lent of 377 whereas that calculated for a cyclic disulfone having one molecule of 10-hendecenoic acid and one of 1-pentene should have the value 382.

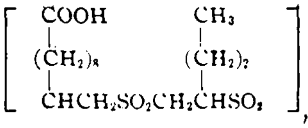
Anal. Calcd. for $C_{16}H_{30}S_2O_6$: S, 16.75. Found: S, 16.97.

No alkali insoluble sulfone was found and no evidence was obtained to indicate that the cyclic disulfone having two units of 10-hendecenoic acid was formed in this reaction.

Summary

1. Mixed olefins and their derivatives or mixtures of an olefin and an acetylene combine with sulfur dioxide to give products which correspond closely in composition to the mixture used and appear to be true copolymers.

2. The copolymer prepared from a mixture of equimolecular quantities of 10-hendecenoic acid and 1-pentene has been shown to have the structure



$$\left[\begin{array}{c} \text{COOH} \qquad\qquad \text{CH}_3 \\ | \qquad\qquad\qquad | \\ (\text{CH}_2)_8 \qquad\quad (\text{CH}_2)_2 \\ | \qquad\qquad\qquad | \\ \text{CHCH}_2\text{SO}_2\text{CH}_2\text{CHSO}_2 \end{array}\right]_n$$

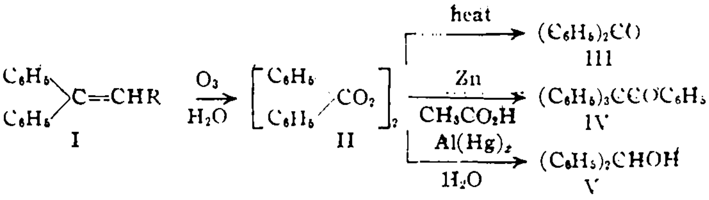
URBANA, ILLINOIS RECEIVED FEBRUARY 14, 1938

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Diaryl Ketone Peroxides

BY C. S. MARVEL AND VELMA E. NICHOLS

Dimeric and trimeric ketone peroxides from dialkyl and alkyl aryl ketones have been known for some time[1] but the corresponding diaryl ketone peroxides apparently have not been described. While studying the ozonolysis of certain 1,1-diphenyl-1-alkenes (I), we isolated a high-melting neutral compound which proved to be dimeric benzophenone peroxide (II). This communication describes the isolation and the properties of the latter and of several analogous compounds.



It is somewhat surprising that diaryl ketone peroxides have not been noted in earlier ozonolysis reactions since both dialkyl and alkyl aryl ketone peroxides have been prepared by this procedure.[1] After our accidental discovery of benzophenone peroxide, a large number of experiments on the ozonolysis of 1,1-diphenyl-1-propene was carried out. Carbon tetrachloride was used as a solvent for the ozonization. Many changes in experimental conditions of ozonization and of hydrolysis did not greatly affect the yield of benzophenone peroxide, which always amounted to 3–7% of the theoretical.

Benzophenone peroxide was also obtained by the ozonolysis of 1,1-diphenylethene and 1,1-diphenyl-1-butene. It was not obtained by ozonolysis of 1,1-diphenyl-4,4-dimethyl-1,2-pentadiene. Ozonolysis of 1,1-di-*p*-tolylethene, 1,1-di-*m*-tolylethene and 1-phenyl-1-*p*-tolylethene gave the respective ketone peroxides in 3–7% yields. No ketone peroxide was obtained in the ozonolysis of 1,1-dibiphenylethene but some *p*-carboxyphenyl biphenyl ketone was isolated. In all of these ozonolysis experiments small amounts of the acids which might be expected from cleavage of the diaryl ketones were isolated.

All of these diaryl ketone peroxides were quite insoluble in ethanol; were difficultly soluble in ether, acetone, ethyl acetate, and acetic acid; and fairly soluble in hot benzene and carbon tetrachloride. They all melted sharply within the limits of 183 to 225° with some liberation of gas and some evidence of sublimation at the melting point. None exploded at the melting point, although some less pure samples gave off gas at a fairly rapid rate in the melting point tubes.

