

II and consequently the latter is preferred (Table I *cf.* B and D.)⁵

Koch and Moffitt⁶ have considered the problem of modes of conjugation between 2p ($C\alpha$) and 3d (SO_2) orbitals in terms of two extreme cases: Case I: axis of p ($C\alpha$) parallel to the sulfone O—O axis, and Case II: p ($C\alpha$) axis in $C\alpha SC\alpha$ plane. Our results exclude the Case I structure for the anion which is involved in proton transfer since this has a plane of symmetry, and indicate a Case II type structure for $L-S^-$ and $D-S^-$ (possibly interconverted *via* the optically inactive Case I anion). Whether the hybridization of $C^- \alpha$ in the Case II anion is sp^2 , sp^3 or intermediate, cannot be decided at present, but experiments to settle this point are now in progress. Probable examples of Case II conjugation with $C\alpha = sp^2$ and $C\alpha = sp^3$ have been recorded.^{7,8} The fact that the ratio of D—H exchange rates in cyclopropyl- and isopropylphenyl sulfone are comparable provides evidence that the hybridization of $C^- \alpha$ in Case II anions may be fairly close to sp^3 .

The stereochemistry of anionic decarboxylation of optically active α -sulfonyl carboxylic acids,¹⁰ the absence of an ortho effect in conjugation of aromatic π -electrons with the sulfonyl group,¹¹ and several other interesting observations are understandable in terms of Case II conjugation and the above findings.

Further studies on the stereoelectronic properties of d -orbital conjugation are in progress and will be reported in due course. We are indebted to the National Institutes of Health and the Higgins Fund of Harvard University for support of this work.¹²

(5) These predictions are based on the kinetic expressions for Scheme I and II with $k_2 + k_3 \cong k_2$ and with correction for the greater base strength of DO^- relative to HO^- and for a small medium effect.

(6) H. P. Koch and W. E. Moffitt, *Trans. Far. Soc.*, **47**, 7 (1951).

(7) J. Toussaint, *Bull. soc. chim. Belg.*, **54**, 319 (1954).

(8) W. E. Doering and L. K. Levy, *J. Am. Chem. Soc.*, **77**, 509 (1955).

(9) H. E. Zimmermann and B. S. Thyagarajan, *ibid.*, **82**, 2505 (1960).

(10) J. E. Taylor and F. H. Verhoek, *ibid.*, **81**, 4537 (1959).

(11) H. Kloosterziel and H. J. Baker, *Rec. trav. chim.*, **72**, 185 (1953).

(12) Prof. D. J. Cram has kindly informed us of studies in his Laboratory which are in part parallel to those reported here.

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E. J. COREY
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THE MOLECULAR STRUCTURE OF $B_9H_{13}NCCH_3$

Sir:

The structure of $B_9H_{13}NCCH_3$ (Fig. 1b) has been established from a complete three dimensional X-ray diffraction study of a single crystal. This compound has only recently been first isolated and characterized,¹ although previous indications of its existence were known.^{2,3} Its heavy atom arrangement as a fragment of decaborane was deduced by Hawthorne⁴; its correct geometrical and valence

(1) M. F. Hawthorne, B. M. Graybill and A. R. Pitochelli, paper 45-N, Abstracts 138th Meeting, American Chemical Society, September 11-16, 1960, New York, N. Y.

(2) S. J. Fitch and A. W. Laubengayer, *J. Am. Chem. Soc.*, **80**, 5911 (1958).

(3) R. Schaeffer, private communication, December, 1958; see R. Schaeffer, *ibid.*, **79**, 1006 (1957).

(4) M. F. Hawthorne, private communication, 1960.

