The proton n.m.r. spectrum of this material in deuteriochloroform showed only a complex resonance due to aromatic protons. The fluorine n.m.r. spectrum had a single unresolved line at 165 p.p.m. from trichlorofluoromethane. The ultraviolet spectrum had λ_{max} 293 mμ, ϵ_{max} 30,000; λ_{max} 242 mμ, ϵ_{max} 53,000; λ_{max} 235 mμ, ϵ_{max} 50,000. The resemblance between the ultraviolet spectra of this material and I, *cis*-stilbene[7] and *cis*-4-chlorostilbene[21] strongly suggests that I and the *p*-chlorophenyl-substituted dimer are structurally related.

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[21] (a) J. F. Codington and E. Mosettig, *J. Org. Chem.*, **17**, 1035 (1952); (b) H. O. House, *J. Am. Chem. Soc.*, **77**, 3070 (1955).

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF YALE UNIVERSITY, NEW HAVEN, CONN., HAVERFORD COLLEGE, HAVERFORD, PA., AND THE JOHNS HOPKINS UNIVERSITY, BALTIMORE, MD.]

Dimers of 1,3-Diphenylcyclobutadiene from the Hofmann Elimination of 1,3-Diphenyl-2,4-bis-(dimethylamino)-cyclobutane Dimethiodide[1]

BY EMIL H. WHITE AND HARMON C. DUNATHAN

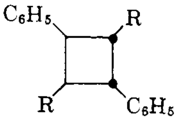
RECEIVED JULY 12, 1963

The reaction of 1,3-diphenyl-2,4-bis-(dimethylamino)-cyclobutane dimethiodide (V) with bases has been examined as part of a study of the chemistry of diphenylcyclobutadiene. The reaction with weak bases yields a cyclobutene derivative, 1,3-diphenyl-4-dimethylaminocyclobutene methiodide (VIa). The reaction with a strong base such as diethylamide ion yields, among other products, two tricyclooctadienes (X and XI), considered to be dimers of 1,3-diphenylcyclobutadiene. The latter compounds (X and XI) undergo an isomerization at room temperature to form 1,3,5,7-tetraphenylcyclooctatetraene (VIII) and 1,2,4,7-tetraphenylcyclooctatetraene (IX), respectively.

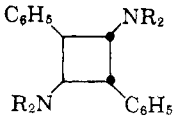
A renewal of interest in the chemistry of cyclobutadiene has occurred in recent years, presumably as one facet of the current interest in cyclic conjugated hydrocarbons. Only a few papers concerning cyclobutadiene appeared in the literature from 1905, the date of Willstätter's pioneering work on the subject,[2] to 1940. The synthesis of dibenzocyclobutadiene[3] in 1941 refocused attention on this problem and led to the current intensive study of the cyclobutadienes.[4]

Although dibenzocyclobutadiene and its homologs are the only cyclobutadiene compounds that have been isolated to date, there is considerable evidence that simple nonring-fused cyclobutadienes may exist as transient reaction intermediates. This evidence includes the isolation of cyclobutadiene dimers,[1,5] butadienes,[6] Diels–Alder adducts[7] and metal complexes[8] of the cyclobutadienes, and the isolation of certain other reaction products.[9] In this paper we present evidence, chiefly of the first kind, for the existence of diphenylcyclobutadiene as a reaction intermediate.

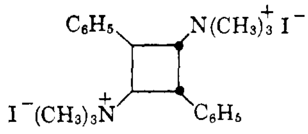
The reaction examined was the Hofmann elimination of 1,3-diphenyl-2,4-bis-(dimethylamino)-cyclobutane dimethiodide (V), a compound readily prepared from cinnamic acid.[10] At the time, it was hoped that the phenyl groups might confer a certain degree of stability on the cyclobutadiene and also increase the rate of the elimination reaction. The stereochemistry of the diamine was such that both *trans* and *cis* elimination could be effected, and therefore, advantage could be taken of both the Hofmann elimination and the amine oxide pyrolysis reactions. It was hoped, furthermore, that the 1,3-arrangement of functional groups would avoid the formation of stable vinyl ammonium salts, a difficulty encountered with 1,2-disubstituted cyclobutanes.[11]



