found to be identical with the salt prepared from an authentic sample of barium ω-styrenesulfonate.

Addition of excess sodium to a liquid ammonia solution of 1-phenyl-1-hydroxyethane-2-sulfonate gave no detectible amount of sodium sulfite, and the hydroxysulfonate was recovered unchanged.

Reduction of Indene Oxide and Bromohydrin.—Sodium was added to a solution of 6.3 g. of indene oxide in 100 ml. of liquid ammonia until the blue color persisted. After one-half hour ammonium chloride was added, the ammonia was evaporated, and the residue extracted with ether. From the ether there was obtained 3.1 g. of crude 2-indanol, which, upon recrystallizing from ligroin, melted at 70°.

To 3 g. of sodium dissolved in 300 ml. of ammonia indene bromohydrin was added slowly with stirring until the blue color disappeared; this required 13 g. Evaporation of the ammonia gave 6.2 g. of 2-indanol, m. p. 70°. This is 75% of the theoretical amount.

Reduction of Sodium Sulfonates in Ammonia Solution.—To the sodium sulfonate dissolved in liquid ammonia was added a liquid ammonia solution of sodium until a permanent blue color resulted. After evaporation of the ammonia the residue was examined for sodium sulfite, unchanged sodium sulfonate, and hydrocarbon or alcohol. The results have been given in the discussion part of the paper.

Summary

1. The reaction of indene bromohydrin with sodium sulfite yields sodium 2-hydroxyindane-1-sulfonate, whereas styrene bromohydrin gives the 1-phenyl-1-hydroxyethane-2-sulfonate.

2. Indene bromohydrin and oxide are reduced by sodium in liquid ammonia to 2-indanol.

3. Sodium sulfonates having a benzyl or allyl type carbon attached to the sulfur are readily cleaved by sodium in ammonia to give sodium sulfite, the sulfonate group being replaced by hydrogen.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

Trivalent Carbon. II. Unsymmetrical Hexaaryldimethylperoxides[1]

BY EMMETT L. BUHLE, SR. MARY LOUIS WHALEN, S.S.N.D., AND F. Y. WISELOGLE

A recently published note from Marvel and Himel prompts us to record some observations on oxygen absorption by solutions containing mixtures of dissociating hexaarylethanes (Equations 1–6).[2] Marvel and Himel, from studies of

$$\begin{aligned} R—R &\rightleftarrows 2R\cdot && (1)\\ R'—R' &\rightleftarrows 2R'\cdot && (2)\\ R\cdot + \cdot R' &\rightleftarrows R—R' && (3)\\ 2R\cdot + O_2 &\longrightarrow R—O—O—R && (4)\\ 2R'\cdot + O_2 &\longrightarrow R'—O—O—R' && (5)\\ R\cdot + O_2 + \cdot R' &\longrightarrow R—O—O—R' && (6) \end{aligned}$$

dissociation equilibria in mixtures of hexaarylethanes (Equations 1–3), have concluded that the radical concentration in a mixture is in general lower than the average of the radical concentrations of the two single, symmetrical ethanes in corresponding formal concentrations. Although this appears to be the first quantitative study of a long discussed problem,[3] it is in agreement with other evidence that unsymmetrical dissociating systems are usually more stable than their symmetrical counterparts.[4]

We have found that the action of oxygen on mixtures of dissociating hexaarylethanes gives surprisingly high yields of unsymmetrical peroxides (Equation 6). Thus, in a representative experiment, a benzene solution 0.2 formal with respect to triphenylmethyl and diphenyl-*p*-biphenylmethyl was exposed to air until the colors of the radicals had disappeared. Removal of the solvent and recrystallization of the residue gave a 60% yield of the unsymmetrical 4-phenylhexaphenyldimethylperoxide, $(C_6H_5)_3C\text{-}O\text{-}O\text{-}C(C_6H_5)_2(C_6H_4\text{-}C_6H_5\text{-}p)$. Neither of the two symmetrical peroxides could be isolated although both are quite insoluble substances and are readily recovered.

The structures of the new unsymmetrical peroxides were confirmed by cleavage with sodium amalgam to the carbinols (Equation 7), or by

$$R—O—O—R' + 2Na \longrightarrow R—O^- + 2Na^+ + {}^-O—R' \quad (7)$$

cleavage with hydrogen iodide in acetic acid which gave the methanes (Equation 8).

$$R—O—O—R' + 6(H) \longrightarrow RH + 2H_2O + HR' \quad (8)$$

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(1) Most of the work reported herein was taken from the Essay of Sister Mary Louis Whalen submitted in partial fulfillment of the requirements for the degree of Master of Arts in The Johns Hopkins University, 1937. We are indebted to the Hynson, Westcott and Dunning Research Fund for a grant-in-aid covering a part of the cost of this research.

(2) Marvel and Himel, THIS JOURNAL, **64**, 2227 (1942).

