Organic Peroxides. XXVIII. Addition of *t*-Butylhydroperoxide and Hydrogen Peroxide to Bicyclo[2.2.1]hepta-2,5-diene

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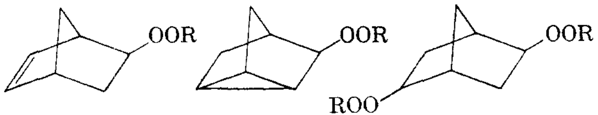
The addition of hydrogen peroxide and *t*-alkylhydroperoxides to carbon-carbon double bonds in the presence of hydrogen ion is well known.[2–4] On the basis of considerations published by Winstein and Shatavsky,[5] the addition of either hydrogen peroxide or *t*-butylhydroperoxide to bicyclo-[2.2.1]hepta-2,5-diene should lead to three possible peroxides (I, II, III) in which R may be hydrogen or *t*-butyl.



I II III

When bicycloheptadiene was allowed to react at room temperature with a large excess of *t*-butylhydroperoxide in the presence of catalytic amounts of sulfuric acid, the crude product, after the excess *t*-butylhydroperoxide had been removed by repeated extractions with 10% potassium hydroxide, showed a single strong spot on a paper chromatogram using dimethylformamide-decalin as the developing solvent and hydriodic acid–glacial acetic acid as the detecting agent.[6] Fractional distillation failed to give an analytically pure peroxide although all the fractions contained the same peroxide mixed with polymeric products of bicycloheptadiene. The peroxide was finally purified by chromatography through a column packed with cellulose powder impregnated with dimethylformamide and developed with cyclohexane.[7]

The analytical data and saturated character of this peroxide together with its infrared spectrum are in favor of the tricyclene structure II. The infrared spectrum in carbon bisulfide showed strong bands at 805 and 1005–1026 cm.$^{-1}$, respectively, which are characteristic for the tricyclene system.[8,9] Moreover, since there is no double bond absorption near 1650 cm.$^{-1}$, the band at 3070 cm.$^{-1}$ is supposed to be diagnostic for hydrogen atoms attached to carbons of the cyclopropane ring. Absorption at 880 and 1135 cm.$^{-1}$, respectively, are attributed to the peroxide group and peaks at 1200 and 1240 cm.$^{-1}$, respectively, are due to the *t*-butyl group.

Reaction of bicycloheptadiene with hydrogen peroxide under various conditions either failed to take place or else gave complex mixtures which contained two different peroxides as detected by paper chromatography.

EXPERIMENTAL

t-Butyl-6-nortricyclanyl peroxide (II). After several trials under various conditions of temperature, stirring, and concentration of reactants and of sulfuric acid,[10] the following procedure is the safest and gives the best results. To a mixture of 34 ml. of 80% *t*-butylhydroperoxide containing 20% di-*t*-butyl peroxide (Lucidol) and 15.4 g. of freshly distilled bicycloheptadiene[11] was added dropwise with stirring 0.15 ml. of concd. sulfuric acid. Stirring was continued at room temperature for 70 hr., then the mixture was diluted with an equal volume of *n*-pentane and extracted several times with 10% aqueous potassium hydroxide until it gave no immediate peroxide test with potassium iodide in glacial acetic acid (hydroperoxides give an immediate reaction). The nonaqueous mixture was then dried over magnesium sulfate, filtered, and the solvent and di-*t*-butyl peroxide removed at room temperature under reduced pressure (0.2 mm.); yield of the crude product, 20 g. Both the solvent distillate and the residue were subjected to paper chromatography using Whatman paper No. 1, dimethylformamide-decalin as the developing solvent, and hydriodic acid–glacial acetic acid as the detecting agent. The paper chromatogram of the solvent distillate gave no spots since under the conditions of these chromatographic tests di-*t*-butyl peroxide evaporates rapidly and cannot be detected. The paper chromatogram of the residue showed a single strong spot with an R_f of 0.87.

