important as electrophilic attack on carbon. This is in agreement with similar conclusions by Winstein based on the reaction of a bis-organomercury with mercuric chloride,[6] and also supports the supposition of Kaufman and Corwin[15] that un-ionized HCl might be an attacking species in the cleavage reaction.

The faster rates of reaction exhibited by the unsaturated groups attached to mercury arise either from an increased electropositivity of the mercury, due to the increased s-character of the attached carbon, or from the ability of these unsaturated groups to stabilize bonding to the incoming hydrogen atom *via* "onium" ion formation.

The lack of significant isotope effect indicates that in the transition state the H–Cl bond is only slightly weakened while the C–H and Hg–Cl bonds are in the process of formation.[16]

The present work would seem to rule out a mechanism in which the rate-determining step is an attack by the solvated proton, analogous to that proposed by Kaufman and Corwin[15] for the perchloric acid cleavage of diphenylmercury. Not only are the reactions over-all second order, regardless of added sulfuric acid or chloride ion, but activation energy calculations for the cleavage of diphenylmercury with HCl and HBr give a difference of over 5 kcal. for the two acids. The reaction of diphenylmercury with HCl in DMSO-dioxane gives the values $-E^*$, 12.2 kcal./mole; ΔS^*, −29 e.u. For diphenylmercury, HBr in DMSO–dioxane the values are $-E^*$, 17.4 kcal./mole; ΔS, −11 e.u.; such differences could not be expected to arise from an attack by the solvated proton alone.

The mechanism as outlined above is consistent with effect of change in structure of R; with the effect of added dioxane, added water, added salt, added sulfuric acid; with the large negative entropies of activation and the deuterium isotope effect, and with the over-all kinetic picture.

Acknowledgments.—The authors wish to acknowledge support of part of this work by The National Science Foundation (Research Grant NSF G-5911).

CINCINNATI 21, OHIO

(15) F. Kaufman and A. H. Corwin, THIS JOURNAL, **77**, 6280 (1955).

(16) K. Wiberg, *Chem. Revs.*, **55**, 713 (1955).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Mechanism of Hypochlorite Decompositions. The Thermal Decomposition of L-(+)-2-Methyl-3-phenyl-2-butyl Hypochlorite

BY FREDERICK D. GREENE

RECEIVED SEPTEMBER 26, 1958

Decomposition of L-(+)-2-methyl-3-phenyl-2-butyl hypochlorite of 53% optical purity in carbon tetrachloride at 80° affords acetone and α-phenylethyl chloride (1-chloroethylbenzene) of 0.71% optical purity (L-configuration) in high yield under conditions in which α-phenylethyl chloride has been shown to be optically stable. The optical results and the marked inhibitory effect of oxygen on rate of decomposition are interpreted in terms of a chain mechanism (equations 2–5) as the principal path of disappearance of hypochlorite.

The organic hypochlorites have received attention principally from the standpoint of synthesis and use as oxidants.[1] Recently a detailed report of the synthesis and isolation of a large number of primary, secondary and tertiary hypochlorites has appeared.[2] Primary and secondary hypochlorites undergo spontaneous decomposition at room temperature to carbonyl compounds and hydrogen chloride. The tertiary hypochlorites, of substantially greater stability, undergo decomposition to carbonyl compounds and alkyl chlorides, equation 1. Isolated examples in the literature, such as

$$R_3C\text{–O–Cl} \longrightarrow R_2CO + RCl \qquad (1)$$

the conversion of 1-methylcyclopentyl hypochlorite to 6-chloro-2-hexanone,[3] are suggestive of considerable selectivity in the decomposition process. The nature of the decompositions[4] represented by equation 1 has received little attention, although the conversion of toluene to benzyl chloride by the action of *t*-butyl hypochlorite and the rapid decomposition of hypochlorites in sunlight are strong indications of the facility with which hypochlorites may enter into free radical reactions. The principal processes, *a priori*, for thermal decomposition of a *t*-hypochlorite in an inert solvent would appear to be unimolecular processes and chain decomposition processes (equations 2–5). Our interest was attracted to this area by the likelihood we attached to the chain process and by the potential use to which such a reaction might be placed in the investigation of stereospecificity and selectivity in free radical chain reactions.[5] This paper presents evidence in support of a chain mechanism as the principal path for the thermal decomposition of the tertiary hypochlorite derived from 2-methyl-3-phenyl-2-butanol.

$$R_3C\text{–O–Cl} \longrightarrow R_3C\text{–O}\cdot + Cl\cdot \qquad (2)$$

$$R_3C\text{–O}\cdot \longrightarrow R_2CO + R\cdot \qquad (3)$$

$$R\cdot + R_3C\text{–O–Cl} \longrightarrow R_3C\text{–O}\cdot + RCl \qquad (4)$$

$$2R\cdot \longrightarrow R\text{–}R \qquad (5)$$

Results and Discussion

The processes on which information was sought were chain decomposition (equations 2–5) and unimolecular four-center decomposition of hypochlorite to alkyl chloride and ketone (equation 6).

