with Silicon SF 96 fluid on firebrick using helium as the effluent gas (60 ml. per minute); only a single peak was observed in each case.

Cuprous Bromide-catalyzed Reactions of *t*-Butyl Perbenzoate and Cyclohexene in Aliphatic Acids.—The reactions were again carried out under similar conditions. Over a period of one hour, *t*-butyl perbenzoate (0.2 mole) was added to a boiling mixture of cyclohexene (40.5 g., 0.49 mole), an aliphatic acid (0.5–1.15 moles) and cuprous bromide (0.1 g., 0.35 mmole). Heating was continued for 3 to 12 hours to assure complete ester interchange. After the addition of an equal volume of petroleum ether to the cooled solution, the mixture was extracted with sodium carbonate to remove benzoic acid and the catalyst. The non-aqueous layer was washed with water until neutral and was then concentrated under reduced pressure. The products were isolated by distillation of the residual oil. The results are summarized in Table III.

A mixture of cyclohexenyl benzoate (19.2 g., 0.1 mole) and glacial acetic acid (50 ml.) was refluxed for 5 hours. After the usual workup, benzoic acid (6.3 g., 53%) was recovered from the carbonate extract, and cyclohexenyl acetate (7 g., 50%), b.p. 58° (9 mm.), was isolated from the organic layer.

Reaction of *t*-Butyl Perbenzoate and Triphenylmethane.—*t*-Butyl perbenzoate (10 ml., 0.05 mole) was added to a refluxing mixture of triphenylmethane (11.7 g., 0.05 mole) and cuprous bromide (0.1 g., 0.35 millimole) in benzene (50 ml.) over a period of one hour. The mixture was heated under reflux for an additional 12 hours. At the end of this period, it was filtered while hot, and 9.5 g. of a colorless solid separated from the filtrate upon cooling. The mother liquor was concentrated and the residue was triturated with a benzene–petroleum ether mixture (1:2), whereby an additional 2.1 g. of crystals was collected. The solid (11.6 g., 99%) was shown to be recovered triphenylmethane by comparison with the starting material.

CHICAGO 37, ILL.

Studies in Organic Peroxides. XXV. Preparation, Separation and Identification of Peroxides Derived from Methyl Ethyl Ketone and Hydrogen Peroxide

BY NICHOLAS A. MILAS AND ALEKSANDAR GOLUBOVIĆ[1]

When methyl ethyl ketone is allowed to react with hydrogen peroxide in the presence of hydrogen ion, seven different peroxides are formed. Three have been separated by standard procedures and four by means of cellulose powder chromatography. 2,2-Dihydroperoxybutane has been shown to be the precursor from which all other peroxides can be formed. All peroxides of this series are highly sensitive to shock and explode with considerable brisance.

Although mixtures of organic peroxides derived from methyl ethyl ketone and hydrogen peroxide have been products of commerce for a long time, the complete separation of the individual peroxides present in these mixtures has never been accomplished and consequently their identity remained obscure. Quite frequently the properties of these peroxides would change on standing without an appreciable loss of active oxygen. This change, too, remained unexplained.

Our recent success in the separation and identification of the peroxides derived from diethyl ketone and hydrogen peroxide[2] prompted us to examine the peroxides derived from other simple ketones and hydrogen peroxide. When methyl ethyl ketone was allowed to react at 0 to −5° with 50% hydrogen peroxide in the presence of mineral acids, a mixture of peroxides was obtained which contained seven different peroxides as detected by paper chromatography[3] using hydrogen iodide–glacial acetic acid as the detecting agent. The probable structures of these peroxides are listed together with their R_f's in Fig. 1.
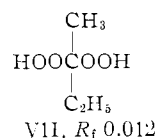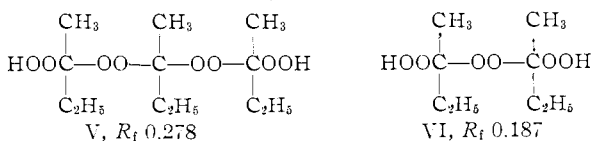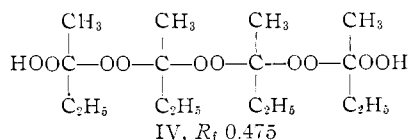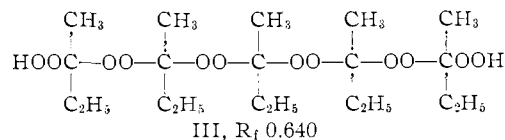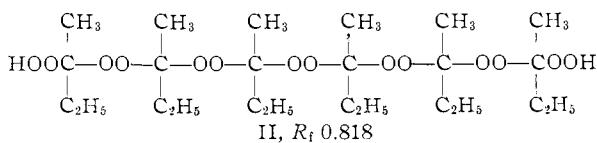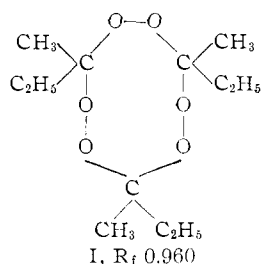

