

carbinol, 6 g. of redistilled *p*-toluenesulfonyl chloride and 15 ml. of dry pyridine. The solution was allowed to stand overnight and then poured into ice-cold 6 *N* sulfuric acid. The 14 g. of crude ester so obtained was crystallized twice from ethyl acetate-hexane to give 9.35 g. of long needles melting at 108°.

*Anal.* Calcd. for  $\text{C}_{22}\text{H}_{22}\text{O}_3\text{S}$ : C, 72.2; H, 6.03; S, 8.76; equiv. wt. on acetolysis, 366. Found: C, 71.9; H, 6.27; S, 8.73; equiv. wt., 373.

The labeled ester was prepared similarly from 2.55 g. of carbinol to give 3.4 g. of purified ester, m.p. 106°. *Anal.* 1.625, 1.650, 1.640  $\mu\text{c}$ . of carbon-14/mmole.

**Acetolysis of 2-Phenyl-2-(*p*-tolyl)-ethyl-1- $\text{C}^{14}$  Tosylate.**—Two 500-mg. samples of the above mentioned labeled tosylate were heated separately 16 hours with dry acetic acid at 100°. Each was then poured into water and the solid precipitates recrystallized from methanol to give about 200 mg. each of 4-methylstilbene, m.p. 110°. This stilbene assayed 1.605, 1.611  $\mu\text{c}$ . of carbon-14/mmole. Each sample of stilbene was then oxidized with alkaline potassium permanganate, and the terephthalic acid isolated as before.<sup>2</sup> Assay of terephthalic acid: (1) 1.150, 1.155, 1.155  $\mu\text{c}$ . of carbon-14/mmole; (2) 1.155, 1.175  $\mu\text{c}$ . of carbon-14/mmole. This corresponds to an average of 71.6% *p*-tolyl group migration or a migration ratio of *p*-tolyl to phenyl of 2.47.

**Reaction of 2-Phenyl-2-(*p*-tolyl)-ethyl-1- $\text{C}^{14}$  Tosylate with Sodium Methoxide in Methyl Cellosolve.**—A 1.00-g. sample of the labeled tosylate was heated at 90° (steam-bath) with 100 ml. of a 0.0460 *M* solution of sodium methoxide in methyl cellosolve. The solution was poured into water and the resultant oil ether-extracted, dried and oxidized with alkaline permanganate. It oxidized with difficulty. The resulting terephthalic acid was filtered from hot dilute hydrochloric acid, washed with alcohol and ether and vacuum sublimed. Assay of this acid showed carbon-14 activity only slightly over background, corresponding at most to 1.9% *p*-tolyl group migration.

**Di-(*p*-tolyl)-ethyl Tosylate.**—The corresponding carbinol was prepared in the usual<sup>2</sup> fashion from di-(*p*-tolyl)-acetonitrile *via* hydrolysis to the acid and reduction of the acid, m.p. 144°, to the carbinol with lithium aluminum hydride. The product of this reaction was an oil which crystallized spontaneously. The over-all yield of carbinol was 44 g. from 110 g. of the corresponding benzhydryl chloride

and 40 g. of cuprous cyanide. It crystallized from low-boiling petroleum ether as a cottony mass which melted at 51°.

*Anal.* Calcd. for  $\text{C}_{16}\text{H}_{18}\text{O}$ : C, 84.9; H, 8.04. Found: C, 84.9; H, 8.13.

The tosylate was prepared as above from 7 g. of the carbinol, 6 g. of tosyl chloride, and 15 ml. of pyridine at room temperature overnight. The crude ester weighed 12 g. and melted at 72°. Recrystallization twice from hexane gave 7.0 g. of ester with an unchanged melting point.

*Anal.* Calcd. for  $\text{C}_{23}\text{H}_{24}\text{O}_3\text{S}$ : C, 72.6; H, 6.33; S, 8.43; equiv. wt. on acetolysis, 380. Found: C, 72.7; H, 6.59; S, 8.41; equiv. wt., 388.

