

TABLE II
ACTIVITIES OF THE COLCHICINE AND DEMECOLCEINE OBTAINED FROM THE L-METHIONINE-METHYL-C¹⁴ FEEDING EXPERIMENT AND THEIR DEGRADATION PRODUCTS (C.P.M./M.M)

	Colchicine	Demecolceine
Free alkaloid	6.0×10^5	2.03×10^5
Colchicine or demecolceine	5.4×10^5	1.50×10^5
3,4,5-Trimethoxyphthalic anhydride	5.4×10^6	1.23×10^5
3,4,5-Trimethoxybenzoic acid	5.5×10^5	1.22×10^5
Gallic acid	0	0
N-Methylbenzamide	0.26×10^5

Further degradation of this anhydride proceeded as for colchicine.

(b) **Demecolceine (V).**¹⁰ Demecolceine (50 mg.) was refluxed for 1 hr. with 2% hydrochloric acid (4 ml.). The cooled solution was neutralized with sodium bicarbonate and extracted with chloroform. The dried extract was evaporated and the residue crystallized from methanol to yield

(10) A. Ufer, O. Schindler, F. Šantavý and T. Reichstein, *Helv. Chim. Acta*, **37**, 18 (1954).

pale yellow needles of demecolceine (44 mg.), m.p. 137–138°. The analytical sample was dried *in vacuo* at 100°.

Anal. Calcd. for C₂₀H₂₈O₆N: C, 67.21; H, 6.49; N, 3.92. Found: C, 67.22; H, 6.43; N, 3.95.

(c) **N-Methylbenzamide.**¹¹—Demecolceine (100 mg.) was heated at 170° with concentrated hydrochloric acid (3 ml.) in a sealed tube for 12 hr. The contents of the tube were filtered and the filtrate evaporated to dryness. The residue was made alkaline with aqueous sodium hydroxide and the solution distilled into dilute hydrochloric acid. This acid solution was evaporated to small bulk and treated with a mixture of benzoyl chloride and sodium hydroxide to yield N-methylbenzamide which was extracted with ether. The dried ether extract was evaporated and the residue crystallized from ether-petroleum ether to yield colorless needles (16 mg.), m.p. 78–79°, not depressed on admixture with an authentic specimen of N-methylbenzamide.

Chromatography of the Alkaloids.—Pure benzene was an excellent solvent for the separation of the *Colchicum* alkaloids, producing discrete spots which were detected by their fluorescence in ultraviolet light. *R_f* values obtained with this solvent on Whatman No. 4 paper were: colchicine 0.58, colchicine 0.67, demecolceine 0.84 and demecolceine 0.92.

(11) F. Šantavý, R. Winkler and T. Reichstein, *ibid.*, **36**, 1319 (1953).

COMMUNICATIONS TO THE EDITOR

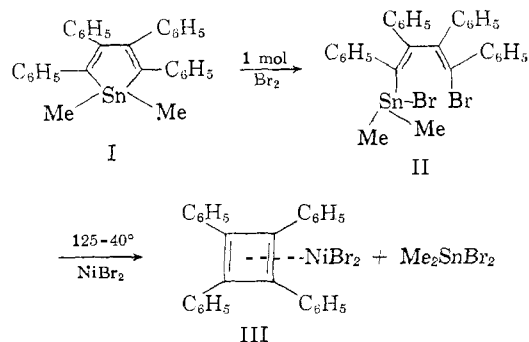
TETRAPHENYLCYCLOBUTADIENE DERIVATIVES. I. TETRAPHENYLCYCLOBUTADIENE NICKEL BROMIDE COMPLEX

Sir:

The preparation of authentic derivatives of cyclobutadiene has been and continues to be the object of many investigations.¹ The suggestion that this highly strained molecule may be stabilized by combination with a transition metal² has culminated in the recent preparation of tetramethylcyclobutadiene nickel chloride complex,³ tetraphenylcyclobutadiene iron tricarbonyl complex,⁴ and the silver nitrate complex of unsubstituted cyclobutadiene itself.⁵ We now wish to report a novel method for the preparation in high yield of tetraphenylcyclobutadiene nickel bromide complex (III) and some preliminary findings on some of its reactions.