Benzophenone peroxide when heated for five minutes at its melting point (214–215°) was decomposed completely to give benzophenone (III). It was noted that recrystallization of these peroxides from various solvents always caused con-

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(1) The literature concerning these compounds has been summarized by Rieche: (a) "Alkylperoxyde und Ozonide, Studien uber peroxydischen Sauerstoff," Steinkopff, Dresden, 1931; (b) "Die Bedeutung der organischen Peroxyde für die chemische Wissenschaft und Technik," Ahrens Sammlung, **34**, 1 (1936), Enke, Stuttgart.

TABLE I

BENZOPHENONE PEROXIDE FROM 1,1-DIPHENYLALKENES

Olefin used	Amount, g.	CCl_4 used as solvent, cc.	Time of ozonization, hrs.	Mixture used to hydrolyze ozonide	Yield benzophenone peroxide, g.
1,1-Diphenylethene	2.5	75	2	50 cc. 30% H_2O_2	0.08
1,1-Diphenylethene	2.5	75	4	50 cc. 30% H_2O_2	.15
1,1-Diphenylethene	2.5	75	6	50 cc. 30% H_2O_2	.165
1,1-Diphenyl-1-propene	2.5	75	4	5 cc. 30% H_2O_2; 25 cc. H_2O	.13
1,1-Diphenyl-1-propene	7.5	100	$4^{3}/_{4}$	17 cc. 30% H_2O_2; 25 cc. H_2O	.4
1,1-Diphenyl-1-propene	7	75	4	25 cc. H_2O	.243
1,1-Diphenyl-1-propene	3	50	1[a]	10 cc. 30% H_2O_2; 20 cc. H_2O	.035
1,1-Diphenyl-1-propene	3	50	2[b]	10 cc. 30% H_2O_2; 20 cc. H_2O	.08
1,1-Diphenyl-1-propene	3	50	3[c]	10 cc. 30% H_2O_2; 20 cc. H_2O	.11
1,1-Diphenyl-1-butene	2.5	75	4	5 cc. 30% H_2O_2; 25 cc. H_2O	.09

[a] The short period of ozonization left considerable olefin unchanged as the solution would still decolorize bromine in carbon tetrachloride at the end of the ozonization. [b] Some unchanged olefin remained after ozonolysis. [c] After three hours of ozonization the solution of olefin no longer decolorized a solution of bromine in carbon tetrachloride.

siderable loss which was probably due to partial decomposition into the ketone.

The diaryl ketone peroxides resemble acetophenone peroxide in their inertness toward reagents which react with the low molecular weight alkyl peroxides (p. 26),[1a] with dialkyl ketone peroxides (p. 76 ff.),[1a] and acyl peroxides (p. 14)[1b]. Reduction of benzophenone peroxide with zinc and acetic acid gave benzopinacolone (IV) and reduction with aluminum amalgam gave benzohydrol (V).

Attempts to prepare benzophenone peroxide from benzophenone by treatment with hydrogen peroxide, with hydrogen peroxide and sulfuric acid, with persulfuric acid or with ozone have been unsuccessful. These general methods have been used for the preparation of dialkyl ketone peroxides but do not work with alkyl aryl ketones (p.86)[1a]. A 3% yield of benzophenone peroxide has been obtained by treating benzophenone dichloride with 30% hydrogen peroxide over a period of two weeks. Further work on the preparation and reactions of these diaryl peroxides is in progress.

Experimental

Benzophenone Peroxide.—Ozonized oxygen from a commercial ozonizer was passed through a solution of the olefin derivative for various periods of time and at varying rates. In some experiments the ozonized oxygen was washed with sodium hydroxide solution and concentrated sulfuric acid before it was introduced into the olefin solution. The ozonide was hydrolyzed with water or water and hydrogen peroxide mixtures. Acidic materials, formed in the ozonolysis, were removed by extraction with 2% sodium hydroxide solution. The solvent was then removed and the benzophenone peroxide was separated from the benzophenone by washing with alcohol and recrystallizing from acetone, benzene or ethyl acetate. A few typical experiments are recorded in Table I.