I, R_f 0.960

Fig. 1.—Peroxides derived from methyl ethyl ketone and hydrogen peroxide.

The percentage of each peroxide present in the mixture was estimated by paper chromatography to be approximately: I, 25; II, 1; III, 2; IV, 5; V, 12; VI, 45; and VII, 10%, respectively. Peroxides I, VI and VII were separated from the mixture without resorting to cellulose powder chromatography, while the other four peroxides were

(1) Lucidol Research Assistant.

(2) N. A. Milas and A. Golubović, THIS JOURNAL, **81**, 3361 (1959).

(3) N. A. Milas and I. Belić, *ibid.*, **81**, 3358 (1959).

separated only by the latter method. All of the peroxides in this series are highly shock sensitive and explode with considerable brisance.

As in the case of the peroxides obtained from the diethyl ketone and hydrogen peroxide,[2] all of the peroxides of the present series are probably formed from the unstable initial addition product VIII, while in the presence of hydrogen ion peroxide VII seems to be the stable precursor of all other peroxides isolated.

$$CH_3CH_2\overset{\displaystyle OH}{\underset{\displaystyle OOH}{C}}-CH_3$$

VIII
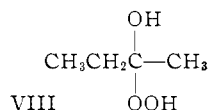
When a pure sample of peroxide VII was allowed to decompose slowly for several weeks in a closed system at room temperature a small amount of oxygen was evolved and the residue was found by paper chromatography to contain, in addition to the original peroxide, peroxides II, III, IV, V and VI but not even a trace of the cyclic trimer (peroxide I). The rate of decomposition as well as the total decomposition of this peroxide for the time measured were much lower than the decomposition of the corresponding peroxide from diethyl ketone. It is significant, however, that the decomposition seems to follow a similar course and it may be general with peroxides of this type.

An attempt was again made to cause the conversion with lead tetraacetate of peroxide VI to a cyclic dimer but again the attempt was unsuccessful. In accordance with our experience dimers of this type are formed only in ozonization reactions of tertiary-tertiary olefin carbon double bonds.

Experimental

2,2′-Dihydroperoxy-2,2′-dibutyl Peroxide (VI).—To 13.6 g. (0.2 mole) of 50% hydrogen peroxide cooled to 0° to −5° was added with stirring 4.8 g. (0.05 mole) of concd. sulfuric acid. To this solution cooled to −5° was added dropwise in the course of one hr. 14.4 g. (0.2 mole) of methyl ethyl ketone. Stirring and cooling was continued for an additional 4-hr. period. The cold mixture was then extracted with about 100 cc. of n-pentane and the extract shaken with 2 × 30 cc. of saturated ammonium sulfate solution followed by 3 × 50 cc. of water, dried over magnesium sulfate then filtered. A paper chromatogram of the filtrate showed the presence of seven different peroxides when sprayed with hydrogen iodide–acetic acid solution. The filtrate was then cooled to −70° and the colorless crystalline solid which separated out was recrystallized three times at low temperatures from pentane and the final crystals sublimed at room temperature under reduced pressure (0.3 mm.). The sublimate gave a single spot on a paper chromatogram with an R_f of 0.187 and a m.p. of 39–42° with softening at 30°. Due to explosiveness of this peroxide, it was impossible to run a combustion analysis. As low as 5 mg. caused a shattering of the combustion tube.

Anal. Calcd. for $C_8H_{18}O_6$: (O), 22.83; mol. wt., 210.2. Found: (O), 22.54 (KI + CH_3COOH method); mol. wt., 204 (in exaltone).