**Rate Measurements.**—Acetic acid was distilled from acetic anhydride and sulfuric acid. It analyzed by titration 99.70% acetic acid. The solution of potassium acetate was prepared from this acetic acid and 4.92 g. of potassium acetate per liter of solution. It was standardized against a solution of *p*-toluenesulfonic acid monohydrate in acetic acid and proved to be 0.0533 *M*. The toluenesulfonic acid was in turn standardized against sodium hydroxide and had an equivalent weight of 190.6. The methyl cellosolve was purified by distillation at atmospheric pressure, and the fraction boiling at 121–122 used. The solutions for solvolysis were prepared by adding a standardized (0.046 *M*) solution of sodium methoxide in this reagent to an accurately weighed amount of the ester in a volumetric flask. In every case the amount of ester was sufficient to make the resulting solution 0.0460 *M* in ester. The measurement of acetolysis rates was accomplished by the sealed ampule technique exactly as previously described.<sup>3</sup> A 5.00-ml. sample was taken for each titration. The measurements of alkoxide solvolysis were also made by the sealed ampule technique. A 5.00-ml. aliquot of each ampule was withdrawn, added to 5.00 ml. of 0.0529 *M* HCl, and the resulting suspension titrated with 0.0514 *M* NaOH, using phenolphthalein as indicator. The thermostat employed used the saturated vapor of a boiling liquid as the constant temperature source of heat. For measurements at 100°, this liquid was water and for measurements at 78°, the liquid was alcohol. Temperatures were measured with a thermometer calibrated in 0.1° steps.

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[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

## The Reaction of Peroxides and Hydroperoxides with Lithium Aluminum Hydride

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Hydroperoxides and polymeric peroxides are much more reactive toward lithium aluminum hydride than are most monomeric dialkyl peroxides. A stepwise chain degradation involving cyclic intermediates has been proposed to explain the facile reduction of polymeric peroxides to glycols. Lithium aluminum hydride will not readily catalyze the basic decomposition of peroxides containing an  $\alpha$ -hydrogen atom activated by a phenyl group.

Prior to the start of this investigation, there had been no reports of the reduction of alkyl peroxides by lithium aluminum hydride although reductions of benzoyl peroxide,<sup>1</sup> 1,2,3,4-tetrahydronaphth-1-yl hydroperoxide<sup>2</sup> and 2-cyclohexen-1-yl hydroperoxide<sup>3</sup> had been noted. Recently, the reduction of several 9,10-diarylanthracene photo-peroxides,<sup>3</sup> triphenylmethyl peroxide,<sup>3</sup> ascaridole,<sup>4</sup> *t*-butyl peroxide,<sup>4</sup> methyl 1,2,3,4-tetrahydronaphth-1-yl peroxide,<sup>4</sup> and the ozonide of phenylskatole<sup>5</sup> have been reported.

To determine the scope of this reaction, we have

- (1) F. A. Hochstein, *THIS JOURNAL*, **71**, 305 (1949).
- (2) D. A. Sutton, *Chemistry and Industry*, 272 (1951).
- (3) A. Mustafa, *J. Chem. Soc.*, 2435 (1952).
- (4) M. Matic and D. A. Sutton, *ibid.*, 2679 (1952).
- (5) B. Witkop and J. B. Patrick, *THIS JOURNAL*, **74**, 3855 (1952).

attempted to reduce a series of hydroperoxides and peroxides, including polymeric peroxides, by lithium aluminum hydride in butyl ether or dioxane solution. It was hoped that the reduction might occur quantitatively at low temperatures and thus provide a general method of analysis for alkyl peroxides.

### Results and Discussion

A number of reductions were attempted or performed on an analytical scale by slowly adding a 0.1 *M* solution of a peroxide or hydroperoxide in butyl ether or dioxane to a 0.1 *M* solution of lithium aluminum hydride in butyl ether. The hydrogen evolved during reaction was collected at constant pressure and measured to  $\pm 2\%$  in a thermostated gas buret. When the gas evolution

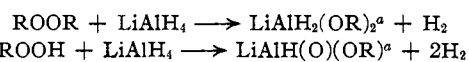
TABLE I  
 REACTION OF LITHIUM ALUMINUM HYDRIDE WITH VARIOUS PEROXIDES AND HYDROPEROXIDES<sup>a</sup>