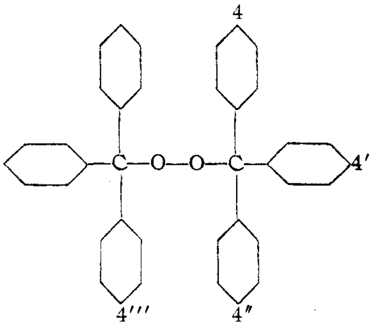
(3) Schmidlin, "Das Triphenylmethyl," Ferdinand Enke, Stuttgart, 1914, p. 101; Bachmann, THIS JOURNAL, **55**, 2135 (1933).

(4) Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1939, p. 58 ff.

In three cases studied the unsymmetrical peroxide was the sole isolable product. From a mixture of triphenylmethyl and tri-*p*-biphenylmethyl, however, the symmetrical peroxides predominated although we were able to isolate the unsymmetrical peroxide in 36% yield.[3] The data are recorded in Table I.

TABLE I

UNSYMMETRICALLY SUBSTITUTED HEXAPHENYLDIMETHYLPEROXIDES, R—O—O—R′



Substituent group and position	Yield, %	Formal ratio [R′·]/[R·]	Calcd. ratio[a] [R′·]/[R·]
4-Phenyl-	60	1	4
4,4′-Diphenyl-	62	1	6
4,4′,4‴-Triphenyl-	65	1	2
4,4′,4″-Triphenyl-	13	1	10
	36	1/3	6

[a] The last column is the ratio of the concentrations of the two free radicals in separate benzene solutions at 25° if the ethanes are in the same formal concentration as in the mixture when first exposed to oxygen. It would represent the actual ratio of radical concentrations in the mixture if none of the unsymmetrical ethane were formed. The following dissociation constants were used in calculating these data: hexaphenylethane,[5] 2.4×10^{-4}; *sym*-tetraphenyldi-*p*-biphenylethane,[6] 4.2×10^{-3}; *sym*-diphenyltetra-*p*-biphenylethane,[7] 1.6×10^{-2}; hexa-*p*-biphenylethane,[7] 3.6×10^{-2}.

The predominant formation of an unsymmetrical peroxide would be readily understandable if the reaction involved a direct attack by oxygen on an unsymmetrical hexaarylethane present in relatively high concentration. Ziegler has proved, however, that any direct reaction between oxygen and hexaphenylethane must be incomparably slower than the dissociation of the ethane into free radicals. The formation of hexaphenyldimethylperoxide, therefore, involves the action of oxygen on triphenylmethyl radicals exclusively.[8] This mechanism has been applied by Bachmann to unsymmetrical dissociating pentaarylethanes.[9] Although the reaction between pentaarylethanes and oxygen likewise involves intermediary free radicals exclusively, the unsymmetrical peroxide was always the predominant product. Under the special reaction conditions the two different trivalent carbon radicals were present in equal concentrations, which were exceedingly small, for they were removed as fast as they were formed by the large excess of oxygen present.

It is highly probable, therefore, that unsymmetrical hexaaryldimethylperoxides are also formed from intermediary free radicals. If two different radicals are present in equal concentrations and if the rates of corresponding steps leading to peroxide formation are identical, then the yield of each of the three possible peroxides should be fifty per cent. of the theoretical. The high yields of unsymmetrical peroxides which we have isolated must indicate, therefore, an unusually high rate for an unsymmetrical as contrasted with a symmetrical coupling reaction.

The highest yield of unsymmetrical peroxide would be expected when the two radicals are present in equal concentrations. The low yield of unsymmetrical peroxide from the triphenylmethyl–tri-*p*-biphenylmethyl mixture is readily understandable, then, for the dissociation constants of the two ethanes are greatly different. Indeed, we were able to raise the yield of unsymmetrical peroxide substantially by increasing the relative concentration of triphenylmethyl with respect to tri-*p*-biphenylmethyl (Table I).

Experimental

4-Phenyl-hexaphenyldimethylperoxide.—A mixture of 2.78 g. of triphenylchloromethane (0.01 mole) and 3.55 g. of diphenyl-*p*-biphenylchloromethane[10] (0.01 mole) was dissolved in 50 cc. of benzene in a glass-stoppered Erlenmeyer flask which was repeatedly evacuated and filled with nitrogen. Twenty grams of mercury was added; the flask was refilled with nitrogen, stoppered and shaken mechanically for seventeen hours. The solution was filtered into a flask and the inorganic residue was washed with benzene. The filtrate was allowed to stand, undisturbed, until the characteristic orange-red color of the radical mixture had disappeared, indicating that oxidation was complete. The product crystallized on evaporation of the solvent at room temperature. The residue was digested with 100 cc. of cold chloroform and filtered; only 0.04 g. of insoluble product remained. Two recrystallizations of the chloroform soluble fraction from chloroform and alcohol gave a 60% yield of colorless prisms melting, with decom-

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[5] Roy and Marvel, THIS JOURNAL, **59**, 2622 (1937); Preckel and Selwood, *ibid.*, **63**, 3401 (1941).

[6] Marvel, Mueller and Ginsberg, *ibid.*, **61**, 2010 (1939).

[7] Marvel, Shackelton, Himel and Whitson, *ibid.*, **64**, 1824 (1942).

[8] Ziegler and co-workers, *Ann.*, **479**, 277 (1930); **504**, 162 (1933); **504**, 182 (1933).

