

gives the known methyl *cis*-dihydrophthalic ester in quantitative yield (m.p. 149–150°, lit.⁴ 149–150°), and dimethyl acetylenedicarboxylate affords dimethyl 3,4,5,6-tetraphenylphthalate (85%, m.p. 260–261°, lit.⁵ m.p. 258°). From diethyl maleate and diethyl fumarate there are obtained, respectively, diethyl *cis*-1,2-dihydro-3,4,5,6-tetraphenylphthalate (85%, m.p. 128–129°; found: C, 81.8; H, 6.1) and diethyl *trans*-1,2-dihydro-3,4,5,6-tetraphenylphthalate (90%, m.p. 110–111°; found: C, 81.8; H, 6.0).

Decomposition of I in triglyme in the presence of thiophenol, a reagent noted for its high reactivity with radicals, leads to a mixture of products, one of which is obtained in 40% yield and, on the basis of its analysis, ultraviolet and n.m.r. spectrum is believed to be 1-thiophenoxy-1,2,3,4-tetraphenylbutadiene (m.p. 132–133°, found: C, 87.9; H, 5.7; S, 6.7; mol. wt., 475). Other radical reagents such as nitric oxide and benzoyl peroxide also lead to mixtures, the resolutions of which are currently under investigation. The absence of products incorporating a cyclobutene ring cannot be interpreted as evidence in favor of IIB and against IIA in view of the ready thermal isomerization of cyclobutenes to butadienes⁶; it seems doubtful that a cyclobutene would survive the reaction temperatures employed in this study.

In the absence of added radical reagents, homolytic extrusion of dimethyltin dibromide from I, either in solution or as a melt, leads to dimerization of the triplet intermediate and the production (85%) of a new colorless hydrocarbon, m.p. 425–427° (found: C, 94.1; H, 5.7; mol. wt. 686 (ebullioscopic in diphenyl ether)). Because of the extreme insolubility of this dimer, chemical elucidation of its structure is a very slow process; however, X-ray work (by D. R. Petersen)⁷ reveals that the molecule possesses unusual symmetry requirements and that these are not satisfied by assuming a cyclooctatetraene or any of the other dimers obtained by previous workers in the cyclobutadiene field.⁸ Further speculation regarding the structure of this interesting new dimer would be premature at this time.

Generation of the triplet state in refluxing diglyme in the presence of one mole of anhydrous ferric bromide leads not to the cyclobutadiene metal complex, as is the case with nickel bromide,¹ but results in near-quantitative reduction of the ferric to ferrous ion with concurrent oxidation of the triplet state to what would appear to be an unusual carbonium ion. Oxidation of radicals by metal salts is not unknown,⁹ but seldom have the organic products been characterized. In our case, aqueous work-up leads to a variety of products in-

cluding tetraphenylfuran and 1-benzal-2,3-diphenylindene, both of which were identified by comparison with authentic material. Among the products whose structures are still under investigation are three unsaturated ketonic compounds, C₂₈H₂₂O, of m.p. 110–111°, 145–146°, and 181–182°, respectively. Comparable results are obtained in the presence of anhydrous cupric and palladium bromides.

An unequivocal choice between IIA and IIB as the triplet intermediate in the reactions reported here cannot be made at this time. Substitution of four phenyl groups should increase the stability of the postulated² cyclobutadiene triplet ground state and there are indications that this stabilization occurs to an unexpectedly large degree¹⁰ in structure IIA. On the other hand, IIB should possess no additional delocalization energy over that of two *cis*-stilbene mono-radicals and the existence of this type of radical has not been confirmed on either an experimental or theoretical level. Alternatively, in the language of the familiar resonance theory, each of the unpaired electrons of IIA may distribute itself over eight carbon atoms, but distribution over only four carbons is possible with IIB. It is hoped that chemical and spectroscopic investigations currently in progress will clarify many of the unresolved questions and, in particular, the nature of the triplet intermediate.

Thanks are due to F. Johnson, F. W. McLafferty, and G. H. Büchi for helpful discussions, to E. B. Baker and J. Heeschen for n.m.r. data, and to A. A. Carlson and A. M. Frantz for experimental assistance.

(10) Personal Communication from J. W. Crump, based on simplified MO-LCAO calculations.

