

506. *The Chemistry of Polymerised Oils. Part III.* Reduction of Some Organic Peroxides with Lithium Aluminium Hydride.*

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Dibenzoyl, methyl α -tetralyl, and di-*tert*.-butyl peroxide, and ascaridole with lithium aluminium hydride give the expected alcohols in good yields. In each case the primary reaction probably involves fission of the O-O linkage. Only one-half of the total hydrogen of lithium aluminium hydride is displaced during reaction with ascaridole and with methyl α -tetralyl peroxide.

THE study reported here was undertaken as a preliminary to an examination of the reduction of peroxidised oils by lithium aluminium hydride. It has already (Sutton, *Chem. and Ind.*, 1951, 272) been reported that cyclohex-2-enyl hydroperoxide and tetralyl hydroperoxide are smoothly reduced by lithium aluminium hydride to the corresponding alcohols. It was suggested that the primary reaction with lithium aluminium hydride involves fission between the oxygen atoms of the $-\text{O}\cdot\text{OH}$ groups, so that the lithium aluminium alkoxides are formed directly. In more precise measurements the volume of hydrogen evolved in the case of pure tetralyl hydroperoxide corresponds very closely to two moles per mole of peroxide, in agreement with the postulated fission.

Four peroxides, of different types, have now been studied. Dibenzoyl peroxide reacts with almost explosive vigour, methyl α -tetralyl peroxide and ascaridole at moderate speeds, and di-*tert*.-butyl peroxide very slowly, the expected alcohols being obtained in good yields.

In agreement with Hochstein (*J. Amer. Chem. Soc.*, 1949, **71**, 305), it was found that one mole of hydrogen was evolved per mole of dibenzoyl peroxide :



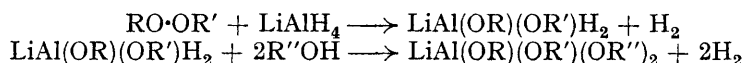
This representation is supported both by the identification of the final product as benzyl alcohol and by Hochstein's report (*loc. cit.*) that approximately 1.5 moles of hydride are consumed per mole of peroxide.

Methyl α -tetralyl peroxide and ascaridole each gave one mole of hydrogen per mole on reaction with excess of hydride, thus supporting the view that the primary reaction involves

* Part II, Clingman and Sutton (*J. Amer. Oil Chem. Soc.*, in the press).

fission of the O-O bond. For the very slow reaction of di-*tert*.-butyl peroxide at room temperature quantitative measurement of hydrogen was impossible.

Unexpectedly, about one half of the ascaridole was recovered unchanged after reaction with slightly more than a half-molar proportion of lithium aluminium hydride, even although the reaction time was greater than that necessary for the evolution of the full amount of hydrogen in small-scale experiments. In the latter experiments an excess of hydride had been used in the usual way. No ascaridole was unchanged when a twice-molar proportion of hydride was used. It therefore seemed possible that only one-half of the hydrogen of lithium aluminium hydride was available for replacement in this case. This was confirmed as follows: an excess of ascaridole was added to a solution of lithium aluminium hydride, the hydrogen evolved being measured; an excess of *n*-octyl alcohol was then added and approximately twice the volume of hydrogen already evolved was given off. Methyl α -tetralyl peroxide behaved in the same way and the following reaction scheme is tentatively suggested :



The finding that only one-half of the total hydrogen of lithium aluminium hydride is available for replacement in the above two examples is paralleled by the behaviour of nitriles (Amundsen and Nelson, *ibid.*, 1951, **73**, 242). Lithium aluminium hydrogen complexes may possibly have greater selective powers of reduction than the parent hydride and may also find applications in asymmetric reductions (cf. Bothner-By, *ibid.*, p. 846).

