

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

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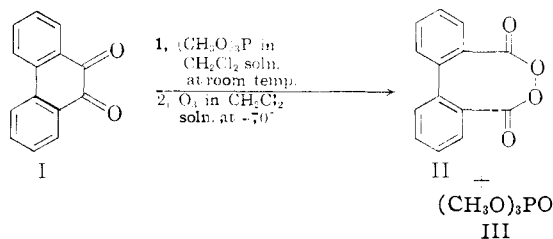
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A NEW SYNTHESIS OF CYCLIC DIACYL PEROXIDES. DIPHENOYL PEROXIDE FROM PHENANTHRENE-QUINONE via A PHOSPHORANE DERIVATIVE¹

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°).

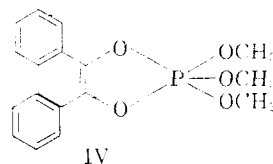
Diphenoyl peroxide (II) is a colorless substance which can be preserved at low temperature but which *explodes violently* when heated to *ca.* 70° or under impact. Calcd. for $C_{14}H_{10}O_4$: C, 70.0; H,

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(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.

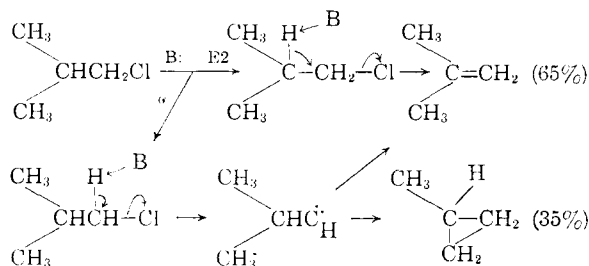
(2) L. Friedman and J. G. Berger, *J. Am. Chem. Soc.*, **83**, 500 (1961).

(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).

TABLE I
 REACTION OF BUTYL HALIDES WITH STRONG BASES

Halide	Base	Dehydrohalogenation Products ^a					Yield, ^b %	% α -Elimination ^c	
		C ₄ Alkane	1-Butene	Isobutene	<i>trans</i> -2-Butene	Methylcyclopropane			<i>cis</i> -2-Butene
<i>n</i> -BuCl-1- <i>d</i> ₁	PhNa ^d	7.7	89		t ^e	3.6	t	30	94 ^f
<i>n</i> -BuCl	PhNa	4.5	91		t	3.7	t	40	94
<i>n</i> -BuBr	PhNa	7	75		7	4	7	25 ^g	94
<i>n</i> -BuI	PhNa	12	71		5.5	2.6	10	20	65
<i>i</i> -BuCl-1- <i>d</i> ₂	PhNa	9.7		57	t	33	t	59	89 ^f
<i>i</i> -BuCl	PhNa	5.0		63	t	32	t	59	89
<i>i</i> -BuBr	PhNa	3.2		73	t	24	t	31	62
<i>i</i> -BuI	PhNa	7.5		86	0.7	5.1	1.1	29	13
<i>s</i> -BuCl	PhNa	t	47		30		23	66 ^h	?
<i>n</i> -BuCl	NaNH ₂	0.5	98		t	1.2	t	27	30
<i>n</i> -BuBr	NaNH ₂	4.5	95		t	0.6	t	45 ^h	15
<i>i</i> -BuCl	NaNH ₂			96	0.7	2.5	0.7	50	7
<i>i</i> -BuBr	NaNH ₂			99	0.3	0.4	t	50 ^h	1
<i>n</i> -BuCl	NaOMe		99		0.4	0.4	t	8	10
<i>i</i> -BuCl	NaOMe			98	1.6		0.4	6 ^h	0

^a % composition. Products analyzed, separated and identified by v.p.c. ^b Conversion of halides $\sim 100\%$. SN2 products account for balance *i.e.*, $100\% - \%$ yield. Average of two or more runs unless noted. ^c Estimated (see text) except where noted. Difference from 100 is extent of E2. Exclusive of SN2 process. ^d Reaction conditions: 10% excess base; PhNa suspension in decane (100°), NaNH₂ in diethyl Carbitol (reflux, *ca.* 180°), NaOMe in diethyl Carbitol (reflux). ^e Trace <0.1%. ^f Mass spectrographic analysis. ^g Total yield of products reproducible, but % composition variable as a result of presently unknown factors. Yield of SN2 product is in good agreement with that obtained by Wurtz-Fittig reaction, using PhBr, *n*-BuBr and Na. See R. R. Read, L. S. Foster, A. Russell and V. L. Simril, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 157. ^h Single experiment.



It is now reported that *n*-butyl chloride and isobutyl chloride^{3b} are dehydrohalogenated by phenyl sodium or sodium predominantly through α -elimination. Thus, 1,1-dideuterobutyl chloride and phenyl sodium give monodeuteromethylcyclopropane (4%) and a mixture of *mono*-($\sim 90\%$) and *di*-($\sim 6\%$) deutero-1-butenes⁴ in 30% overall yield. 1,1-Dideuteroisobutyl chloride and phenyl sodium give monodeuteromethylcyclopropane (37%) and a mixture of *mono*-($\sim 52\%$) and *di*-($\sim 11\%$) deuteroisobutylenes⁴ in 60% overall yield. Therefore, exclusive of SN2 reaction, α -elimination occurs in the former case to the extent of 94%, while in the latter to 89%. Using the yield of methylcyclopropane in each series as the criterion, the extent of α -elimination occurring with undeuterated butyl halides can be estimated (Table I).⁵

Thus, it may be inferred from the experimental data that *n*-butyl halides (X = Cl, Br, I) undergo α -elimination with phenyl sodium to the extent of 94, 94 and 61%, respectively, whereas with the corresponding isobutyl halides α -elimination occurs to the extent of 89, 62 and 13%. Similar data are

(4) By mass spectrographic analysis.

(5) For yield of methylcyclopropane from corresponding tosylhydrazones see: L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **81**, 5512 (1959).

obtained when sodium [Wurtz reaction] is used. These results indicate how steric more than inductive factors affect the course of dehydrohalogenation.⁶ With weaker bases such as sodamide the extent of α -elimination is markedly reduced. However, *n*-butyl chloride undergoes α -elimination ($\sim 10\%$) with sodium methoxide while isobutyl chloride does not. Hence, in addition to steric factors, the extent of α -elimination appears to be proportional to the strength of the base employed.

n-Propyl halides (X = I, Br, Cl) react with phenyl sodium to give dehydrohalogenation products (20–50% yield) of which 2–4% is cyclopropane. Similarly, ethylcyclopropane (4.5%) is obtained from *n*-amyl chloride.⁷ It is of interest to note that *n*-propyl benzenesulfonate reacts with phenyl sodium to give elimination products in only 1% yield of which 4% is cyclopropane. *sec*-Butyl halides do not yield methylcyclopropane. The degree of α -elimination with secondary halides is presently under investigation.

It is therefore apparent that dehydrohalogenation of primary halides with strong base in suitable media occurs predominantly via α -elimination.⁸

(6) These factors are amply discussed and documented with respect to E2 vs. SN2 reactions. C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, chap. VIII.

(7) Cf. G. L. Closs, Abstracts of Papers, 138th Meeting of the American Chemical Society, New York, N. Y., Sept., 1960, p. 9-O.

(8) For earlier work in this area see: D. G. Hill, W. A. Judge, P. S. Skell, S. W. Kantor and C. R. Hauser, *J. Am. Chem. Soc.*, **74**, 5599 (1952); S. M. Luck, D. G. Hill, A. T. Stewart, Jr. and C. R. Hauser, *ibid.*, **81**, 2784 (1959).

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