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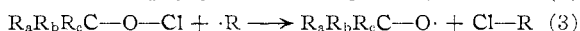
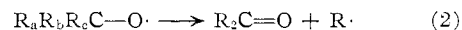
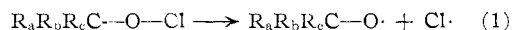
H. H. FREEDMAN

RECEIVED FEBRUARY 8, 1961

DECOMPOSITION OF TERTIARY ALKYL HYPOCHLORITES

Sir:

We wish to report the results of decomposition of a number of tertiary alkyl hypochlorites¹ (a class of compounds readily accessible from the corresponding alcohols) which serve to outline the general usefulness and scope of this alcohol degradation reaction. In isolated examples² the mechanism of decomposition has been shown to be a free radical chain reaction.



Principal questions concern direction of cleavage in the alkoxy radical (eq. 2) and reactions of the alkoxy radical competitive with fragmentation, such as inter- and intramolecular hydrogen abstraction.³ The products obtained in this study

(1) For leading references, see C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 386–388.

(2) See F. D. Greene, *J. Am. Chem. Soc.*, **81**, 2688 (1959), and references cited therein.

(3) For a discussion of thermochemistry and reactivity of alkoxy radicals, see P. Gray and A. Williams, *Chem. Revs.*, **59**, 239 (1959).

(4) C. F. H. Allen and L. J. Sheps, *Can. J. Res.*, **11**, 171 (1934).

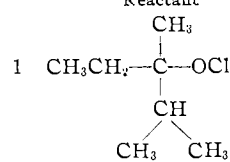
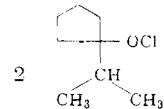
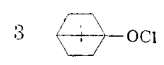
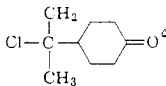
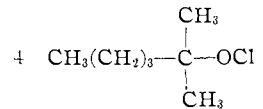

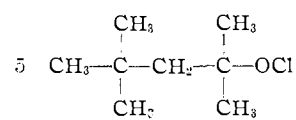




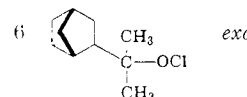
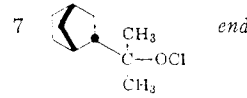
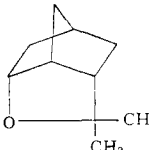
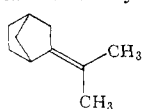
(5) W. Dilthey, I. Thewalt and O. Trosken, *Ber.*, **67**, 1959 (1934).

(6) E. Vogel, *Angew. Chemie*, **66**, 640 (1954).

(7) Dr. Petersen is currently carrying out a complete X-ray structure determination, the results of which will be published when available.

(8) (a) M. P. Cava, *Bull. Chem. Soc., France*, 1744 (1959); (b) R. Criegee and G. Louis, *Ber.*, **90**, 417 (1957); (c) M. Avram, *et al.*, *Ber.*, **93**, 1789 (1960); (d) F. R. Jensen and W. E. Coleman, *Tetrahedron Letters*, No. 20, 7 (1959); (e) E. H. White and H. C. Dunathan, Abstracts ACS Meeting, Chicago, September, 1958, p. S-41P.

(9) E. Collinson, *et al.*, *Disc. Faraday Soc.*, 188 (1960), and references cited therein.

TABLE I: PRODUCTS OF DECOMPOSITION OF TERTIARY ALKYL HYPOCHLORITES				
Reactant	Solvent	Products	Yield, %	
1 	CCl ₄ ^a	CH ₃ CH ₂ COCH ₃ , (CH ₃) ₂ CHCl (CH ₃) ₂ CHCOCH ₃ , CH ₃ CH ₂ Cl (CH ₃) ₂ CHCOCH ₂ CH ₃ , CH ₃ Cl	95 4 <0.5	
2 	CFCl ₃ ^b	(CH ₃) ₂ CHCO(CH ₂) ₃ CH ₂ Cl Cyclopentanone, (CH ₃) ₂ CHCl	94 3.4	
3 	CCl ₄ ^a		>95	
4 	CFCl ₃ ^b 	CH ₃ CHClCH ₂ CH ₂ C(CH ₃) ₂ OH ^d <i>n</i> -BuCl, acetone <i>n</i> -BuCOCH ₃ , CH ₃ Cl CH ₃ CHClCH ₂ CH ₂ C(CH ₃) ₂ OH ^d <i>n</i> -BuCl 2,2,5-Trimethyltetrahydrofuran 3-Chlorocyclohexene	55 15 <0.5 75 14 2 8	
5 	CFCl ₃ ^b 	Neopentyl chloride, acetone (CH ₃) ₂ CCH ₂ C(CH ₃) ₂ OH ^f  Neopentyl methyl ketone Neopentyl chloride, acetone (CH ₃) ₂ CCH ₂ C(CH ₃) ₂ OH ^f  (CH ₃) ₂ CCH ₂ C(CH ₃)=CH ₂  3-Chlorocyclohexene	55 20 5 <0.5 55 25 4 2 8	
6 	CCl ₄ ^{b, g}	<i>exo</i> -Norbornyl chloride, acetone	37	
7 	CCl ₄ ^{b, g}	 <i>exo</i> -Norbornyl chloride 	33 4 9	