I, R = CO_2H
II, R = NCO



III, R = H
IV, R = CH_3



V

The conversion of α-truxillic acid (I) into 1,3-diphenyl-2,4-diaminocyclobutane (III) by the Curtius reaction has been described in an earlier paper.[10] Methylation of this amine by the Eschweiller–Clark method[12] yielded 1,3-diphenyl-2,4-bis-(dimethylamino)-cyclobutane (IV)[13]; the stereochemistry assigned (IV) follows from the method of synthesis[10] and the n.m.r. spectrum, which showed a typical A_2B_2 multiplet. It was found, subsequently, that the hydrolysis step II → III could be by-passed, and that good yields of the tetramethyldiamine IV could be obtained through treatment of the diisocyanate II directly with formaldehyde and formic acid.[14] Quaternization of the

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[1] Presented, in part, before the Division of Organic Chemistry at the 134th National Meeting of the American Chemical Society, Chicago, Ill., September, 1958 (p. 41P of the abstracts). Taken in part from a thesis submitted by Harmon C. Dunathan to the faculty of the Graduate School of Yale University in partial fulfillment of the requirements for the Ph.D. degree.

[2] R. Willstätter and W. von Schmaedel, *Ber.*, **38**, 1992 (1905).

[3] W. C. Lothrop, *J. Am. Chem. Soc.*, **63**, 1187 (1941).

[4] For reviews of the cyclobutadiene literature, see W. Baker and J. F. W. McOmie, "Non-Benzenoid Aromatic Compounds," D. Ginsberg, Ed., Interscience Publishers, Inc., New York, N. Y., 1959, Chapter II; E. Vogel, *Angew. Chem.*, **72**, 4 (1960); and R. Criegee, *ibid.*, **74**, 703 (1962).

[5] (a) R. Criegee and G. Louis, *Ber.*, **90**, 417 (1957); (b) M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, **79**, 1701 (1957); M. P. Cava and J. F. Stucker, *ibid.*, **79**, 1706 (1957); (c) M. Avram, D. Dinu, G. Mateescu, and C. D. Nenitzescu, *Ber.*, **93**, 1789 (1960); (d) R. Criegee, G. Schröder, G. Maier, and H. G. Fischer, *ibid.*, **93**, 1553 (1960); (e) G. Wittig and U. Mayer, *ibid.*, **96**, 342 (1963).

[6] (a) M. Avram, C. D. Nenitzescu, and E. Marica, *ibid.*, **90**, 1857 (1957); (b) R. Criegee and G. Schröder, *Ann.*, **623**, 1 (1959).

[7] C. D. Nenitzescu, M. Avram, and D. Dinu, *Ber.*, **90**, 2541 (1957); C. E. Berkoff, R. C. Cookson, J. Hudec, and R. O. Williams, *Proc. Chem. Soc.*, 312 (1961); R. C. Cookson and D. W. Jones, *ibid.*, 115 (1963).

[8] (a) R. Criegee and G. Schröder, *Angew. Chem.*, **71**, 70 (1959); (b) A. T. Blomquist and P. M. Maitlis, *J. Am. Chem. Soc.*, **84**, 2329 (1962); (c) M. Avram, E. Marica, and C. D. Nenitzescu, *Ber.*, **92**, 1088 (1959).

[9] (a) H. H. Freedman, *J. Am. Chem. Soc.*, **83**, 2195 (1961); (b) C. M. Sharts and J. D. Roberts, *ibid.*, **83**, 871 (1961).

[10] E. H. White and H. C. Dunathan, *ibid.*, **78**, 6055 (1956).

[11] E. R. Buchman, A. O. Reims, T. Skei, and M. J. Schlatter, *ibid.*, **64**, 2696 (1942); see also p. 2701.

[12] M. L. Moore, "Organic Reactions," Coll. Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 307.

[13] The bis-oxide of this compound was prepared and pyrolyzed; a complex mixture was obtained from which no pure olefinic material could be isolated. A possible side reaction in this case would be a rearrangement of the monoeliminated material to the corresponding O-alkylhydroxylamine [A. C. Cope, T. T. Foster, and P. H. Towle, *J. Am. Chem. Soc.*, **71**, 3929 (1949)].

[14] Less efficient synthetic sequences involved reduction of II to the dimethyldiamine followed by the Eschweiller–Clark methylation to IV, on the one hand, and formation of the benzyl alcohol derivative of II followed by catalytic hydrogenation to give the diamine III, on the other.

