tetraphenylfuran.[8] Aqueous sodium nitrite oxidation of tetramethylcyclobutadiene nickel chloride complex to *cis*-dihydroxytetramethylcyclobutene was utilized by Criegee[3] to establish the identity of the organic portion of his cyclobutadiene metal complex. An analogous diol has not been isolated in our work to date, but its ready dehydration to tetraphenylfuran is perhaps not unexpected.

In general, III is quite soluble in solvents which can further complex with the available d orbitals of the nickel, yielding deep blue or violet solutions which are readily decomposed by the application of heat or the addition of water. In contrast, attempts to remove the nickel by treatment of a dimethylformamide solution of III with aqueous sodium acetate or sodium hydroxide led only to exchange of the bromide with the production of the red, ether-soluble, oxygen-sensitive nickel acetate or nickel hydroxide complex of tetraphenylcyclobutadiene.

Catalytic hydrogenation of the complex III in tetrachloroethane proceeded only at high pressures (PtO_2, 800 lb. H_2, 75°) and afforded an 80% yield of white needles, m.p. 122–123°. The mass spectral pattern of this product unequivocally assigns to it a molecular formula of $C_{28}H_{22}$ and this is supported by analysis (Found: C, 93.6; H, 6.4). The choice between the two most likely possibilities, 1,2,3,4-tetraphenylcyclobutene or 1,2,-3,4-tetraphenylbutadiene, was resolved in favor of the former on the basis of the spectral properties. Thus, the ultraviolet spectrum in heptane (λ max. 293 mμ, ϵ 26,000) resembles that of stilbene and not that of phenyl-substituted 1,3-dienes. The infrared spectrum in carbon tetrachloride solution shows absorption at 2915 cm.$^{-1}$, characteristic of alkane hydrogen, effectively eliminating the possibility that the hydrogenation product is a 1,2,3,4-tetraphenylbutadiene. The n.m.r. spectrum in carbon tetrachloride shows no bands in the region characteristic of the olefinic protons, but absorption does occur in the region characteristic for protons on a cyclobutane ring.[9] However, the n.m.r. spectrum shows, besides phenyl protons, *two* singlet bands at −4.90 and −4.03 p.p.m. (relative to tetramethylsilane as an internal standard) in the relative ratio of approximately 1:2. Inasmuch as the molecular formula does not allow the presence of more than two non-phenyl equivalent protons, we are forced to conclude that the hydrogenation product is in fact a mixture of the *cis* and *trans*-tetraphenylcyclobutenes.[10] Rigorous proof of this conclusion is in progress.

Attempts to prepare complexes analogous to III with other metal bromides, as well as some preliminary findings in regard to the intermediate involved in the formation of III, is given in a separate communication.

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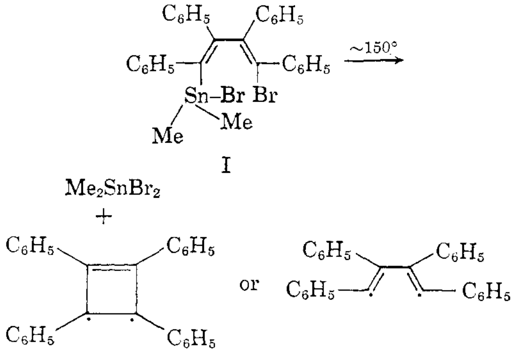
TETRAPHENYLCYCLOBUTADIENE DERIVATIVES. II.[1] CHEMICAL EVIDENCE FOR THE TRIPLET STATE

Sir:

Theoretical considerations suggest that cyclobutadiene will have a triplet ground state.[2] The method employed for the preparation of tetraphenylcyclobutadiene nickel bromide complex described in the accompanying report,[1] presents a unique opportunity for experimental evidence bearing on these theoretical predictions, since here the complex is formed in solution from an intermediate of finite lifetime.

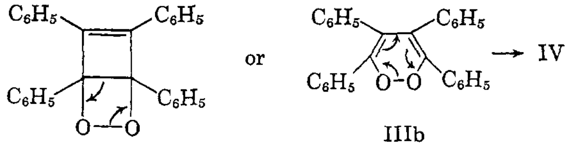
This intermediate, formed by the loss of dimethyltin dibromide from the stannole dibromide I[1] at approximately 150°, exhibits properties consistent with either structure IIa, the predicted[2] triplet ground state of tetraphenylcyclobutadiene, or, less likely, its open chain equivalent, IIb.



I

IIa IIb

Evidence that the intermediate in question is indeed a diradical species is inferred from the transient green color observed when I is decomposed in solution and its avid reactivity with characteristic radical reagents. The ready reaction of the intermediate with oxygen (itself in a triplet state) is particularly significant and affords an 80% yield of *cis*-dibenzoylstilbene[3] (IV) *via* the indicated electron redistribution of the postulated intermediate peroxide, IIIa or b.



IV

IIIa IIIb

Addition of II to dienophiles takes place stereospecifically and in high yields. Dimethyl maleate

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(8) We are grateful to Prof. R. K. Summerbell for a sample of tetraphenylfuran.

(9) The n.m.r. spectrum of a tetraphenylcyclobutane has been reported by J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959, p. 291.

(10) It is conceivable that rearrangement has occurred during the hydrogenation with the production of 1,2,3-triphenyl-1,4-dihydronaphthalene, a structure which would fit all the data reported above and, in particular, the n.m.r. spectrum. However, this compound has been prepared previously (E. Bergmann and O. Zwecker, *Ann.*, **487**, 155 (1931)), and is reported to melt at 165°.

(1) H. H. Freedman, Part I, *J. Am. Chem. Soc.*, **83**, 2194 (1961).

(2) (a) J. D. Roberts, A. Streitweiser, Jr., and C. M. Regan, *ibid.*, **74**, 4579 (1952), and references cited therein; (b) W. D. Hobey and A. D. McLachlan, *J. Chem. Phys.*, **33**, 1695 (1960).

(3) We are indebted to Prof. Peter Yates for the sample of *cis*-dibenzoylstilbene used for comparison purposes.

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. 110–11°; 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 butadienes[6]; 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 cycloöctatetraene 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 including 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, $C_{28}H_{22}O$, 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 postulated[2] cyclobutadiene triplet ground state and there are indications that this stabilization occurs to an unexpectedly large degree[10] 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.

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(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.

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

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DECOMPOSITION OF TERTIARY ALKYL HYPOCHLORITES

Sir:

We wish to report the results of decomposition of a number of tertiary alkyl hypochlorites[1] (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 examples[2] the mechanism of decomposition has been shown to be a free radical chain reaction.

$$R_aR_bR_cC{-}O{-}Cl \longrightarrow R_aR_bR_cC{-}O\cdot + Cl\cdot \qquad (1)$$

$$R_aR_bR_cC{-}O\cdot \longrightarrow R_2C{=}O + R\cdot \qquad (2)$$

$$R_aR_bR_cC{-}O{-}Cl + \cdot R \longrightarrow R_aR_bR_cC{-}O\cdot + Cl{-}R \quad (3)$$

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

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(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 alkoxyl radicals, see P. Gray and A. Williams, *Chem. Revs.*, **59**, 239 (1959).