The infrared spectrum 10% in chloroform showed the following bands in cm.$^{-1}$; the number in parentheses gives the intensity of each band: 3400(8.5), 2990(6.5), 2980(5.5), 2800(3.5), 1460(7); 1430(4.5); 1365(9); 1330(5); 1290-(4.5); 1250(5); 1205–1230(6.5); 1170(8.5); 1125(8.5); 1115(7.5); 1050(6); 1010(6.5); 995(4.5); 915(6.5); 885-(6.5); 860(6.5).

Using the procedure of Brewster and Cotte,[4] the bis-*p*-nitrobenzoate of peroxide VI was prepared; m.p. 103° (explosive).

---

(4) J. H. Brewster and C. J. Cotte, Jr., THIS JOURNAL, **77**, 6214 (1955).

Anal. Calcd. for $C_{22}H_{24}N_2O_{12}$: C, 51.97; H, 4.76; N, 5.51; (O), 9.44. Found: C, 52.20; H, 4.87; N, 5.32; (O), 9.50.

The reaction of peroxide VI with lead tetraacetate in glacial acetic acid is highly exothermic with evolution of oxygen, but it was not possible to isolate the cyclic dimeric peroxide from the reaction products.

2,2-Dihydroperoxybutane (VII).—This peroxide is much more soluble in water than in pentane so that a crude reaction product in pentane was washed twice with saturated ammonium sulfate solution to remove the unreacted hydrogen peroxide, then extracted several times with water and the water extracts combined and extracted with ethyl ether, dried over magnesium sulfate and filtered. The ether was removed under reduced pressure and the oily residue subjected to a high vacuum (0.3 mm.) at 50° for 1 hr. The residue showed a single spot on the paper chromatogram with an R_f of 0.012. It was not possible to crystallize this peroxide and it failed to form a crystalline hydrate as in the case of 3,3-dihydroperoxypentane.

Anal. Calcd. for $C_4H_{10}O_4$: (O), 26.2; mol. wt., 122.1. Found: (O), 25.7 (KI + CH_3COOH method); mol. wt., 120 (in exaltone).

The infrared spectrum 10% in chloroform showed the following bands in cm.$^{-1}$: 3400(7), 2990(4), 2980(4), 1610-(2.5); 1455(5); 1370(7); 1355(5); 1290(4); 1205–1240-(3.5); 1175(5); 1130(7.5); 1090(4); 1050(3.5); 1040(3.5); 1050(3.5); 995(3); 945(2.5); 885(3.5); 845(6).

The bis-*p*-nitrobenzoate was prepared and recrystallized from methyl alcohol, m.p. 109° dec.

Anal. Calcd. for $C_{18}H_{16}N_2O_{10}$: C, 51.43; H, 3.84; N, 6.67. Found: C, 51.47; H, 3.89; N, 6.84.

1,4,7-Trimethyl-1,4,7-triethyl-1,4,7-cyclononatriperoxane (I).—The mother liquors from the crystallization of peroxide VI were combined and the solvent removed under reduced pressure. The residue was dissolved in methyl alcohol and cooled to −70°; a voluminous white precipitate separated. This was recrystallized several times from methyl alcohol at low temperatures and the final product subjected to a vacuum (0.3 mm.) at 40° for 3 hr. to remove traces of methanol; m.p. 30–32° with softening at 20°. This product showed a single spot on the paper chromatogram when sprayed with hydrogen iodide–acetic acid reagent with an R_f of 0.960. This peroxide does not liberate iodine from potassium iodide–acetic acid reagent; it is highly sensitive to shock and explodes with considerable brisance.

Anal. Calcd. for $C_{12}H_{24}O_6$: (O), 18.16; mol. wt., 264.3. Found: (O), 17.80 (HI–CH_3COOH method); mol. wt., 270 (in exaltone).

It is significant that this cyclic peroxide is formed only in the presence of hydrogen ion and therefore must be formed by an ionic rather than a free-radical mechanism.

The infrared spectrum of this peroxide 10% in chloroform showed the following bands in cm.$^{-1}$: 2990(7.5), 2980(6.5), 2800(4.5), 1460(7.5); 1360(8); 1325(5); 1285(5); 1260-(6.5); 1200–1225(6); 1170(9); 1140(9.5); 1105(5); 1045 (6); 1010(7); 990(5); 910(7); 885(7.5); 860(5).