Peroxide	Purity, %	Peroxide used <sup>b</sup>	LAH used	Temp., °C.	Time, hr.	H <sub>2</sub> <sup>c</sup>	LAH destroyed <sup>c</sup>	Peroxide, % From H <sub>2</sub> <sup>d</sup>	From LaH <sup>e</sup>
Styrene <sup>f</sup>	96.2 <sup>g</sup>	0.961	1.006	25	12	0.875	0.471	91.1	99.2
$\alpha$ -Methylstyrene <sup>h</sup>	96.0 <sup>g</sup>	.982	1.006	25	6	.919	.457	94.0	93.0
Indene <sup>i</sup>	100.0 <sup>g</sup>	.912	1.006	25	6	.821	.453	90.0	99.4
Cumyl hydroperoxide	99.2 <sup>j</sup>	.695	1.03	25	3	1.408	.518	101 <sup>k</sup>	100 <sup>l</sup>
8- <i>p</i> -Cymyl hydroperoxide	95-96 <sup>j</sup>	.793	1.03	25	3	1.533	.567	96.7 <sup>k</sup>	96.5 <sup>l</sup>
<i>t</i> -Butyl	>95	1.04	0.696	{ 25 55	{ 2 0.5	0.01	<.01	<2	<4
<i>t</i> -Butyl ethyl	100 <sup>g</sup>	2.82	1.006	25	6				
Cumyl	100 <sup>m</sup>	1.11	0.940	{ 25 55	{ 3 1	.10	.07	<10	<15
<i>t</i> -Butyl $\alpha$ -phenylethyl	>95	0.461	.503	{ 25 55	{ 4 1				
Benzyl <i>t</i> -butyl	>95	.820	.503	25	5	.025	.014	<4	<4
Triphenylmethyl	>95	.626 <sup>n</sup>	.826	{ 25 55	{ 4 1	.012	.026	<2	<8

<sup>a</sup> All quantities in millimoles. <sup>b</sup> Assuming peroxide to be 100% pure. <sup>c</sup> Blank correction and vapor correction for solvent applied. <sup>d</sup> Hydrogen evolved/peroxide used. <sup>e</sup> (LAH destroyed) 2/peroxide used. <sup>f</sup> Mol. wt., 3900. <sup>g</sup> From carbon and hydrogen analysis. <sup>h</sup> Mol. wt., 5000. <sup>i</sup> Mol. wt., 1500. <sup>j</sup> Analysis by acetic acid and potassium iodide in isopropyl alcohol. (V. R. Kokatnur and M. Jelling, *ibid.*, **63**, 1432 (1941)). <sup>k</sup> Hydrogen evolved/(peroxide used)2. <sup>l</sup> (LAH destroyed) (4/3)/peroxide used. <sup>m</sup> Analysis by sodium iodide and hydrochloric acid in glacial acetic acid. <sup>n</sup> Slurry in butyl ether.

had ceased, the unreacted lithium aluminum hydride was destroyed by *t*-amyl alcohol and the hydrogen evolved on hydrolysis measured. In Table I, the results obtained for nine peroxides and two hydroperoxides are summarized, wherein the purities of the peroxides as determined by known analytical methods or by combustion are compared with the values obtained from the amounts of hydrogen evolved and lithium aluminum hydride destroyed during reduction.

The results obtained for the polymeric peroxides of styrene,  $\alpha$ -methylstyrene and indene and for cumyl and 8-*p*-cymyl hydroperoxides clearly indicate that the stoichiometry of the reaction of peroxides and hydroperoxides with lithium aluminum hydride is



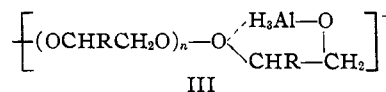
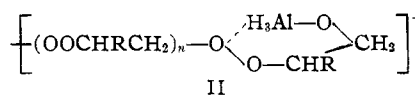
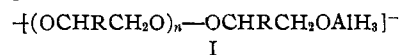
<sup>a</sup> Or its equivalent.

From the results obtained with cumyl, 8-*p*-cymyl, 2-cyclohexen-1-yl<sup>2</sup> and 1,2,3,4-tetrahydronaphth-1-yl<sup>2</sup> hydroperoxides, it seems safe to assume that nearly all hydroperoxides are easily reduced to alcohols by lithium aluminum hydride. Alkyl peroxides do not react nearly as readily. It is of interest that of the alkyl peroxides that can be reduced easily, not one contains the tertiary butyl group. Matic and Sutton<sup>4</sup> were able to reduce *t*-butyl peroxide only at 135°—a temperature at which lithium aluminum hydride itself slowly decomposes.<sup>6</sup> *t*-Butyl ethyl peroxide was prepared and its reduction attempted particularly to see if decreasing the size of an alkyl group increased the reactivity of an alkyl peroxide toward lithium aluminum hydride, but, as shown in Table I, neither *t*-butyl nor *t*-butyl ethyl peroxide underwent noticeable reduction at temperatures up to 55°.