The treatment of 1,1-dimethyl-2,3,4,5-tetraphenylstannole⁶ with one mole of bromine in the cold leads to the cleavage of one of the ring carbon-tin bonds and the quantitative production of (4-bromo-1,2,3,4-tetraphenyl-*cis,cis*-1,3-butadienyl)-dimethyltin bromide (II); m.p. 142–143° (Found: C, 54.32; H, 4.13; Sn, 17.56; Br, 24.19). Proof of structure of II is provided by its further reaction with an additional mole of bromine to

give, in 80% yield, *cis,cis*-1,4-dibromo-1,2,3,4-tetraphenylbutadiene, obtained in two crystalline modifications, m.p. 147–148° or 151–152° (Found: C, 65.2; H, 3.5; Br, 31.0). Heating a suspension of one mole of anhydrous nickel bromide in a triglyme solution of II under nitrogen at $130 \pm 10^\circ$ for one hour, furnishes an 80% yield⁷ of 1,2,3,4-tetraphenylcyclobutadiene nickel bromide complex (III), as thin, shiny, blue-black plates. Its n.m.r. spectrum in dimethyl sulfoxide shows only phenyl hydrogen and its analysis, after recrystallization from bromobenzene, is correct for C₂₈H₂₀NiBr₂ (Found: C, 58.4; H, 3.6; Br, 27.9; Ni, 10.0).



The complex III is thermally stable to approximately 300° at which temperature it decomposes to nickel bromide and as yet unidentified hydrocarbon products. It is stable to air oxidation, but is readily oxidized by sodium nitrite in aqueous dimethylformamide, yielding nickel hydroxide and

(7) By modifications of the method given in ref. 6 we have been able to prepare the stannole I in yields of better than 80%; the overall yield of the complex III from diphenylacetylene is, therefore, 65%.

(1) For a review of the literature through 1958 see: W. Baker and J. F. W. McOmie in "Non-Benzenoid Aromatic Compounds" (Ed. D. Ginsburg), Interscience Publishers, Inc., New York, N. Y., 1959, pp. 43–105.

(2) H. C. Longuet-Higgins and L. E. Orgel, *J. Chem. Soc.*, 1959 (1956).

(3) R. Criegee and G. Schröder, *Ann.*, **623**, 1 (1959).

(4) W. Hubel, *et al.*, *J. Inorg. Nucl. Chem.*, **9**, 204 (1959).

(5) M. E. Avram, E. Marica and C. D. Nenitzescu, *Ber.*, **92**, 1088 (1959).

(6) F. C. Leavitt, T. A. Manuel, F. Johnson, L. U. Matternas and D. S. Lehman, *J. Am. Chem. Soc.*, **82**, 5099 (1960).

tetraphenylfuran.⁸ Aqueous sodium nitrite oxidation of tetramethylcyclobutadiene nickel chloride complex to *cis*-dihydroxytetramethylcyclobutene was utilized by Criegee³ 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 (PtO₂, 800 lb. H₂, 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 C₂₈H₂₂ 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

(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°.

involved in the formation of III, is given in a separate communication.

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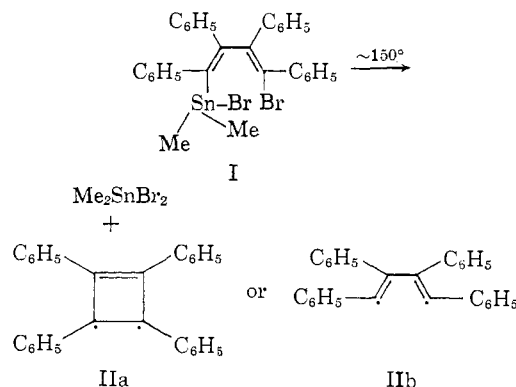
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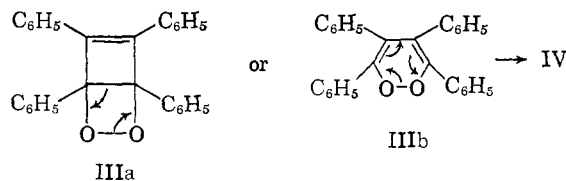
TETRAPHENYLCYCLOBUTADIENE DERIVATIVES. II.¹ CHEMICAL EVIDENCE FOR THE TRIPLET STATE Sir:

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 I¹ at approximately 150°, exhibits properties consistent with either structure IIa, the predicted² triplet ground state of tetraphenylcyclobutadiene, or, less likely, its open chain equivalent, 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*-dibenzoylstilbene³ (IV) via the indicated electron redistribution of the postulated intermediate peroxide, IIIa or b.



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

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

(2) (a) J. D. Roberts, A. Streitwieser, 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.