1,4,7,10,13,16-Hexamethyl-1,4,7,10,13,16-hexaethyl-1,4,7,10,13-pentaperoxy-1,16-dihydroperoxide (II).—Of the seven peroxides detected by paper chromatography only three were separated by standard procedures. The remaining four peroxides were separated only by the use of a chromatographic column packed with cellulose powder. The technique used has been described in a previous publication.[2] The tube best suited for the separation of the peroxides of this series had the dimensions of 3 × 50 cm. with a cellulose packing of 37 cm. About 2.5–3 g. of the original mixture of peroxides, from which most of peroxides I, VI and VII had been removed, was dissolved in 5 cc. of pentane and sprayed evenly on the top of the cellulose column. Pentane previously saturated with dimethylformamide was then allowed to flow through the column at the rate of 0.5 cc. per min. and with a positive dry air pressure of 50 mm. Twenty cc. fractions were collected and analyzed by means of paper chromatography. Fraction 1 was pure peroxide I; fractions 2–4 were mixtures of I and II, while fractions 5–8 gave a single spot on the paper chromatogram with an R_f of 0.818. From these fractions was isolated 17.8 mg. of a highly viscous, highly explosive product which failed to crystallize at −70° either in methanol or pentane. Since the quantity was too small only molecular weight and infrared spectrum were

taken; calcd. for $C_{24}H_{30}O_{14}$: mol. wt., 563. Found: mol. wt., 576 (in exaltone).

The infrared spectrum 10% in chloroform is typical of this type of peroxides and showed the following bands in cm.$^{-1}$: 3400(3), 2990(4.5), 2980 (4.5); 2800 (3); 1460 (4.5); 1430(2.5); 1365(5.5); 1335(3); 1290(3); 1260- (4); 1210–1230(2.5); 1170(6); 1130(6.5); 1115(6.5); 1055(5); 1010(5); 995(4); 920(3); 875–885(4.5); 860- (5.5).

1,4,7,10,13-Pentamethyl-1,4,7,10,13-pentaethyl-1,4,7,10-tetraperoxy-1,13-dihydroperoxide (III).—The fractions 12–16 from the chromatographic separation which gave a single spot on the paper chromatogram with an R_f of 0.640 were combined and the peroxide (28 mg.) recovered and recrystallized at low temperatures from methanol. At room temperature this peroxide is a gum and is highly sensitive to shock and explodes with brisance.

Anal. Calcd. for $C_{26}H_{42}O_{12}$: (O), 20.23; mol. wt., 474.6. Found: (O), 20.4 (KI + CH_3COOH method); mol. wt., 453 (in exaltone).

The infrared spectrum 10% in chloroform showed the following bands in cm.$^{-1}$: 3400(4), 2990(5), 2980(5); 2800(3); 1465(5.5); 1430(3); 1365(7); 1335(4); 1290(3.5); 1250- (3); 1210–1230(3); 1170(6.5); 1130(7.5); 1115(7.5); 1055(5.5); 1010(5); 995(4); 920(4); 870–885(6); 860(6.5).

1,4,7,10-Tetramethyl-1,4,7,10-tetraethyl-1,4,7-triperoxy-1,10-dihydroperoxide (IV).—The fractions (22–33) from the chromatographic column which gave a single spot on the paper chromatogram with an R_f of 0.475 were combined and the peroxide recovered and recrystallized at 70° from pentane. The crystals melted at room temperature to give a highly viscous and explosive liquid.

Anal. Calcd. for $C_{18}H_{34}O_{10}$: (O), 20.71; mol.wt., 386.4. Found: (O), 21.50 (KI + CH_3COOH method); mol.wt., 372.0 (in exaltone).

The infrared spectrum 10% in chloroform showed the following bands in cm.$^{-1}$: 3400(5.5), 2990(5), 2980(5),

2800(3.5); 1460(5.5); 1430(3); 1365(7.5); 1335(4); 1290(3.5); 1250(3); 1210–1230(3.5); 1170(6.5); 1130- (7.5); 1115(6.5); 1055(5); 1010(5); 995(4); 875–885(6); 860(6.5).