---

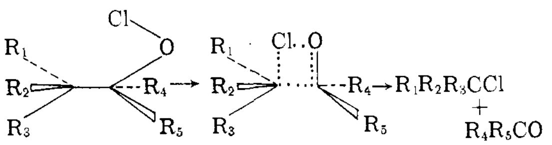
(1) M. Anbar and D. Ginsburg, *Chem. Revs.*, **54**, 925 (1954).

(2) R. Fort and L. Denivelle, *Bull. Soc. chim. France*, 1109 (1954); 534 (1955).

(3) T. L. Cairns and B. E. Englund, *J. Org. Chem.*, **21**, 140 (1956).

(4) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 386–388.

(5) F. D. Greene, W. A. Remers and J. W. Wilson, THIS JOURNAL, **79**, 1416 (1957).



(6)

A stereochemical method utilizing optically active compounds was considered to be the one that would afford the most information in the event that both processes were occurring simultaneously, in that the chain mechanism would be expected to give *dl*-alkyl chloride while the four-center reaction would give optically active chloride of retained configuration. Selection of the system employed in this study, L-2-methyl-3-phenyl-2-butyl hypochlorite, was based on the expectation that the decomposition of the hypochlorite, by either mechanism, would strongly favor rupture of only one of the three possible carbon–carbon bonds and on the known configurational relationships between reactants and products.[6]

A sample of L-(+)-2-methyl-3-phenyl-2-butanol was prepared by the reaction of methyl hydratropoate (optical purity 53%) with methylmagnesium iodide. Conversion to the desired hypochlorite was achieved by the action of aqueous hypochlorous acid on a concentrated solution of the alcohol in carbon tetrachloride. The decompositions were carried out in the dark on diluted anhydrous solutions of the hypochlorite in carbon tetrachloride at reflux. Decomposition of a 0.075 M solution of the hypochlorite afforded acetone, characterized as the 2,4-dinitrophenylhydrazone, α-phenylethyl chloride (98% yield based on alcohol consumed) and recovered 2-methyl-3-phenyl-2-butanol (presumably due to incomplete conversion of alcohol to hypochlorite). Examination of the infrared absorption spectra of all distillation fractions after removal of the acetone–carbon tetrachloride fraction showed only very minor absorption in the 1700–1730 cm.$^{-1}$ region indicating a negligible amount, if any, of 3-phenyl-2-butanone. The weakness of absorption in the ultraviolet at 280–300 mμ for the fractions also renders unlikely the presence of 2,2,3-trimethyldihydrobenzofuran, a possible cyclization product of the 2-methyl-3-phenyl-2-butoxy radical.[7] From an experiment with optically active hypochlorite of 53% optical purity L-configuration, was obtained α-phenylethyl chloride of 0.75% optical purity, L-configuration. In a second experiment, decomposition of a solution of the hypochlorite sixfold more dilute than the above afforded α-phenylethyl chloride of 0.71% optical purity. Assignment of the observed rotations to α-phenylethyl chloride rather than to an impurity is based on the identity of infrared spectra and physical constants of these samples with authentic material and on their chromatographic behavior. The active samples were chromatographed on acid-washed alumina using petroleum ether as eluent. The first fraction contained the α-phenylethyl chloride which had retained 86% of the optical activity. In a control experiment, a sample of authentic optically active α-phenylethyl chloride retained 90% of its activity under comparable chromatographic conditions.

In order to establish the degree of optical stability of α-phenylethyl chloride under the experimental conditions of the hypochlorite decomposition, a sample was prepared by the action of nitrosyl chloride on L-(+)-α-phenylethylamine[8] (α-methylbenzylamine). From this reaction at room temperature in dioxane was obtained α-phenylethyl chloride of 58% retention, 42% inversion of configuration.[9] Decomposition of optically active hypochlorite in carbon tetrachloride in the presence of an added amount of L-(+)-α-phenylethyl chloride of known degree of optical purity was allowed to proceed to completion. The solution was divided into two parts, to one of which was added a portion of *dl*-α-phenylethyl chloride. From the rotations of α-phenylethyl chloride recovered from the two fractions and the rotation of the chloride obtained from an experiment involving no added optically active chloride one may calculate the extent of racemization of α-phenylethyl chloride under the experimental conditions and the optical rotation of the α-phenylethyl chloride produced from the active hypochlorite. (The data of these calculations, summarized in Table II, and the method of analysis of the data, equations 7–9, are reported in the Experimental section.) Analysis of the data indicates that there is less than 2% racemization of optically active α-phenylethyl chloride under the experimental conditions and that the α-phenylethyl chloride produced from L-2-methyl-3-phenyl-2-butyl hypochlorite has 1.1–1.3% retention of optical activity and is of retained configuration.