Although the crude product seemed fairly homogeneous, its active oxygen was somewhat low as determined by the hydriodic acid–glacial acetic acid method. Fractional distillation failed to improve the active oxygen so that a portion (3.5 g.) was chromatographed through a column packed with cellulose impregnated with dimethylformamide and developed with cyclohexane saturated with dimethylformamide. Twenty-six fractions were collected and the purification was followed by paper chromatography. Fractions 13–20, which showed a single spot on the paper chromatogram with the same R_f, were combined, washed with water, dried, and the solvent removed under reduced pressure. The residual oil distilled at 42–43° (0.1 mm.); n_{D}^{25}, 1.4591; R_f, 0.86.

Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95; (O), 8.78; mol. wt., 182.3. Found: C, 72.60; H, 9.95; (O), 8.90; mol. wt., 184 (exaltone).

The infrared spectrum of this peroxide 10% in carbon bisulfide showed the following bands in cm.$^{-1}$; the number in parenthesis gives the intensity of each band: 3070(3.8); 3000(8.4); 2990(8); 2900(5.8); 1430(4); 1380(4.5); 1368 (8.5); 1335(5); 1305(3.6); 1284(3.8); 1262(3.5); 1240(4.8); 1200(8.2); 1135(5.5); 1082(7.3); 1060(4.3); 1040(3.1); 1026 (4.4); 1005(3.6); 955(2.8); 910(3.5); 880(5.0); 805(7.6); 800(7.3).

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(3) N. A. Milas, *Ency. Chem. Technology*, **10**, 70 (1953).

(4) N. A. Milas, R. L. Peeler, Jr., and O. L. Mageli, *J. Am. Chem. Soc.*, **76**, 2322 (1954).

(5) S. Winstein and M. Shatavsky, *Chem. & Ind. (London)*, **1956**, 56.

(6) N. A. Milas and I. Belič, *J. Am. Chem. Soc.*, **81**, 3358 (1959).

(7) N. A. Milas and A. Golubović, *J. Am. Chem. Soc.*, **81**, 3361 (1959).

(8) J. D. Roberts, E. R. Trumbull, W. Bennett, and R. Armstrong, *J. Am. Chem. Soc.*, **72**, 3116 (1950).

(9) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 2nd ed., John Wiley & Sons, New York, 1958, pp. 29–30.

(10) Large concentrations of sulfuric acid should be avoided since they lead invariably to explosions.

(11) We are indebted to Shell Chemical Corporation for a generous supply of bicycloheptadiene.

Attempted addition of hydrogen peroxide to bicycloheptadiene. When bicycloheptadiene was allowed to react for 24 hr. at room temperature with hydrogen peroxide (50%) in a two-phase system with stirring using chloroform or carbon tetrachloride as solvents and catalytic amounts of sulfuric acid, no organic peroxides were formed. Even in the absence of inert solvents with traces of the acid present no reaction was observed after 24 hr. of stirring. However, when the concentration of the acid was increased to about 50% and the reaction carried out at 0° with stirring but without the use of inert solvents, the mixture exploded at the end of 2 hr.; even when carbon tetrachloride was used under these conditions, the reaction produced black tars and no organic peroxides.

The following experiment led to the isolation in very small yields of a mixture of two peroxides. To a mixture of 10 g. of hydrogen peroxide (50%) and 5 g. of concd. sulfuric acid maintained at 0° was added dropwise with stirring 11 g. of bicycloheptadiene. Stirring was continued at 0° for 2.5 days, then to the mixture was added 25 ml. of saturated ammonium sulfate solution and the resulting mixture extracted several times with cyclohexane. The cyclohexane extracts were shaken again with saturated ammonium sulfate to remove traces of hydrogen peroxide, dried over magnesium sulfate, then the solvent and unused bicycloheptadiene removed under reduced pressure. A small amount of oil remained which failed to crystallize. A paper chromatogram using dimethylformamide-decalin as the developing solvent and hydriodic acid–glacial acetic acid as the detecting agent showed two strong spots; one with R_f, 0.08, and the other with an R_f, 0.76. The spot with the lower but not the one with the higher R_f was also observed when the paper chromatogram was sprayed with potassium iodide–glacial acetic acid detecting agent. This indicates that the peroxide with the lower R_f must be a hydroperoxide while the one with the higher R_f, a dialkyl peroxide. This was also confirmed by the infrared spectrum of the mixture which showed bands at 3400 and 880 cm.$^{-1}$, respectively. The amount available of the mixture was too small for separation and further investigation of these two peroxides.