The influence of the activated  $\alpha$ -hydrogen atoms

present in indene, styrene and methyl 1,2,3,4-tetrahydronaphth-1-yl peroxides was considered since it has been shown that *t*-butyl  $\alpha$ -phenylethyl peroxide undergoes a base-catalyzed decomposition.<sup>7</sup> A similar process involving lithium aluminum hydride as the base was considered possible. However, the failure of the attempted reduction of benzyl *t*-butyl and *t*-butyl  $\alpha$ -phenylethyl peroxides (Table I) shows that the presence of activated  $\alpha$ -hydrogen atoms is not a sufficient condition for reduction.

Of the three polymeric peroxides investigated, all were reduced in a nearly quantitative manner. The fact that polymeric peroxides react more readily than most monomeric peroxides with lithium aluminum hydride can be explained by a stepwise reductive chain degradation. Thus, if a peroxide bond of a polymeric peroxide is broken by the action of lithium aluminum hydride, I is a probable product. By cyclization of I, intermediates similar to II or III, containing 5- or 6-membered rings, may be formed. Transfer of a hydride ion with cleavage of the peroxide bond in II or III will produce carbinols which will react readily with lithium aluminum hydride to produce hydrogen and compounds similar to I or capable of exchanging with lithium aluminum hydride to produce I. It is postulated that the scission of a peroxide bond occurs more readily by such a cyclic mechanism than by the attack of  $\text{AlH}_4^-$  ions on isolated peroxide links. The initial formation of I



(6) A. E. Finholt, A. C. Bond and H. I. Schlesinger, *THIS JOURNAL*, **69**, 1199 (1947).

(7) N. Kornblum and H. E. DeLaMare, *ibid.*, **73**, 880 (1951).

from a polymeric peroxide molecule may be aided by the end-groups present (e.g., carbonyl, hydroxyl and hydroperoxide).

The isolation of phenylglycol in nearly quantitative yields (88% of purified material) from the reaction of styrene peroxide and lithium aluminum hydride at 0–5° offers excellent proof that the structure of styrene peroxide is that of a 1:1 copolymer of oxygen and styrene and represents a considerable improvement over catalytic or electrolytic reduction.<sup>8</sup> However, the exact peroxide contents of the polymers used are not known since conventional methods of analysis fail and it is possible that a small amount of the oxygen of polymeric peroxides is present in a form other than peroxide. Furthermore, the nature of the end-groups of polymeric peroxides is not known. Because of the latter, polymers with molecular weights as high as easily obtainable were used to mask any complicating reactions due to end-groups. From the data given in Table I it is apparent that for styrene and indene peroxides a discrepancy above experimental error exists between the amount of hydrogen evolved on reduction and the amount of lithium aluminum hydride consumed (an excellent agreement was found for cumyl and 8-*p*-cymyl hydroperoxides). This discrepancy may indicate that the polymeric peroxides contain oxygen in some form other than peroxide. If, for example, the styrene peroxide used contained 3.7% of its oxygen in the form of carbonyl (one carbonyl group per 13 peroxide groups),<sup>9</sup> this discrepancy would vanish and a peroxide containing 91% of the theoretical peroxide groups, should analyze 91% peroxide by the amount of hydrogen evolved on reduction and 95% peroxide by combustion, while destroying lithium aluminum hydride equivalent to 99% of the theoretical peroxide.

**Acknowledgment.**—Samples of *t*-butyl  $\alpha$ -phenylethyl peroxide and benzyl *t*-butyl peroxide were generously furnished by Professor N. Kornblum. Purified samples of cumyl peroxide, cumyl hydroperoxide and 8-*p*-cymyl hydroperoxide were obtained from the Hercules Powder Company.

### Experimental<sup>10</sup>

**Materials.**—Dioxane and butyl ether were distilled from lithium aluminum hydride under reduced pressure at 60–70°. The dioxane was stored over lithium aluminum hydride and vacuum transferred at room temperature immediately before use. A centrifuged solution of lithium aluminum hydride was used. The peroxides of indene, styrene and  $\alpha$ -methylstyrene were prepared by the partial autoxidation

(<10%) at 50° of the monomers initiated by  $\alpha, \alpha'$ -azodiisobutyronitrile (0.01 *M*). The polymeric peroxides were precipitated by methyl alcohol, thrice precipitated from benzene by petroleum ether and evacuated to constant weight from a frozen benzene solution at  $10^{-4}$  mm.