TABLE I

RATE OF DECOMPOSITION OF 2-METHYL-3-PHENYL-2-BUTYL HYPOCHLORITE IN CARBON TETRACHLORIDE AT 80°

Decomposition conditions	Decomposition, %, in 50 min.	120 min.	180 min.
Atmospheric pressure	<1	1.4	3.5
Degassed, sealed *in vacuo*	14	60	80

The formation of racemic α-phenylethyl chloride from the optically active hypochlorite is strong evidence for the chain decomposition (equations 3 and 4). Kinetic evidence in support of free radical chain decomposition is found in the powerful inhibitory effect of oxygen on the rate of the decomposition. The magnitude of the inhibitory effect is indicative of a long chain length.

With respect to the origin of the small (1.1–1.3%) but definite optical activity in the α-phenylethyl chloride produced from active hypochlorite, several alternatives exist. On the assumption that the four-center process (eq. 6) would give chloride of completely retained configuration and that alkyl chloride produced by all other processes would be inactive, this value of 1.1–1.3% represents the

---

(6) See H. Hart and H. S. Eleuterio, THIS JOURNAL, **76**, 516 (1954), and earlier references cited therein for the correlation of (−)-hydratropic acid with (+)-α-phenylethyl chloride.

(7) The data of this paper are uninformative on the question of a finite existence for this alkoxy radical, *i.e.*, on the activation energy associated with equation 3 in these experiments.

(8) H. Felkin, *Compt. rend.*, **236**, 298 (1953).

(9) The above method of preparation of the optically active chloride was chosen because of the facile resolution of the corresponding amine by the method of W. Theilacker and H. Winkler, *Chem. Ber.*, **87**, 690 (1954), and the unimportance to the present work of the degree of optical purity of the chloride. For experiments in which α-phenylethyl chloride of high optical purity is needed, the method of choice is that of Burwell, Shields and Hart (ref. 16).

upper limit to the amount of hypochlorite that may be consumed by the four center process, with the remaining 98.7% being consumed largely by chain decomposition (eq. 4) and in small measure by homolytic fission (eq. 2). However, the chain-carrying step envisioned for the formation of the alkyl chloride is one in which an α-phenylethyl radical (planar or undergoing rapid interconversion between *d*- and *l*- configurations) abstracts a chlorine atom from *optically active* alkyl hypochlorite, a step in which the asymmetry of the hypochlorite may exert an influence on the orientation of the α-phenylethyl moiety in the transition state. Although this chain-carrying step is probably one of low activation energy and one in which the attacking radical and the region of asymmetry in the substrate need not be at close quarters in the transition state, it does not seem unreasonable to attribute some or all of the 1% of activity of the α-phenylethyl chloride to asymmetric induction in this step. An alternate path for formation of optically active α-phenylethyl chloride would be geminate ("cage") recombination of chlorine atoms and α-phenylethyl radicals, a process that might possibly be expected to yield optically active chloride in view of the demonstrated stereospecificity shown in a number of decompositions of diacyl peroxides.[10] However, the invariance of optical rotation of α-phenylethyl chloride to a sixfold change in initial concentration of hypochlorite is more in accord with the chain process (*via* slight asymmetric induction) than with the geminate recombination process or four-center process in that the latter two processes should be favored relative to the chain process at the lower concentration.[11]

Experimental

Methyl Methylphenylacetate.—A sample of methylphenylacetic acid[12] of b.p. 121–123° (0.5 mm.), n^{25}_{D} 1.5211, $\alpha^{32.5}_{\mathrm{D}}$ −52.31 (*l* 1 dm., neat), was converted by the action of an ethereal solution of diazomethane to the methyl ester, b.p. 62–63° (0.2 mm.), n^{32}_{D} 1.4967, $\alpha^{31.4}_{\mathrm{D}}$ −57.98 (*l*, 1 dm., neat).