TABLE I

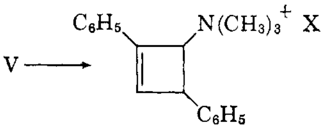
PHYSICAL PROPERTIES OF CYCLOOCTATETRAENES VIII AND IX AND TRICYCLOOCTADIENES X AND XI

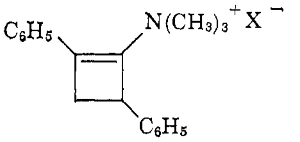
Compound	Ultraviolet spectra, λ_{max}, mμ (log ε)	Infrared spectra,[a] μ	N.m.r. Spectra	
			τ[b]	Weighting
VIII	261 (4.73)[c]	6.15 (weak)	2.63	5
IX		11.60	3.30 s	1
	263 (4.66)[d]	6.15 (weak)	2.67	10
	325 (3.81)	7.46	3.12 s	1
		9.85	3.39 s	1
		11.35		
X	262 (4.46)[e]	12.10	2.58	5
		13.00	2.68	5
		13.85	3.57 d (J = 2.5 c.p.s.)	1
			6.13 d (J = 2.5 c.p.s.)	1
XI	261 (4.20)[e]	7.60	2.58	5
		8.35	2.74 s	5
			3.30 d (J = 2.5 c.p.s.)	1
			6.20 d (J = 2.5 c.p.s.)	1

[a] KBr spectra; the bands listed are those absent in the spectra of the isomeric forms. [b] s = singlet, d = doublet; the unlabeled entries are center positions of broad multiplets. [c] In 95% ethanol. [d] In heptane. [e] In ether.

tetramethyldiamine IV with methyl iodide in methanol then gave the dimethiodide V[15] in high yield.

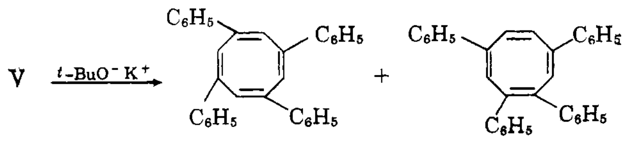
The Hofmann Elimination of Dimethiodide V.—Treatment of dimethiodide V with silver oxide in aqueous ethanol led to the rapid elimination of one mole of trimethylamine and the development of a maximum in the ultraviolet spectrum at 242 mμ. Neutralization of the resulting monohydroxide with hydrochloric acid yielded compound VIb which was assigned the structure 1,3-diphenyl-4-dimethylaminocyclobutene methochloride on the basis of the method of preparation, the elementary analysis, the ultraviolet absorption at 242 mμ, and the n.m.r. spectrum, which showed, in particular, a broad singlet at 3.49 τ (1 vinyl hydrogen) and a set of doublets at 3.77 and 5.34 τ (J = 5 c.p.s.; 2 cyclobutenyl hydrogens). Pips in the spectrum indicated that a small amount of the isomeric species VII might have been present. In comparison to VIb, 1-phenylcyclobutene has an ultraviolet maximum at 255 mμ[16a] and an n.m.r. spectrum with a triplet at 3.80 τ for the vinyl hydrogen (J = 1.25 c.p.s.).[16b] In our case, the splitting of the vinyl hydrogen peak was not resolved.


VIa, X = I⁻
b, X = Cl⁻
c, X = OH⁻


VII

In our efforts to carry out the Hofmann elimination of dimethiodide V, the solution obtained from the silver oxide treatment of V was filtered free of silver salts and freeze dried. The resulting oil was pyrolyzed under high vacuum in a sublimator to yield a volatile oil which contained a number of compounds containing carbonyl groups; these compounds came, presumably, from various substitution and ring opening reactions involving hydroxide ion.[11] No pure compounds could be separated, and this approach was abandoned.

In an effort to suppress the side reactions and encourage the elimination reaction, V was treated with the much stronger base, but sterically hindered nucleophile, potassium *t*-butoxide. When dimethiodide V and potassium *t*-butoxide were refluxed in *t*-butyl alcohol, two major products and at least four minor products were formed. The two major products, a white crystalline solid, m.p. 189°, and a yellow crystalline solid, m.p. 133°, were assigned structures VIII (1,3,5,7-tetraphenylcyclooctatetraene) and IX (1,2,4,7-tetraphenylcyclooctatetraene), respectively; current work is directed toward the identification of the minor products.[17] The yields of these compounds are strongly affected by the concentrations of the reactants and by traces of water and oxygen; the highest yields that we obtained for cyclooctatetraenes VIII and IX were 34 and 24%, respectively.