TABLE II  
PROPERTIES OF POLYMERIC PEROXIDES

Peroxide	Mol. wt. <sup>a, b</sup>	C, %	H, %	Peroxide, % <sup>c</sup>
Styrene	3800	71.3	6.4	96.2
$\alpha$ -Methylstyrene	5300	72.9	7.0	96.0
Indene	1500	92.7	5.7	100.0

<sup>a</sup> Av. of two determinations. <sup>b</sup> Determined cryoscopically in benzene solution. <sup>c</sup> Calculated from the carbon analysis.

Cumyl hydroperoxide, 8-*p*-cymyl hydroperoxide and cumyl peroxide were obtained in a purified form from the Hercules Powder Company. Lucidol brand *t*-butyl peroxide was distilled at reduced pressure, b.p. 52° (91.5 mm.). Benzyl *t*-butyl and *t*-butyl  $\alpha$ -phenylethyl peroxides were obtained from Professor N. Kornblum.<sup>11</sup> *t*-Butyl ethyl peroxide was prepared according to the directions of Rust and Dickey.<sup>12</sup> The material used for reduction was tensimetrically homogeneous, v.p. 14 mm. (0°), 45 mm. (20°).

*Anal.* Calcd. for  $\text{C}_8\text{H}_{14}\text{O}_2$ : C, 61.0; H, 11.9. Found: C, 60.8; H, 12.1.

Triphenylmethyl peroxide, prepared by the oxidation of triphenylmethyl,<sup>13</sup> was recrystallized from carbon disulfide, m.p. 184.5–185.5° (lit.<sup>13</sup> 185–186°).

**Reduction of Styrene Peroxide.**—A solution of 3.35 g. of styrene peroxide (containing 0.0240 mole of oxygen by analysis) in 50 ml. of dry, peroxide-free dioxane was added slowly to 0.0207 mole of lithium aluminum hydride in 50 ml. of ethyl ether at 0°. The gas evolved during the reaction corresponded to 0.0236 mole of hydrogen. Hydrolysis of the unreacted lithium aluminum hydride indicated that 0.0089 mole remained and that 0.0118 mole of lithium aluminum hydride had reacted with the styrene peroxide to produce 0.0236 mole of hydrogen. The solution was acidified with hydrochloric acid and evaporated to dryness. From the ether extract of the residue there was obtained 3.30 g. of crude phenylglycol (m.p. 55–62°). One recrystallization from benzene gave 2.90 g. (87.5%) of pure phenylglycol (m.p. 64–65°). Of the remaining 0.40 g., only 0.17 g. (5%) could not be distilled at 1 mm. pressure.

**Analytical Reduction of Peroxides.**—A sample of standardized lithium aluminum hydride in butyl ether was pipetted under nitrogen into a reaction flask attached to a gas buret while the system was flushed by prepurified nitrogen dried over phosphorus pentoxide. A sample of standard peroxide solution was placed in a pressure-equalized dropping funnel attached to the reaction flask and the system evacuated and filled with nitrogen several times. By means of stopcocks, the system was sealed and the pressure regulated to atmospheric by a mercury leveling bulb and a differential manometer. The lithium aluminum hydride solution was stirred by a stirring bar and after equilibration, the peroxide solution was added slowly. The dropping funnel was calibrated and would deliver 9.95 ml. of a 10-ml. sample. When hydrogen was no longer evolved, *t*-amyl alcohol diluted with butyl ether was added through the dropping funnel and the hydrogen evolved on hydrolysis measured. The reaction flask and gas buret were thermostated and vapor pressure corrections were applied to the hydrogen collected.

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(11) The preparation and properties of these peroxides will be described in papers to appear in *THIS JOURNAL* by Kornblum, Clark and DeLaMare.

(12) F. F. Rust and F. H. Dickey, U. S. Patent No. 2,414,769 (1947).

(13) M. Gomberg, *Ber.*, **33**, 3150 (1900).

(8) C. E. Barnes, R. M. Eloffson and G. D. Jones, *THIS JOURNAL*, **72**, 210 (1950).

(9) Polymeric styrene and indene peroxides show an infrared carbonyl absorption even after several precipitations from benzene and thorough evacuation. In the case of styrene peroxide, it is very difficult to ascertain whether the carbonyl adsorption is due to the peroxide or a decomposition product of the peroxide (e.g., benzaldehyde).

(10) Molecular weight determination by Mrs. P. Morrison, Carbon and hydrogen analyses by Mrs. J. Martin.