[9] Bachmann and Wiselogle, *J. Org. Chem.*, **1**, 354 (1936).

[10] Schlenk, *Ann.*, **368**, 300–303 (1909).

position, at 177° to a yellow liquid. If the melting point tube was inserted in the bath at room temperature and slowly warmed the compound decomposed at temperatures as low as 155°.

That the product was not a mixture of two symmetrical peroxides was established by separating such a mixture through fractional crystallization, the triphenylmethylperoxide being the less soluble in chloroform and alcohol. A mixture of triphenylmethylperoxide and the unsymmetrical peroxide was also easily separated.

Anal. Calcd. for $C_{44}H_{34}O_2$: C, 88.8; H, 5.8. Found: C, 88.6; H, 5.9.

Cleavage.—The unsymmetrical peroxide dissolved in concentrated sulfuric acid, giving an orange-red color, but no crystalline products could be isolated from the hydrolyzed mixture. The peroxide was slowly cleaved by shaking 1.0 g. in 20 cc. of ether and 40 cc. of benzene with 2.5 g. of 45% sodium amalgam for two weeks. Hydrolysis of the reaction mixture gave a 20% yield (0.08 g.) of triphenylcarbinol; the other alcohol was not isolated.

A mixture of 0.2 g. of iodine and 0.6 g. of red phosphorus was allowed to reflux in 20 cc. of acetic acid until the iodine color had disappeared; then 0.3 cc. of water and 0.5 g. of the unsymmetrical peroxide were added and the mixture was refluxed for one hour. The filtrate, after removal of the phosphorus, was diluted with benzene and the acetic acid was extracted with water. The diphenyl-*p*-biphenylmethane crystallized from an alcohol solution; recrystallization from acetone and petroleum ether gave a product melting at 110.5–112.5°. Triphenylmethane crystallized when the filtrate was taken up in benzene. Both methanes were compared with authentic specimens.

4,4′-Diphenyl-hexaphenyldimethylperoxide.—A 62% yield, 1.6 g., of the unsymmetrical peroxide melting at 186° (instant immersion) was obtained from a mixture of 1.0 g. of triphenylchloromethane, 1.5 g. of phenyl-di-*p*-biphenylchloromethane[10] and 20 g. of mercury in 50 cc. of benzene. Neither of the two possible symmetrical peroxides was found. *Anal.* Calcd. for $C_{50}H_{38}O_2$: C, 89.5; H, 5.7. Found: C, 89.6; H, 5.8.

Cleavage.—The unsymmetrical peroxide gave an orange-red color with concentrated sulfuric acid. Cleavage of 1.0 g. with hydrogen iodide gave 0.58 g. of phenyl-di-*p*-biphenylmethane, m. p. 163–164°, and 0.2 g. of triphenylmethane.

4,4′,4″-Triphenyl-hexaphenyldimethylperoxide.—A mixture of 2.79 g. of triphenylchloromethane (0.01 mole), 5.07 g. of tri-*p*-biphenylchloromethane[10] (0.01 mole) and 30 g. of mercury was shaken in 50 cc. of benzene for nine hours. The solution was filtered in an atmosphere of carbon dioxide and the filtrate allowed to stand in the dark until colorless. After removal of the solvent at room temperature the partially crystalline residue was extracted with 25 cc. of cold chloroform. The chloroform was evaporated and the resulting unsymmetrical peroxide was recrystallized from acetone. The yield of product melting at 148° was 0.961 g. (13%).

When 5.07 g. of tri-*p*-biphenylchloromethane and 8.36 g. of triphenylchloromethane (0.03 mole) were shaken with 30 g. of mercury in 100 cc. of benzene a 36% yield (2.69 g.) of the unsymmetrical peroxide was obtained. *Anal.* Calcd. for $C_{56}H_{42}O_2$: C, 90.0; H, 5.7. Found: C, 90.0; H, 5.8.

Cleavage.—The peroxide gave a red color with concentrated sulfuric acid. Hydrogen iodide cleavage of 1.0 g. gave 29% of triphenylmethane (m. p., 91.5–92.0°) and 80% of tri-*p*-biphenylmethane (m. p. 235.5–236°).

4,4′,4‴-Triphenyl-hexaphenyldimethylperoxide.—A 65% yield of the unsymmetrical peroxide was obtained from 1.2 g. of phenyldi-*p*-biphenylchloromethane and 1.0 g. of diphenyl-*p*-biphenylchloromethane. The product after recrystallization from chloroform melted at 175° (instant immersion). *Anal.* Calcd. for $C_{56}H_{42}O_2$: C, 90.0; H, 5.7. Found: C, 89.9; H, 5.8.

Cleavage.—The peroxide gave a purple-red color with concentrated sulfuric acid. Cleavage with hydrogen iodide gave a 50% yield of phenyl-di-*p*-biphenylmethane but the other methane was not isolated.

Summary

The action of oxygen on mixtures of triarylmethyl radicals generally gives predominantly the unsymmetrical hexaaryldimethyl-peroxide, R–O–O–R′.

BALTIMORE, MD.

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