VIII IX

The proof of structure of VIII and IX rests on the elemental analysis, the molecular weight determination, the absorption of four moles of hydrogen on catalytic hydrogenation, and the physical data listed in Table I. The infrared spectra of both VIII and IX showed a weak band at 6.15 mμ attributed to the carbon–carbon double bond stretching frequency of the cyclooctatetraene ring. The intense ultraviolet absorptions near 260 mμ compare with those reported by Cope and Moore for 1,3- and 1,2-diphenylcyclooctatetraene (λ_{max} 250 mμ (log ε 4.4)[18a] and λ_{max} 260 mμ (log ε 4.4), respectively).[18b] The yellow color of cyclooctatetraene IX is presumably due to the long wave length tail of the weak absorption at 325 mμ (which is missing in compound VIII). In this connection, Cope and Moore report that 1,3-diphenylcyclooctatetraene is colorless whereas the 1,2-isomer is yellow in color.[18c] In the n.m.r. of cyclooctatetraene IX (Table I), one vinyl resonance (τ 3.12) is assigned to the equivalent ring hydrogens at C_3 and C_8 and the other (τ 3.39) to the equivalent hydrogens at C_5 and C_6. Since the hydrogens of these pairs are equivalent in both double bond isomers of IX (IXa and IXb), the n.m.r. offers no basis for a choice between them; n.m.r. spectra taken over a range of temperatures from −40 to 95° were practically identical, showing either that the cyclo-

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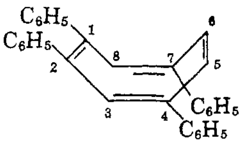
(15) Attempts to form the monomethiodide of IV with 1 mole of methyl iodide were unsuccessful; starting material and compound V were obtained.

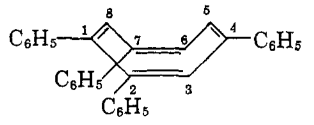
(16) (a) J. W. Wilt and D. D. Roberts, *J. Org. Chem.*, **27**, 3430 (1962); (b) private communication from Professor P. Schleyer.

(17) $C_{20}H_{22}O$, $C_{36}H_{34}O$, and $C_{48}H_{35}$ (unpublished work, R. L. Stern). A $(C_6H_{12})_n$ compound was also isolated by one of the authors (H. C. D.) from a run containing dimethylbutadiene.

(18) (a) Private communication from Professor A. C. Cope; (b) A. C. Cope and D. S. Smith, *J. Am. Chem. Soc.*, **74**, 5136 (1952); (c) A. C. Cope and W. R. Moore, *ibid.*, **77**, 4939 (1955).



IXa



IXb

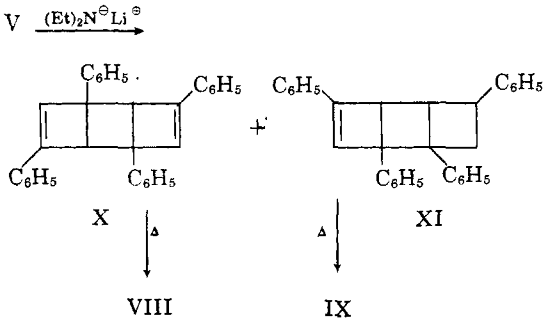
octatetraene is a single species or that the rate of interconversion is still high at −40°.[19]

Further evidence for the arrangement of the phenyl groups in cyclooctatetraene IX comes from photochemical studies which show that *p*-terphenyl and diphenylacetylene are the principal products of the irradiation of IX in solution.[20]

Both VIII and IX react with one mole of perbenzoic acid, following the behavior of cyclooctatetraene itself.[21] Ozonolysis of VIII or IX on a small scale yielded benzoic acid as the only identifiable product and attempts to form Diels–Alder adducts of VIII and IX with maleic anhydride and other dienophiles were unsuccessful.

It was assumed that the monoeliminated salt VI was an intermediate in the production of the dimers VIII and IX, and in fact both dimers were isolated from a reaction in which VIa was treated with potassium *t*-butoxide.