The samples of benzophenone peroxide isolated from different reaction mixtures had different melting points ranging from 206.5–207.5° to 214.5–215.5°. The melting point of a sample seemed to be influenced by the size of the crystal, the rate of heating and to a slight extent by the solvent used in the recrystallization of the peroxide. Some samples on analysis were found to contain more carbon and hydrogen than expected, thus indicating some decomposition into the ketone.

Anal. Calcd. for $(C_{13}H_{10}O_2)_2$: C, 78.77; H, 5.09; mol. wt., 396. Found: C, 78.52, 79.45, 79.37; H, 4.86, 5.16, 5.23; mol. wt. (ebullioscopic in benzene), 410, 423, 415.

Reactions of Benzophenone Peroxide.—A 0.13-g. sample of the peroxide was suspended in a solution of ether and acetic acid. To this mixture zinc dust was added. When the suspended peroxide had disappeared, the ether layer was separated and evaporated to dryness. The residue after recrystallization from alcohol melted at 174.5–179° and the melting point was not changed when this material was mixed with an authentic specimen of benzopinacolone.

An 0.11-g. sample of the peroxide in ether suspension was shaken with aluminum amalgam and water for two days. The unchanged peroxide remaining was separated and the ether evaporated. Some needle-shaped crystals, melting at 64–65°, were isolated. When these were mixed with an authentic specimen of benzohydrol, m. p. 68–69°, the mixture melted at 65–67°.

An 0.11-g. sample of the peroxide was melted and held at the melting point for five minutes. The product was cooled and recrystallized from alcohol and ether. It then melted at 47–48° and when mixed with an authentic specimen of benzophenone did not depress the melting point.

Solutions of potassium iodide, in acetone, acetic acid, dilute aqueous sodium hydroxide, concentrated hydrochloric acid and in water were shaken with benzophenone peroxide but no free iodine could be detected in these reaction mixtures. Aqueous solutions of potassium iodide were also treated with solutions of the peroxide in both carbon tetrachloride and carbon disulfide without reaction. Solutions of hydroquinone in benzene or dioxane and water were not affected by this peroxide. Boiling the peroxide with 4% aqueous sodium hydroxide left it essentially unchanged.

A 0.05-g. sample of the peroxide was added to a standard reaction mixture of 10 g. of 2-pentene, 10 g. of liquid sulfur dioxide and 2 g. of alcohol.[2] No polysulfone was produced in forty hours.

Attempted Syntheses of Benzophenone Peroxide from Benzophenone.—Mixtures of 1 g. of benzophenone with various proportions of concentrated sulfuric acid and hydrogen peroxide were allowed to stand for two weeks; no evidence of peroxide formation was found. Likewise benzophenone in 30% hydrogen peroxide gave no benzophenone peroxide. Attempts to oxidize benzophenone with potassium persulfate and sulfuric acid gave no ketone peroxide. Ozonized oxygen was passed into a solution of 2.5 g. of benzophenone in 75 cc. of carbon tetrachloride for one and one-half hours and the mixture treated with water. Benzophenone (2 g.) was recovered and some benzoic acid was isolated, but there was no evidence of peroxide formation.

Synthesis of Benzophenone Peroxide from Benzophenone Dichloride.—A mixture of 1 cc. of benzophenone dichloride and 2 cc. of 30% hydrogen peroxide was allowed to stand for two weeks. The dichloride was converted largely to benzophenone but 0.03 g. (3%) of benzophenone peroxide was obtained. Various modifications of the reaction involving stirring, alkaline medium, etc., gave no better results.

Di-*p*-tolyl Ketone Peroxide.—Ozonized oxygen was passed through a solution of 3 g. of 1,1-di-*p*-tolylethene in 75 cc. of carbon tetrachloride for three and one-fourth hours and the reaction mixture was then hydrolyzed with 50 cc. of 30% hydrogen peroxide. The neutral material from the ozonolysis was recrystallized from benzene and 0.215 g. (6.7%) of di-*p*-tolyl ketone peroxide, m. p. 210.5–211.5°, was obtained. In addition 2.3 g. of di-*p*-tolyl ketone, m. p. 91–93°, was isolated.