1,4,7-Trimethyl-1,4,7-triethyl-1,4-diperoxy-1,7-dihydroperoxide (V).—The fractions (38–48) from the chromatographic column which gave a single spot on the paper chromatogram with an R_f of 0.278 were combined and the peroxide recovered. This was recrystallized at −70° from pentane, but at room temperature it exists as a highly viscous liquid which is sensitive to shock and explodes with brisance.

Anal. Calcd. for $C_{12}H_{26}O_3$: (O), 21.40; mol.wt., 298.3. Found: (O), 21.10 (KI + CH_3COOH method); mol.wt., 289.0 (in exaltone).

The infrared spectrum 10% in chloroform showed the following bands in cm.$^{-1}$: 3400(5.5), 2990(5), 2980(5); 2800- (3); 1460(6); 1430(3.5); 1365(7.5); 1330(4); 1290(3.5); 1250(3); 1210–1230(3); 1170(7); 1125(8); 1115(7); 1055- (5); 1010(5); 995(3.5); 915(4); 885(6.5); 875(6.5); 860(6.5).

This peroxide also formed a bis-*p*-nitrobenzoate, m.p. 77–78° from ethyl alcohol.

Anal. Calcd. for $C_{26}H_{32}N_2O_{14}$: C, 52.34; H, 5.41; N, 4.70. Found: C, 52.66; H, 5.59; N, 4.75.

These results complete the list of the seven different peroxides originally detected in the crude mixture.

The Alkyl Nitration of Active Methylene Compounds. II.[1,2] The Nitration of Aliphatic Nitriles and Ketones
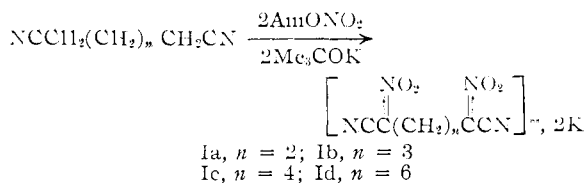
BY HENRY FEUER AND CHRISTOS SAVIDES

The nitration of aliphatic nitriles, dinitriles and ketones with amyl nitrate in the presence of potassium *t*-butoxide afforded in good yields the potassium salts of the corresponding α-nitronitriles, α,α'-dinitrodinitriles and α,α'-dinitroketones. Dipotassium α,α'-dinitroadiponitrile was hydrolyzed to 1,4-dinitrobutane and was found to react readily with methyl vinyl ketone to give 5,8-dicyano-5,8-dinitro-2,11-dodecanedione.

In a previous publication[2] it was shown that cyclic ketones are effectively nitrated with amyl nitrate in the presence of sublimed potassium *t*-butoxide to give the dipotassium salts of the corresponding α,α'-dinitrocyclic ketones. We have now found that the reaction is generally applicable for aliphatic mononitriles, α,ω-dinitriles, aliphatic ketones and aryl alkyl ketones.

Adiponitrile was chosen as a model compound for the study of the nitration of nitriles since the product, dipotassium α,α'-dinitroadiponitrile (Ia), was not very hygroscopic and could be readily purified. As in the case of cyclic ketones, it was found that the nitration of adiponitrile was most successful in the presence of a strong base and in the absence of hydroxylic solvents. Thus the yield of Ia was 16% when potassium ethoxide was the

base and tetrahydrofuran the solvent. However, with the stronger base, sublimed potassium *t*-butoxide in tetrahydrofuran, the yield of compound Ia was increased to 93%.

By following the latter procedure (which afforded the best yield with adiponitrile), pimelonitrile, suberonitrile, sebaconitrile, butanenitrile and hexanenitrile were nitrated.[3]

$$NCCH_2(CH_2)_n CH_2CN \xrightarrow[2Me_3COK]{2AmONO_2} \left[NCC(CH_2)_nCCN \right]^{--}, 2K$$

Ia, $n = 2$; Ib, $n = 3$
Ic, $n = 4$; Id, $n = 6$

Except for compound Ia, the potassium salts of I and α-nitronitriles II were very hygroscopic and could not be purified. Conversion of these

(1) From the Ph.D. thesis of Christos Savides, Purdue University, 1958.

(2) For the previous publication see H. Feuer, J. W. Shepherd and C. Savides, THIS JOURNAL, **78**, 4364 (1956).

(3) Evidence of nitration was observed with acetonitrile; however, the product could not be isolated.