On hydrogenation of the crude *cis-p*-menthene-1 : 4-diol resulting from reduction of ascaridole, a small amount of an unidentified substance of m. p. 125–128° was obtained, in addition to the expected *cis*-1 : 4-terpin. Examination of molecular models showed that the formation of *trans-p*-menthene-1 : 4-diol is not to be expected from the reduction of ascaridole, so that the substance is unlikely to be *trans*-1 : 4-terpin (m. p. 137°); it probably arose from traces of an impurity in the ascaridole, the preparation of which in absolutely pure condition is known to be extremely difficult (Paget, *J.*, 1938, 829). Some difficulties were encountered during the preparation, for comparison, of *cis-p*-menthene-1 : 4-diol by partial hydrogenation of ascaridole, owing to the incomplete descriptions given in the older literature; it was found that the method of preparation of the palladium catalyst and the catalyst : ascaridole ratio are extremely important (see Experimental section).

Reduction of di-*tert*.-butyl peroxide was carried out at 135°, the yield of *tert*.-butyl alcohol recovered being 67%, based on the total hydrogen content of the lithium aluminium hydride used. Presumably the much higher temperature of reaction was responsible for the yield being higher than the 50% to be expected on the basis of the above reaction scheme.

EXPERIMENTAL

M. p.s are uncorrected.

Reductions with Lithium Aluminium Hydride.—On the preparative scale ether was used as solvent, except where otherwise stated; the procedure is given fully below for the case of dibenzoyl peroxide. Gas volumes quoted for small-scale experiments, in which di-*n*-butyl ether was used as solvent, are corrected to N.T.P., the vapour pressure of di-*n*-butyl ether at the temperatures used being taken into account.

Determination of Active Hydrogen.—The lithium aluminium hydride method was used (cf. Hochstein, *loc. cit.*), di-*n*-butyl ether being the solvent.

Reaction of Tetralyl Hydroperoxide with Lithium Aluminium Hydride.—Pure tetralyl peroxide was added to an excess of lithium aluminium hydride in di-*n*-butyl ether at room temperature [0.0093 g. gave 2.56 c.c. of H₂ (N.T.P.); 0.0068 g. gave 1.82 c.c. of H₂ (N.T.P.). Calc. for 2H₂ per C₁₀H₁₂O₂ : 2.54 c.c. and 1.86 c.c. respectively].

Reduction of Dibenzoyl Peroxide.—Dibenzoyl peroxide (4.84 g., 0.02 mole), purified by Nozaki and Bartlett's method (*J. Amer. Chem. Soc.*, 1946, **68**, 1686), in dry ether (50 c.c.) was added slowly with stirring to lithium aluminium hydride (1.52 g., 0.04 mole) in ether (75 c.c.).

After a further 30 minutes' refluxing the complex was decomposed in the usual way (Nystrom and Brown, *ibid.*, 1947, **69**, 1197, 2548) with dilute sulphuric acid, and the product extracted with ether, to yield benzyl alcohol (3.78 g., 87.5%) which was distilled (b. p. 110°/32 mm.) (Found: C, 77.8; H, 7.65; active H, 0.94. Calc. for C_7H_8O : C, 77.8; H, 7.4; active H, 0.925%) and characterised as its α -naphthylurethane (m. p. and mixed m. p. 134°).

Dibenzoyl peroxide was treated with excess of lithium aluminium hydride in di-*n*-butyl ether [0.0352 g. gave instantaneously 3.26 c.c. of H_2 (N.T.P.)]. Calc. for H_2 per $C_{14}H_{10}O_4$: 3.26 c.c.]. Addition of a larger quantity (*ca.* 0.2 g.) of benzoyl peroxide to lithium aluminium hydride solution resulted in an explosion of moderate violence.