Anal. Calcd. for $(C_{15}H_{14}O_2)_2$: C, 79.62; H, 6.23; mol. wt., 452. Found: C, 79.68; H, 6.39; mol. wt. (ebullioscopic in benzene), 452.

Di-*m*-tolyl Ketone Peroxide.—1,1-Di-*m*-tolylethene was prepared by adding 20.1 g. of ethyl acetate to the Grignard reagent prepared from 86 g. of *m*-bromotoluene and 12.4 g. of magnesium and after the addition reaction was complete, separating the carbinol in the usual way. The crude carbinol was dehydrated by dropping it into a flask in an oil-bath held at 210–215° and then heating for one-half hour at that temperature. On distillation under reduced pressure, the 1,1-di-*m*-tolylethene was obtained as a liquid boiling at 134–139° at 5 mm.; 118° at 3 mm.; n^{20}_D 1.5922; d^{20}_4 1.0003. The yield was about 20 g.

Anal. Calcd. for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.01; H, 7.78.

A solution of 2.8 g. of 1,1-di-*m*-tolylethene in 70 cc. of carbon tetrachloride was treated with a rapid stream of ozonized oxygen for about three and three-fourths hours and then the solution was treated with 10 cc. of 30% hydrogen peroxide and 20 cc. of water. An excess of 2% sodium hydroxide solution was added to take up any acidic products. The solvent was evaporated and the residue was recrystallized from acetone. The di-*m*-tolyl ketone peroxide melted at 183–184°.

Anal. Calcd. for $(C_{15}H_{14}O_2)_2$: C, 79.62; H, 6.23. Found: C, 79.09; H, 6.59.

The residual acetone solutions from several such ozonolysis mixtures were combined and distilled. The fraction boiling from 135 to 140° at 3 mm. was collected, dissolved in ether and cooled in a dry ice–acetone bath. The crystals thus obtained were collected on a filter and recrystallized from absolute alcohol again using a dry ice–acetone bath for cooling. The product melted at 51°.

Anal. Calcd. for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 86.10; H, 6.33.

***p*-Tolyl Phenyl Ketone Peroxide.**—A 7-g. sample of 1-*p*-tolyl-1-phenylethene in 75 cc. of carbon tetrachloride was treated with ozonized oxygen which had been washed with aqueous sodium hydroxide and concentrated sulfuric acid for four and one-half hours. The reaction mixture was then hydrolyzed with water, extracted with aqueous alkali, and the peroxide was recrystallized from acetone. The yield of crude material was 0.5 g. (6.5%) but there was much loss on purification. The recrystallized peroxide melted at 186.5–187.5°.

Anal. Calcd. for $(C_{14}H_{12}O_2)_2$: C, 79.23; H, 5.70. Found: C, 79.15; H, 5.80.

Ozonolysis of 1,1-Dibiphenylethene.—An attempt to prepare dibiphenyl ketone peroxide by ozonolysis of 1,1-dibiphenylethene gave a difficultly soluble acid which melted at 287–288° after recrystallization from acetone or dioxane. This appeared to be *p*-carboxyphenyl biphenyl ketone which has been mentioned by Schlenk and Brauns[3] but has not been characterized definitely.

Anal. Calcd. for $C_{20}H_{14}O_3$: C, 79.45; H, 4.67; mol. wt., 302. Found: C, 78.71; H, 4.59; mol. wt. (ebullioscopic in acetic acid), 294.

Summary

Ozonolysis of a number of 1,1-diarylalkenes has produced the corresponding dimeric diaryl ketone peroxides in yields of 3–7%. These peroxides are much more stable than the known dialkyl ketone peroxides.

URBANA, ILLINOIS RECEIVED MARCH 14, 1938

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[2] Ryden and Marvel, THIS JOURNAL, **57**, 2311 (1935).

[3] Schlenk and Brauns, *Ber.*, **46**, 4063 (1913).