2-Methyl-3-phenyl-2-butanol.—To a cooled ethereal solution of methylmagnesium iodide, prepared from 42.6 g. of methyl iodide and 7.3 g. of magnesium, was added a solution of 16.9 g. (0.103 mole) of the above ester in 60 ml. of ether over a period of 30 min. The mixture was heated at reflux for an additional 45 min., cooled and the excess Grignard reagent was decomposed by the addition of saturated aqueous ammonium chloride solution. Water was added and the mixture was extracted three times with ether. The ether layers were washed with 5% sodium bisulfite solution, with sodium bicarbonate solution and dried over magnesium sulfate. Filtration, removal of the ether and distillation of the residual oil afforded 14.1 g. (0.086 mole) of pure 2-methyl-3-phenyl-2-butanol, b.p. 72–73° (0.35 mm.), n^{28}_{D} 1.5131,[13] α^{32}_{D} +10.16 (*l*, 1 dm., neat). After storage at 0° the material solidified, m.p. 36–45°, $[\alpha]^{31.4}_{\mathrm{D}}$ +10.1° (*l* 1 dm., 9% in carbon tetrachloride). A sample of racemic alcohol prepared by this method melted sharply at 45–46°.

Anal. Calcd. for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.23; H, 9.86.

L-(+)-α-**Phenylethyl chloride** was prepared by the method indicated by Felkin.[8] (The procedure is described here in detail because of the lack of detail in ref. 8.) To a solution of 11.8 g. of L-(+)-α-phenylethylamine, b.p. 82.5–83° (18 mm.), n^{28}_{D} 1.5224, α^{28}_{D} +14.40° (*l* 1 dm., neat), partially resolved by the method of Theilacker and Winkler,[9] in 100 ml. of dry dioxane cooled to 10° was added dropwise a solution of nitrosyl chloride[14] in dioxane until a slight excess of the nitrosyl chloride had been added. The cooled solution was poured into 300 ml. of ice-water and extracted with ether. The ether layers were washed with 5% aqueous hydrochloric acid, with water, three times with 5% sodium carbonate solution and dried over magnesium sulfate. Filtration, removal of ether and distillation of the residue afforded a forerun of 1.1 g., b.p. 50–83.5° (19 mm.), and a main fraction of 3.5 g., b.p. 80.5–82.5° (17 mm.), n^{30}_{D} 1.5210, α^{28}_{D} +7.21° (*l* 1 dm., neat). In a second experiment α-phenylethyl chloride of $\alpha^{27.5}_{\mathrm{D}}$ +8.69° (*l* 1 dm., neat) was obtained.

Preparation and Decomposition of 2-Methyl-3-phenyl-2-butyl Hypochlorite.—To an 80-ml. sample of Clorox (0.745 *M* in sodium hypochlorite by iodometric analysis), cooled to 0°, was added a cooled solution of 5.0 g. (0.0305 mole) of 2-methyl-3-phenyl-2-butanol [α^{32}_{D} +10.16 (*l* 1 dm., neat)] in 10 ml. of carbon tetrachloride containing 5.0 g. of acetic acid (reagent grade). After a 90-min. period of vigorous stirring at 0° the layers were separated and the aqueous phase was extracted with a 10-ml. portion of carbon tetrachloride. The organic phases were combined, extracted three times with 3% aqueous sodium bicarbonate and dried over magnesium sulfate. The pale yellow filtered solution was diluted to exactly 25 ml.

A 20-ml. portion was added to 214 ml. of carbon tetrachloride (freshly distilled from phosphorus pentoxide directly into the reaction vessel). To the solution was added 3.492 g. of α-phenylethyl chloride, α^{28}_{D} +7.21° (*l* 1 dm., neat). The resulting solution (approx. 0.075 *M*) in hypochlorite) was heated at reflux for 18 hr. Titration (iodometric) of 10-ml. aliquots indicated 99% decomposition after 18 hr.

A 110-ml. portion was withdrawn, placed in a dry flask, and the bulk of the solvent was removed at atmospheric pressure through a 1-ft. Vigreux column. The first 50 ml. of distillate was shaken with a solution of 1 g. of 2,4-dinitrophenylhydrazine in 20 ml. of 75% ethanol containing 4 ml. of concd. sulfuric acid. The carbon tetrachloride layer was separated, washed with water and dried over magnesium sulfate. Filtration and removal of solvent afforded a residue of 1.2 g. of acetone 2,4-dinitrophenylhydrazone, m.p. 122–124°, mixed m.p. with an authentic sample, 123–125°. After removal of the rest of the solvent from the 110-ml. aliquot, the residual oil was distilled yielding a forerun of 0.74 g., b.p. 80–83° (15 mm.); a main fraction of 1.26 g. of α-phenylethyl chloride, b.p. 83–85° (15 mm.), n^{28}_{D} 1.5225, α^{27}_{D} +4.55° (*l* 1 dm., neat); and a 0.45-g. fraction consisting largely of 2-methyl-3-phenyl-2-butanol, b.p. 70–73° (0.1 mm.), identified by infrared absorption spectrum. All three fractions showed negligible absorption in the 1700–1730 cm.$^{-1}$ region, indicating the absence of 3-phenyl-2-butanone. The third fraction was inert toward a solution of bromine in carbon tetrachloride indicating the absence of 2-methyl-3-phenyl-2-butene.