Reduction of Methyl α -Tetralyl Peroxide.—(a) *With an equimolar proportion of lithium aluminium hydride.* Methyl α -tetralyl peroxide (2.4 g., 0.0135 mole) (Hock and Lang, *Ber.*, 1942, **75**, 310) and lithium aluminium hydride (0.5 g., 0.013 mole) were used. After 2.5 hours' refluxing, the complex was decomposed and the ethereal extract washed with water (5×4 c.c.). The combined aqueous layer and washings were distilled until pure water came over, and the distillate was divided into two portions. Determination of the methanol in one portion (method adapted from Lomond, *Analyst*, 1949, **74**, 560) gave 0.224 g. (52%) for the methyl alcohol content of the total distillate. The other portion was oxidised with acid permanganate (Wright, *Ind. Eng. Chem.*, 1927, **19**, 750) and then distilled into dimerone solution; the dimerone derivative of formaldehyde slowly separated and was recrystallised from aqueous alcohol (m. p. and mixed m. p. 188°).

The ethereal extract yielded crude α -tetralol (1.9 g., 95%) which on distillation gave a main fraction (1.5 g.; b. p. 144—5°/28 mm.) which solidified (m. p. 33—34°, from pentane) (Found: C, 80.9; H, 8.2; active H, 0.67. Calc. for $C_{10}H_{12}O$: C, 81.0; H, 8.2%; active H, 0.675%) and was characterised as its phenylurethane (m. p. and mixed m. p. 121—122°).

(b) *Measurements of hydrogen from methyl α -tetralyl peroxide and lithium aluminium hydride.* Methyl α -tetralyl peroxide was treated with an excess of lithium aluminium hydride in di-*n*-butyl ether [0.0281 g. gave, during 3 hours, 3.48 c.c. of H_2 (N.T.P.)]. Calc. for H_2 per $C_{11}H_{14}O_2$: 3.53 c.c.].

An excess of methyl α -tetralyl peroxide (0.05 g.) was added at room temperature to a solution of lithium aluminium hydride (*ca.* 3 mg.) in di-*n*-butyl ether; after evolution of hydrogen had ceased (3 hours) an excess of *n*-octyl alcohol (>0.1 g.) was added [1.62 c.c. of H_2 (N.T.P.) were evolved after addition of peroxide; 2.78 c.c. after subsequent addition of *n*-octyl alcohol].

Reduction of Di-tert.-butyl Peroxide.—Di-tert.-butyl peroxide (10 g., 0.0685 mole) (Milas and Surgenor, *J. Amer. Chem. Soc.*, 1946, **68**, 205) and lithium aluminium hydride (1.5 g., 0.0395 mole) were refluxed in boiling (135°) di-*n*-butyl ether (70 c.c.) for 4 hours. After acid decomposition, the ethereal layer was washed with water (10×20 c.c.); the combined aqueous solutions were distilled at 650 mm. through a column (48×1 cm.) packed with Cannon rings, to give fractions (a) b. p. 75—80° (4.2 g.), (b) b. p. 80—94° (7.3 g.), and (c) b. p. 94—96° (12.5 g.). On redistillation, fraction (c) gave a small fraction (d), b. p. <85°, which was combined with (a) and (b); the combined fractions were dried (KOH) and redistilled, to yield tert.-butyl alcohol, b. p. 76—78° (7.97 g.) which from refractive-index measurements contained 2.2% of water, so that the yield recovered was 77% (67% based on the hydrogen content of the lithium aluminium hydride). The alcohol was characterised as its phenylurethane (m. p. and mixed m. p. 135°) (Found: C, 68.6; H, 7.9; N, 7.2. Calc. for $C_{11}H_{15}O_2N$: C, 68.4; H, 7.8; N, 7.25%).