^a Thermal initiation. ^b Weak ultraviolet initiation at 0°. ^c Structure established by conversion to the known dibenzal derivative (O. Wallach, *Ann.*, **437**, 187 (1924)). ^d Structure established by conversion to 2,2,5-trimethyltetrahydrofuran. ^e Initial ROCl concn., 1.4 *M*. ^f Structure established by conversion to 2,2,4,4-tetramethyltetrahydrofuran. ^g Unde-gassed conditions, yields not optimum.

are summarized in Table I. Identification of products was made by isolation from gas liquid phase chromatography and comparison with authentic material. Satisfactory analytical data have been obtained on all new compounds tabulated. Examples 2, 4, 5, 6 and 7 have been shown to proceed by radical chain reactions of long chain length and this is presumably the case for 1 and 3 as well. Product compositions are fairly insensitive of solvent in the series trichlorofluoromethane, carbon

tetrachloride and cyclohexene, of initiating source (heat, light, added radicals), and of initial concentration of hypochlorite (optimum yields were obtained in the region of 0.5–1.5 *M* hypochlorite in the absence of oxygen). The relative importance of intermolecular *vs.* intramolecular hydrogen abstraction was assessed by product analyses from decompositions in cyclohexene (no. 4 and 5).

Direction of Cleavage in Alkoxy Radical.—The examples illustrate the importance of factors

such as relative radical stability and ring strain in dictating direction of cleavage.³ Rate of cleavage of *n*-alkyl *vs.* methyl is greater than 10 to 1 (no. 1, 4, 5). Rate of cleavage of *sec*-alkyl (isopropyl) exceeds *n*-alkyl (ethyl) by 20 to 1 (no. 1). This latter order is reversed when cleavage of "*n*-alkyl" is part of a five-membered ring, *i.e.*, rate of cleavage of isopropyl *vs.* cleavage of one of the two equivalent ring carbon-carbon bonds in 1-isopropylcyclopentoxyl (no. 2) is 1 to 14. The bulk of this difference probably is associated with relief of ring strain in the five-membered ring (6 kcal. per mole from heat of combustion data).

Hydrogen Abstraction⁴ *vs.* Fragmentation.—Examples 4, 5 and 7 indicate that intramolecular hydrogen abstraction may compete successfully with fragmentation. The preferred point of abstraction is four carbon atoms removed from the oxygen atom.⁵ (Intermolecular attack on cyclohexene by the alkoxy radicals of Table I competes poorly with 1,5-intramolecular hydrogen abstraction or fragmentation⁴.) Rate of 1,5-intramolecular abstraction of secondary C-H (per hydrogen) *vs.* fragmentation of *n*-alkyl (butyl) is 2.7 to 1 (no. 4); rate of 1,5-abstraction of primary C-H (per H) *vs.* fragmentation of neopentyl is 1 to 16 (no. 5). If one makes the assumption that the rate constant for abstraction of hydrogen from cyclohexene is the same for the alkoxy radicals in examples 4 and 5, then the data may be extended to indicate a preference for 1,5-abstraction of secondary C-H *vs.* primary C-H of 10 to 1⁶ and a preference for cleavage of neopentyl *vs.* *n*-butyl of 4 to 1.

Acknowledgment.—We are indebted to the National Science Foundation and the Sloan Foundation for support of this work.