To the remaining 107 ml. of the original carbon tetrachloride solution was added 2.041 g. of *dl*-α-phenylethyl chloride. Removal of the solvent through the 1-ft. Vigreux column and distillation of the residual oil afforded a forerun of 0.64 g., b.p. 80–83° (15 mm.), and a 2.5-g. fraction of α-phenylethyl chloride, b.p. 83–85° (15 mm.), n^{28}_{D} 1.5223, α^{27}_{D} +2.58° (*l* 1 dm., neat). In another experiment a 4.35-g. sample of 2-methyl-3-phenyl-2-butanol, α^{32}_{D} +10.16° (*l* 1 dm., neat), was converted to the hypochlorite by the above procedure and heated at reflux in 230 ml. of carbon tetrachloride for 18 hr. The α-phenylethyl chloride isolated from this experiment (1.37 g.) had n^{28}_{D} 1.5234, α^{28}_{D} +0.90°. A 0.85-g. portion was chromatographed on 15 g. of alumina (Merck, acid-washed) eluting with petroleum ether (b.p. 30–60°). Removal of the petroleum ether from the first fraction of 20 ml. of eluent afforded 0.65 g. of colorless oil, n^{30}_{D} 1.5210, $[\alpha]^{28}_{\mathrm{D}}$ +0.68° (*l* 1 dm., 27% in carbon tetrachloride). The infrared absorption spectrum was identical with that of pure α-phenyl-

---

[10] (a) D. F. DeTar and C. Weis, THIS JOURNAL, **79**, 3045 (1957); (b) F. D. Greene, *ibid.*, **77**, 4869 (1955).

[11] The pertinent rate expression for decomposition by unimolecular and by chain processes, assuming the highly probable termination step of equation 5, is $-\mathrm{d\,ROCl}/\mathrm{d}t = k[\mathrm{ROCl}] + k_i\,[\mathrm{ROCl}]^{3/2}$.

[12] A. Campbell and J. Kenyon, *J. Chem. Soc.*, 25 (1946).

[13] S. Winstein and B. K. Morse, THIS JOURNAL, **74**, 1137 (1952), prepared the racemic alcohol by a different method, b.p. 85–87° (4.5 mm.), n^{25}_{D} 1.5158.

[14] J. R. Morton and H. W. Wilcox, "Inorganic Syntheses," Vol. IV, 1953, p. 48.

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 decompn. of hypochlorite
$x = +7.21°$ = 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 *dl*-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
$\alpha_1 = +4.55°$ = opt. rotation of chloride isolate from aliquot containing chloride *a* and *b*
$\alpha_2 = +2.58°$ = opt. rotation of chloride isolated from aliquot containing chloride *a*, *b* and *c*
$\alpha_3 = +0.90°$ = 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, $\alpha^{27.5}$D +8.69° (*l* 1 dm., neat), $[\alpha]^{27}$D +7.86° (*l* 1 dm., 7.4% in carbon tetrachloride) to the same chromatographic procedure afforded 0.52 g. of recovered α-phenylethyl chloride, n^{29}D 1.5214, $[\alpha]^{28}$D +7.24° (*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, $\alpha^{31.4}$D +1.00° (*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.

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

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

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

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°. The lower limit to *y*, ascertained by solution of equations 7 and 8 with θ of unity, is +0.726°. 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).

CAMBRIDGE 39, MASSACHUSETTS

[CONTRIBUTION FROM THE SHELL DEVELOPMENT CO.]

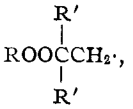
Intramolecular Radical Reactions. Decomposition of Pure Bis-(2-methyl-2-hexyl) Peroxide in the Liquid Phase

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 studies[1] on the thermal and photochemical decomposition of liquid di-*t*-butyl peroxide demonstrated that a peroxide radical, of the type  $\mathrm{ROO}\underset{\mathrm{R'}}{\overset{\mathrm{R'}}{\mathrm{C}}}\mathrm{CH_2}\cdot$, 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 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 pentane[4] and hexane[5] in the cool flame region. Not only tetrahydrofurans but also trimethylene oxides have been isolated as products of the higher

---

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

[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).