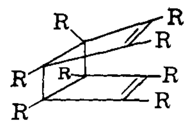
Preparation of the Tetraphenyltricyclo$[4.2.0.0^{2,5}]$octadienes (X and XI).—Reaction of dimethiodide V with lithium diethylamide in ether at room temperature yielded two new hydrocarbons, X and XI. The new compounds proved to be rather unstable; at room temperature, they underwent an isomerization to yield the same cyclooctatetraenes VIII and IX that had been isolated earlier from the butoxide runs. The half-life for this isomerization in solution at 25° is about 12 hr. for compound X and somewhat longer for compound XI. The rates are much lower in the solid state.



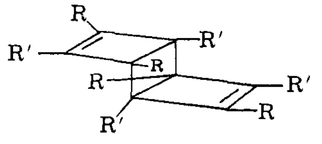
The structures shown were assigned to compounds X and XI on the basis of the analytical data, the physical data of Table I, and the ready conversion of each to the corresponding cyclooctatetraene. The ultraviolet spectra of X and XI show maxima between 260 and 265 mμ with intensities appropriate to two styrene chromophores. This is a definite shift from the 255 mμ maximum observed for 1-phenylcyclobutene[16] and one concludes that there is some interaction between the double bonds and the central cyclobutane ring in X and XI; similar interactions have been commented on by Wren.[22] The n.m.r. spectrum of X and also that of XI consists of two aromatic proton multiplets and two doublets (Table I). The narrower, high-field aromatic multiplet is assigned to the two bridgehead phenyl groups and the broader low-field multiplet is assigned to the phenyl groups attached to the double bonds. The higher-field doublet at 6.1–6.2 τ is assigned in both compounds to the tertiary, bridgehead hydrogen[23] and the remaining doublet at 3.3–3.6 τ to the vinyl hydrogens. The coupling constant of 2.5 c.p.s. is of the magnitude expected for such systems.[24]

The conversion of the tricyclooctadienes to the cyclooctatetraenes may be thought of as two simultaneous or successive cyclobutene–butadiene isomerizations. This particular reaction of cyclobutenes is well known.[25] Although a high temperature is usually required for the isomerization, in this system the relief of strain and the participation of the phenyl substituents in stabilizing the transition state leading to the products may account for the room temperature isomerization. Several other examples of the conversion of compounds of this type to the corresponding cyclooctatetraenes have been reported recently.[5c,6b]

Some of the known tricyclo$[4.2.0.0^{2,5}]$octadienes have been assigned a definite stereochemistry. The tricyclooctadiene XII obtained by Criegee on treating 1,2,3,4-tetramethyl-3,4-dichlorocyclobutene with lithium amalgam was shown by oxidative degradation to have the *syn* arrangement of groups on the central cyclobutane ring, whereas the isomeric dimer XIII obtained by decomposition of the nickel chloride–tetramethylcyclobutadiene complex was assigned the *anti* configuration.[5d] Recently, a dimer of triphenylfluorocyclobutadiene was shown to be 1,2-difluoro-3,4,5,6,7,8-hexaphenyltricyclo$[4.2.0.0^{2,5}]$octadiene with an *anti* arrangement of groups about the central ring.[26] We have no direct evidence for the stereochemistry of our dimers, but we suggest that it is *anti* (XIV).[27] Our reaction conditions were more similar to those employed in the formation of the two *anti* dimers cited above than in the formation of the *syn* dimer. It is possible that the *syn* dimer may have come from the dimerization of a mercury complex of tetramethylcyclobutadiene.[8c] In the dimerization of benzocyclobutadiene, it has been shown that metals can profoundly influence the course of the dimerization.[28]



XII, $R = CH_3$



XIII, $R = R' = CH_3$

XIV, $R = H$; $R' = C_6H_5$ (*Isomer*-X)

In addition to the dimeric species, we have isolated 1,3,5-triphenylbenzene[29] and a $C_{16}H_{14}$ compound from the Hofmann elimination of dimethiodide V with diethylamide ion in furan. The C_{16} compound, with an absorption maximum at 314 mμ, is probably *trans*-1,3-

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(19) F. A. L. Anet, *J. Am. Chem. Soc.*, **84**, 671 (1962).

(20) E. H. White and R. L. Stern, Abstracts, 141st National Meeting of the American Chemical Society, Washington, D. C., March, 1962, p. 7D.

(21) A. C. Cope and B. D. Tiffany, *J. Am. Chem. Soc.*, **73**, 4158 (1951).