(4) See C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6108, 6113 (1960), for a study of intermolecular hydrogen abstraction by the *tert*-butoxyl radical (hydrocarbon chlorination by *tert*-butyl hypochlorite).

(5) Compare with the Hofmann-Löffler-Freytag reaction, E. J. Corey and W. R. Hertler, *J. Am. Chem. Soc.*, **82**, 1657 (1960).

(6) Compare with intermolecular abstraction by *tert*-butoxyl of tertiary C-H *vs.* secondary C-H *vs.* primary C-H of 44 to 8 to 1 (ref. 4).

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MECHANISM OF THE DIELS-ALDER REACTION¹

Sir:

The thermal interconversions of α - and β -1-hydroxydicyclopentadiene with *syn*- and *anti*-8-hydroxydicyclopentadiene, respectively, with retention of optical activity² suggest that other Diels-Alder dimers³ might undergo analogous rearrangements. The conversions of 8-ketodicyclopentadiene⁴ and a chlorinated derivative⁵ to the

(1) Supported in part by the Office of Naval Research.

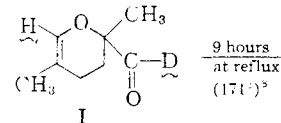
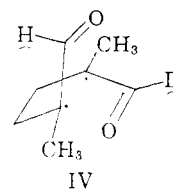
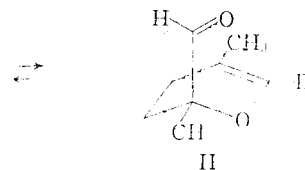
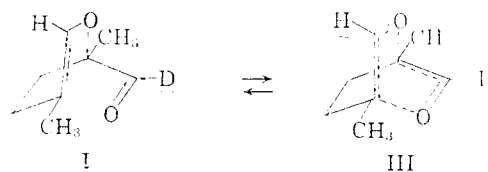
(2) R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

(3) Products of Diels-Alder additions in which a single component serves both as diene and dienophile.

(4) R. C. Cookson, J. Hudec and R. O. Williams, *Tetrahedron Lett.*, No. 22, 29 (1960).

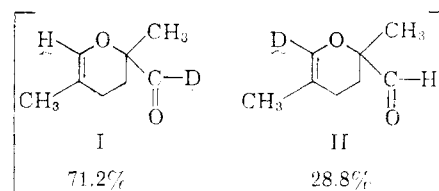
(5) P. Yates and P. Eaton, *ibid.*, No. 11, 5 (1960).

corresponding 1-ketodicyclopentadienes support this prediction; we now report that optically active deuterium-labeled (at the aldehyde hydrogen) methacrolein dimer,⁶ I, rearranges to II in a similar manner, under conditions where there is substantial competitive formation of methacrolein by the reverse Diels-Alder reaction. A possible course of the rearrangement is



$$\alpha_D^{27} - 71.35 \pm 0.05^\circ$$

(neat, $l = 1$ dm)

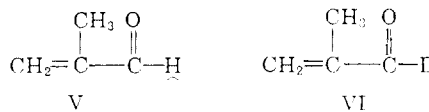


71.2%

28.8%

$$\alpha_D^{26} - 71.00 \pm 0.04^\circ$$

(neat, $l = 1$ dm)



Species III might be the transition state or else an intermediate, but in either case its geometry is formulated as being highly restricted.⁷ The over-

(6) Prepared from inactive unlabeled methacrolein dimer by a Cannizzaro oxidation to the corresponding acid,^{a,b} then resolution through the brucine salt, conversion of the sodium salt of the acid to the acid chloride with oxalyl chloride,^c formation of the corresponding *N*-methylanilide and reduction with lithium aluminum deuteride.^d
^a R. R. Whetstone, U. S. Patent 2,479,283 (1949); ^b G. G. Stoner and J. S. McNulty, *J. Am. Chem. Soc.*, **72**, 1531 (1950); ^c A. L. Wilds and C. H. Shunk, *ibid.*, **70**, 2427 (1948); ^d F. Weygand, G. Eberhardt, H. Linden, F. Schäfer and I. Eigen, *Angew. Chem.*, **65**, 525 (1953).

(7) The bicyclooctane formalism (I-IV) is used only to make clear the general character of the transformation which is taking place and should not be taken as a description of the precise geometry of the species involved. Actually, as has been pointed out to us by Professor