7) and the 2-methyl-2-hexanol value is high (lower limit $\sim 41\%$ w.).

n-Octane was identified by correlation with emergence time of an authentic sample on both TEG and ODPN chromatographic columns.

2,4-Epoxy-2-methylhexane (1,1-dimethyl-3-ethyltrimethylene oxide, trap product III from TEG) gave a mass spectrum consistent with the postulated structure. Principal masses were 99, 85, 59, etc., and a small parent ion (114) was present as would be expected. Further identification was made by comparison of its infrared spectrum (strong bands at 7.95, 8.70, 10.33, ~ 10.75 and 11.72) with that of an authentic spectrum of 2,2-dimethyl-trimethylene oxide¹¹ which has strong absorption at ~ 7.9 , ~ 8.7 , ~ 10.3 and ~ 11.9 . The bands at ~ 8 and 10.2 to 10.3 μ are said to be characteristic of trimethylene oxide structures.^{11,12} Further, the emergence time (GLC) is consistent with such a structure. Minor impurities present in trap III were water, an ester (5.76 μ), acetone and possibly trimethyl-tetrahydrofuran.

1,1-Dimethyl-1,2-epoxypentane (1,1-dimethyl-2-propyl ethylene oxide trap IV from TEG).—Part of this material was identified as an α -epoxide by virtue of its positive reaction to the periodic acid, silver nitrate test.¹³ The specific

(11) G. M. Barrow and Scott Searles, *THIS JOURNAL*, **75**, 1175 (1953).

(12) See also F. F. Rust and D. O. Collamer, *ibid.*, **76**, 1055 (1954). The latter work indicates that the band in the 10.2 to 10.3 μ region is the more characteristic band for the 4-membered ring containing oxygen.

(13) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 115. Quantitative functional group analysis for

structural identification was based on its infrared spectrum (characteristic bands at 7.24, 7.32(s), 8.0, 8.92, 9.18, 11.13 and 11.8 μ). The latter two bands are in the region expected for the α -epoxide structure¹⁴; the 7.24 and 7.32(s) bands are indicative of the α -gem-dimethyl substitution and by direct comparison isobutylene oxide shows characteristic bands at 7.24, 7.40(s), 7.88, 8.95, 11.1 and ~ 12.5 . The isomeric epoxide (1-methyl-1-butyl ethylene oxide) may also be present; the infrared data do not permit its exclusion.

2-Hexanone (trap product VI, TEG) was identified by its infrared spectrum in CHCl₃ (strong absorption bands at 5.83, 8.13 and ~ 8.55), and conversion to a 2,4-DNP (recryst., m.p. 108-110°); mixture with authentic 2-hexanone 2,4-DNP (m.p. 106°) gave m.p. 106-108°.

High Boiling Products.—The partial identification was based on physical properties, elemental analyses and functional group and spectral analyses summarized in Table III. The hydroxyl values are low (theory for C₇H₁₄OH = 0.87 equiv./100 g.) due to some carbonyl contamination, and possibly some ether formation between epoxide and hydroxyl groups. Molecular weights were determined by micro ebullioscopic methods in dichloroethane, and hydroxyl values by a conventional method using lithium aluminum hydride.

Acknowledgment.—The authors are greatly indebted to Mr. Horace Knight whose help and advice were invaluable in the resolution of the complex reaction mixtures by gas-liquid chromatography.

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α -epoxide (footnote in Table I) was also obtained on the crude "volatile" fraction.

(14) See O. D. Shreve, M. R. Heether, H. B. Knight and Daniel Swern, *Anal. Chem.*, **23**, 278 (1951). Other workers say that a band at $\sim 8 \mu$ is most characteristic of α -epoxide (see L. J. Bellamy, "The Infra-red Spectra of Complex Molecules." Methuen and Co., Ltd., London, 1954, pp. 102-103).