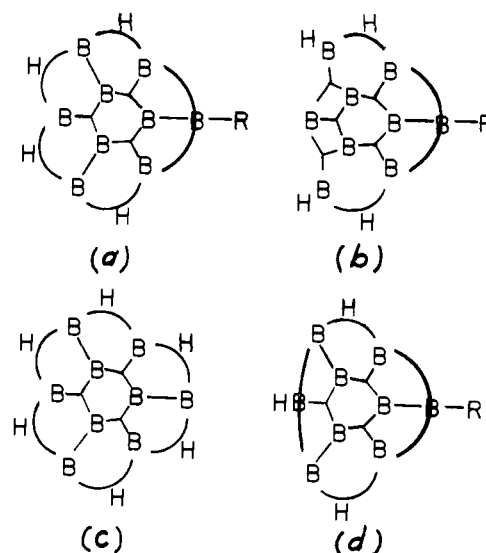


FIG. 1.—One terminal H has been omitted from each B atom in these drawings: (a) starting structure for the final Fourier and least squares refinement; (b) final structure after refinement; (c) hypothetical B_9H_{15} , which violates a topological rule, as does the starting structure (a related $B_9H_{12}^{-3}$ of symmetry C_{3v} and topology⁵ 0633 does not); (d) a probable $B_9H_{12}R^-$ structure. A transformation of the (a) \rightarrow (b) type or some intermediate structure involving a very unsymmetrical B—H—B bond is possible here.

structure was deduced by Lipscomb on the basis of the topological theory and the high field doublet of the B^{11} nuclear magnetic resonance spectrum⁴ which indicated three B atoms in apex environments. In the course of the three dimensional refinement Structure (a) of Fig. 1 refined to Structure (b), hitherto unreported, which definitely has two BH_2 groups to help absorb the extra electrons contributed by the Lewis base, acetonitrile. We suggest that an intermediate type of structure between (a) and (b) might possibly occur when the donating power of the Lewis base is not so large. Even though Structure (a) and its parent hypothetical hydride,⁵ B_9H_{15} of C_{3v} symmetry (Structure (c)), both violate the weakest topological rule,⁵ concerning the improbability of finding two bridge H atoms to a B connected to four other B atoms, we find it useful to think of these structures as related to the most nearly correct form, Structure (b). These relations lead us to consider Structure (d) as a safe prediction for the $B_9H_{12}R^-$ ion, recently isolated,¹ but we are quite uncertain about the structure of the unstable, and even possibly dimerized, $B_9H_{12}^-$ ion: topology⁵ 2621 is conceivable.

The unit cell of the crystal is monoclinic with $a = 5.64 \text{ \AA}$, $b = 9.22 \text{ \AA}$, $c = 9.81 \text{ \AA}$, and $\beta = 90^\circ$, and contains two molecules. Extinction of $0k0$ when k is odd leads to either $P2_1$ or $P2_1/m$ as possible space groups, but very clear indication of the linear $B-N\equiv C-CH_3$ groups in the three dimensional Patterson function immediately suggested that the space group is $P2_1/m$, later confirmed. All H atoms including H's on the methyl group have been located by three dimensional difference syntheses.

(5) R. E. Dickerson and W. N. Lipscomb, *J. Chem. Phys.*, **27**, 212 (1957).

The present agreement factor is $R = \Sigma \|F^o - |F_c|/\Sigma |F_c| = 0.14$ 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.

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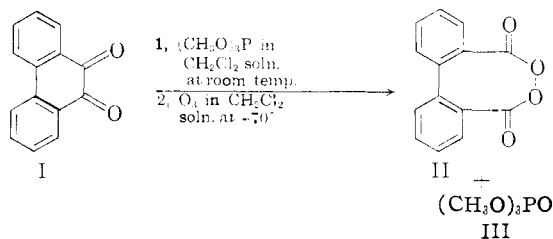
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RECEIVED NOVEMBER 18, 1960

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°).

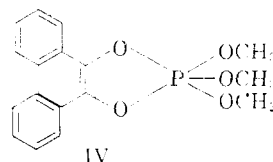
Diphenoyl peroxide (II) is a colorless substance which can be preserved at low temperature but which *explodes violently* when heated to *ca.* 70° or under impact. Calcd. for $C_{14}H_{10}O_4$: C, 70.0; H,

(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).

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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).