Reduction of Ascaridole.—(a) *With an approximately half-molar proportion of lithium aluminium hydride.* Ascaridole (8.91 g., 0.053 mole) prepared from chenopodium oil (Paget, *J.*, 1938, 829) and lithium aluminium hydride (1.2 g., 0.0316 mole) were used. After 4.5 hours' refluxing, the complex was decomposed and the aqueous layer was extracted ten times with ether; the combined ethereal solutions yielded an oil (8.43 g.), some of which (7.23 g.) was distilled at 0.5 mm. to give: (a) b. p. <57° (0.15 g.), (b) b. p. 57° (3.1 g.), (c) b. p. 57—92° (0.4 g.), (d) b. p. 92° (2.4 g.), and (e) residue *ca.* 1 g. Fractions (a) and (b) were unchanged ascaridole, fraction (d) crystallised, to give *cis-p*-menthene-1:4-diol, m. p. 82° after recrystallisation from isohexane-ethyl acetate (Bodendorf *Arch. Pharm.*, 1933, **271**, 1; Paget, *loc. cit.*) (Found: C, 70.6; H, 10.8; active H, 1.19. Calc. for $C_{10}H_{18}O_2$: C, 70.6; H, 10.6; active H, 1.18%); on hydrogenation in the presence of Adams's catalyst it gave *cis*-1:4-terpin (m. p. and mixed m. p. 116—117°).

(b) *With an approximately twice-molar proportion of lithium aluminium hydride.* Ascaridole (2.99 g., 0.0178 mole) and lithium aluminium hydride (1.5 g., 0.0395 mole) were used. Working up as above, after 4.5-hours' reaction, and distillation gave an oil (b. p. 96°/0.5 mm.; 2.2 g. 73%), no ascaridole being detected. The distillate crystallised, 65% of it being recovered as pure

cis-p-menthene-1 : 4-diol, m. p. 82° after crystallisation from *isohexane*–ethyl acetate (m. p. 80–82° in admixture with *cis-p*-menthene-1 : 4-diol of m. p. 79–80° prepared by partial hydrogenation of ascaridole, see below); the filtrate was hydrogenated and a small amount of a substance, m. p. 125–128°, was recovered in addition to *cis*-1 : 4-terpin arising from residual *cis-p*-menthene-1 : 4-diol.

(c) *Measurements of hydrogen evolution from ascaridole and lithium aluminium hydride.* Ascaridole was treated with an excess of lithium aluminium hydride in di-*n*-butyl ether [0.0219 g. gave, during 4 hours, 2.94 c.c. of H₂ (N.T.P.). Calc. for H₂ per C₁₀H₁₆O₂ : 2.92 c.c.].

In duplicate experiments an excess of ascaridole (>0.1 g.) was added at room temperature to a solution of lithium aluminium hydride (3–5 mg.) in di-*n*-butyl ether; after evolution of hydrogen had ceased (4 hours) an excess of *n*-octyl alcohol (>0.1 g.) was added [2.38 c.c., 2.07 c.c. of H₂ (N.T.P.) evolved after addition of ascaridole; 4.89 c.c., 3.86 c.c. of H₂ after subsequent addition of *n*-octyl alcohol].

(d) *Semi-hydrogenation of ascaridole.* When ascaridole was hydrogenated (one mole/mole) in methanol in the presence of palladium black (10% by wt. of the ascaridole; made by the action of formaldehyde and potassium hydroxide on palladium chloride) the chief products were ascaridole and *cis*-1 : 4-terpin. Hydrogenation over palladium chloride and charcoal (hydrochloric acid not removed by washing) with the same palladium–ascaridole ratio as was used by Bodendorf (*loc. cit.*) resulted in a product containing ascaridole, *cis*-1 : 4-terpin, and *cis-p*-menthene-1 : 4-diol; the last two could not be satisfactorily separated by several recrystallisations from ethyl acetate–heptane or *cyclohexane*–heptane. Fairly pure *cis-p*-menthene-1 : 4-diol was prepared as follows : 1 c.c. of a 1% palladium chloride solution and 0.1 g. of charcoal in 50 c.c. of distilled water and 1 c.c. of 33% formaldehyde solution were decomposed at 0° with 2 c.c. of 50% potassium hydroxide solution. The catalyst was well washed (water and then ethanol), dried, and used to hydrogenate (0.5 mole/mole) ascaridole (15 g.) in ethanol (50 c.c.); the diol fraction recovered by distillation had m. p. 74–78° and was three times recrystallised from *cyclohexane*–heptane (1 : 5), giving *cis-p*-menthene-1 : 4-diol, m. p. 79–80°.

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