

The present agreement factor is $R = \Sigma \|F_o - |F_c|/\Sigma |F_o| = 0.14$ for the 889 observed reflections.

Acknowledgments.—We wish to thank Dr. M. F. Hawthorne for supplying us with several $B_9H_{15}R$ derivatives until this favorable X-ray problem was chosen. We also thank the Office of Naval Research and the Office of Ordnance Research for support.

DEPARTMENT OF CHEMISTRY
HARVARD UNIVERSITY
CAMBRIDGE 38, MASSACHUSETTS

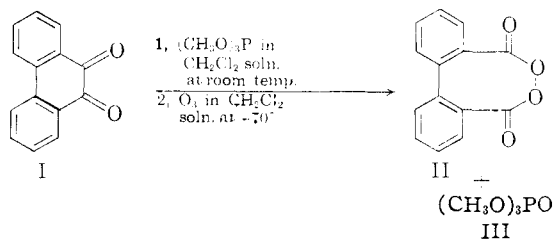
FREDERICK E. WANG
PAUL G. SIMPSON
WILLIAM N. LIPSCOMB

RECEIVED NOVEMBER 18, 1960

A NEW SYNTHESIS OF CYCLIC DIACYL PEROXIDES. DIPHENOYL PEROXIDE FROM PHENANTHRENE-QUINONE via A PHOSPHORANE DERIVATIVE¹

Sir:

We have developed a convenient method for the preparation of certain cyclic diacyl peroxides,² for instance diphenoyl peroxide (II), a substance in which the peroxidic linkage is part of an eight-membered ring.



The results of a typical experiment are: a mixture of phenanthrenequinone (I, 4.16 g.), trimethyl phosphite (2.48 g., one mole equivalent; an excess should be avoided) and methylene chloride (100 ml.) was kept 0.5 hr. at room temperature, under nitrogen. The pale yellow solution was cooled to -70° and treated with ozone from a Welsbach T-23 ozonator. The reddish-brown color of the solution was discharged sharply as the ozone consumption reached the value of one mole equivalent. The reaction mixture was flushed with nitrogen and filtered to remove some phenanthrenequinone (0.41 g.). The methylene chloride was removed *in vacuo* at temperatures not exceeding 20° . The residue was extracted with cold methanol, which left 3.8 g. of crude peroxide, contaminated with some phenanthrenequinone. From this material, 2.4 g. (50% over-all yield) of crystalline diphenoyl peroxide (II) of over 96% purity (iodimetric assay) was obtained after one recrystallization from methylene chloride-methanol (a solution containing 10 ml. of methylene chloride and 10 ml. of methanol per gram of crude peroxide was concentrated *in vacuo*, below 20°).

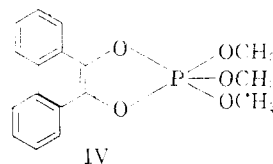
Diphenoyl peroxide (II) is a colorless substance which can be preserved at low temperature but which *explodes violently* when heated to *ca.* 70° or under impact. Calcd. for $C_{14}H_{10}O_4$: C, 70.0; H,

(1) Acknowledgment is made to the Donors of the Petroleum Research Fund administered by the American Chemical Society for partial support of this Research (Grant 286-A) and to the National Cancer Institute of the National Institutes of Health (Grant CY-47(9)).

(2) For a discussion of cyclic diacyl peroxides, see F. D. Greene and W. W. Rees, *J. Am. Chem. Soc.*, **82**, 893 (1960) and references therein.

3.3; 0, 26.7; mol. wt., 240; found C, 70.0; H, 3.2; 0, 26.5; mol. wt., 219 (cryoscopic in benzene); a single, sharp and strong band at 5.68μ . 2,2'-Diphenic anhydride was produced in over 80% yield from the reaction of the peroxide II with triphenylphosphine³ (or trimethyl phosphite). 2,2'-Diphenic acid was obtained in the iodimetric assay of the peroxide II.

A crystalline 1:1 adduct IV can be isolated⁴ from the reaction of phenanthrenequinone I with trimethyl phosphite. Ozonolysis of the adduct IV in methylene chloride as described above gave a mixture shown to contain diphenoyl peroxide (II, *ca.* 77% yield), phenanthrenequinone (I, *ca.* 20% yield) and trimethyl phosphate (III, *ca.* 95% yield), by a combination of infrared spectrometric and iodimetric assays. (Pure peroxide, II, was again isolated in 46-50% yields after one recrystallization.) The product of a comparable ozonolysis⁵ of the crystalline 1:1 adduct derived from benzil and trimethyl phosphite consists of benzoyl peroxide (*ca.* 37%) benzil (*ca.* 52%) and trimethyl phosphate. A possible mechanism for this new reaction has been advanced.⁵



(3) M. A. Greenbaum, D. B. Denney and A. K. Hoffmann, *ibid.*, **78**, 2563 (1956).

(4) F. Ramirez and N. B. Desai, *ibid.*, **82**, 2652 (1960).

(5) F. Ramirez, R. B. Mitra and N. B. Desai, *ibid.*, **82**, 5763 (1960).

DEPARTMENT OF CHEMISTRY
STATE UNIVERSITY OF NEW YORK
LONG ISLAND CENTER
OYSTER BAY, N. Y.

FAUSTO RAMIREZ
N. B. DESAI
R. B. MITRA

RECEIVED NOVEMBER 29, 1960

DEHYDROHALOGENATION OF SIMPLE ALKYL HALIDES BY STRONG BASE; EVIDENCE OF CARBENE INTERMEDIATES, EXTENT OF α -ELIMINATION¹

Sir:

It was shown that neoalkyl halides react with strong base via α -elimination and subsequent insertion to give cyclopropanes.² Since^{3a,c} isobutyl chloride and sodium or propyl sodium yields methylcyclopropane and isobutylene as major products it was of interest to determine the mechanism by which they are formed. Methylcyclopropane can arise via α -elimination, whereas isobutylene may result by either E2 (β) elimination and/or α -elimination, followed by hydride transfer.

(1) (a) Presented in part at the Meeting-in-Miniature, New York Section, A.C.S., March 11, 1960, paper H-9. (b) J. G. Berger, M.S. Thesis, New York University, June 1960.

(2) L. Friedman and J. G. Berger, *J. Am. Chem. Soc.*, **83**, 500 (1961).

(3) (a) F. E. Condon and D. E. Smith, *ibid.*, **69**, 965 (1947). (b) Recently, W. Kirmse, German Chemical Society Local Section Meeting, Mainz-Weisbaden, July 21, 1960; abstracted in *Angew. Chem.*, **72**, 716 (1960), reported that α,α -dideuteroisobutyl chloride reacts with sodium or potassium but not with lithium to give methylcyclopropane *via* α -elimination and isobutylene by concurrent α and β elimination. These results complement those of the present investigation. (c) NOTE ADDED IN PROOF.—For a complete account see W. Kirmse and W. von E. Doering, *Tetrahedron*, **11**, 266 (1960).