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Action of Acid on *o*-Aroyldiarylcarbinols. A New Route to Isobenzofurans[1]

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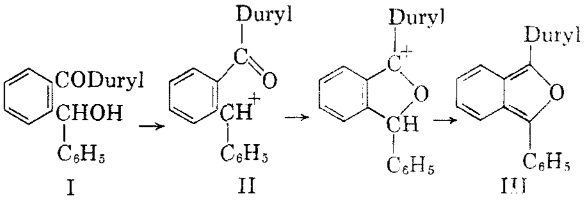
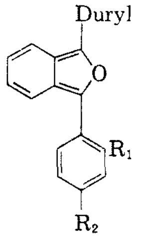
o-Duroylphenylphenylcarbinol (I) prepared by condensation of *o*-duroylphenyllithium[3] with benzaldehyde, undergoes conversion to 1-duryl-3-phenylisobenzofuran (III) when treated with strong mineral acid. The cyclodehydration presumably proceeds by way of the *o*-duroyldiphenylcarbonium ion (II).



I II III

The yield of the isobenzofuran from the carbinol was 83%, but the overall yield from the lithium reagent was only 19%. A higher overall yield may be achieved by omitting the isolation of the carbinol and using strong acid in the workup of the original reaction mixture. From the lithium compound the isobenzofuran was made by this method in a yield of 43%. This latter procedure served also to prepare 1-duryl-3-(2-methoxyphenyl)isobenzofuran (IVa), 1-duryl-3-(4-methoxyphenyl)isobenzofuran (IVb), 1-duryl-3-(2-chlorophenyl)isobenzofuran (IVc), and 1-duryl-3-(4-chlorophenyl)isobenzofuran (IVd).



IVa. $R_1 = OCH_3, R_2 = H$
IVb. $R_1 = H, R_2 = OCH_3$
IVc. $R_1 = Cl, R_2 = H$
IVd. $R_1 = H, R_2 = Cl$

The intervention of *o*-aroyldiarylcarbonium ions in the formation of isobenzofurans has not been suggested previously, but would seem to account for several of the most important syntheses of these heterocycles.[4] Thus, the formation of isobenzofurans by reductive cyclodehydration of *o*-diaroylbenzene derivatives, by treatment of α-arylphthalides with aromatic Grignard reagents, and by condensation of *o*-cyanobenzaldehyde with aromatic Grignard reagents, can be explained on this basis.

EXPERIMENTAL[5]

1-Duryl-3-phenylisobenzofuran. An ether solution of *o*-duroylphenyllithium, blanketed with dry nitrogen and maintained at −30° to −35°, was prepared by the method previously described[3] from 6.3 g. (0.02 mole) of *o*-duroylbromobenzene and 10.7 ml. of 1.86*N* *n*-butyllithium solution. To the cooled solution of the lithium reagent was added all at once, with stirring, a solution of 2.14 g. (0.02 mole) of benzaldehyde in 25 ml. of anhydrous ether. The reaction mixture was stirred at bath temperature for 15 min.; then the bath was removed, and stirring was continued for an additional 15 min. The contents of the flask

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[2] Union Carbide Fellow, 1958–1959.

[3] R. C. Fuson, W. C. Hammann, and W. E. Smith, *J. Org. Chem.*, **19**, 674 (1954).

[4] See R. Adams and M. H. Gold, *J. Am. Chem. Soc.*, **62**, 2038 (1940).

[5] All melting points are corrected.