(22) J. J. Wren, *J. Chem. Soc.*, 2208 (1956).

(23) Bands at 6.46 and 6.93 τ have been assigned to similar protons in two benzocyclobutene derivatives (H. E. Simmons, *J. Am. Chem. Soc.*, **83**, 1657 (1961)).

(24) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959.

(25) E. Vogel, *Ann.*, **615**, 14 (1958); see also W. G. Dauben and G. J. Fonken, *J. Am. Chem. Soc.*, **81**, 4060 (1959), and M. P. Cava and R. Pohlke, *J. Org. Chem.*, **28**, 1012 (1963).

(26) E. W. Hughes and C. J. Fritchie, to be published. We thank Professor J. D. Roberts for bringing this information to our attention.

(27) We have irradiated the tricyclooctadienes X and XI (and also the corresponding cyclooctatetraenes) at temperatures ranging down to −180° and have followed the irradiation at these temperatures in the hope of forming and detecting various photoisomers, in particular tetraphenylcubane (octaphenylcubane has been reported by H. H. Freedman and D. R. Peterson, *J. Am. Chem. Soc.*, **84**, 2837 (1962); see, however, R. C. Cookson and D. W. Jones, *Proc. Chem. Soc.*, 115 (1963)). The compounds are quite stable in the *solid state*,[20] however, and no new isomers were found.

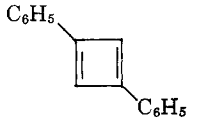
(28) Reference 5c; see, however, C. D. Nenitzescu, *et al.*, *Tetrahedron*, **19**, 187 (1963).

(29) Unpublished work of Dr. Jack Rosenbaum. The triphenylbenzene has also been isolated from a run in piperidine as the solvent.

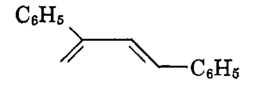
diphenylbutadiene. *cis*-1,3-Diphenylbutadiene has been synthesized by Jacobs[30] but the *trans* isomer has not been reported.[31] The best ultraviolet model that we have found is 1,3-diphenyl-1,3-cyclohexadiene, which has absorption maxima at 255 and 311 mμ.[32] Butadienes have been isolated from other reactions in which cyclobutadienes were probable intermediates[6] and their formation may be among the best of the criteria used for deciding whether or not a reaction proceeds *via* a cyclobutadiene intermediate.

In attempts to provide further proof for the transient existence of 1,3-diphenylcyclobutadiene, we have carried out the Hofmann elimination of dimethiodide V in the presence of reagents such as furan, 2,3-dimethyl-1,3-butadiene, diphenylacetylene, and 1,3-diphenylisobenzofuran[33]; these compounds might have been expected to form adducts with the cyclobutadiene.[7] To date, however, we have not been able to isolate an adduct. It is interesting to note that in a related case (a reaction in which a dimer of triphenylfluorocyclobutadiene was formed)[34] attempts to isolate an adduct have also been unsuccessful.[35] Possibly these phenyl substituted cyclobutadienes are relatively stable and thus selective in their reactions.

The most direct interpretation of our results for the Hofmann elimination of dimethiodide V involves 1,3-diphenylcyclobutadiene (XV) as a reaction intermediate. The 1,2–2′,1′ dimerization of this species would yield tricyclooctadiene X and the 1,2–1′,2′-dimerization would yield tricyclooctadiene XI. In the reactions at higher temperatures (*e.g.*, in refluxing butanol), the isomerization of these compounds would yield the corresponding cyclooctatetraenes. The formation of 1,3-diphenylbutadiene could be accounted for by a cleavage of the cyclobutadienyl ring to form the butadienyl diradical XVI, followed by the abstraction of hydrogen from the solvent by this intermediate.[6,9a] It should be pointed out, however, that on the basis of the data available to date, we cannot rule out a mechanism for the reaction in which the dimers are formed by a series of displacement reactions involving two moles of the cyclobutene derivative VI. This type of reaction (involving metalloorganic intermediates in certain cases) may well be involved, furthermore, in the formation of the other dimers and adducts of the cyclobutadienes reported in the literature.[5,7]



XV



XVI

Experimental[36]

1,3-Diphenyl-2,4-bis-(dimethylamino)-cyclobutane (IV). (A) From 1,3-Diphenyl-2,4-diaminocyclobutane (III).—1,3-Diphenyl-2,4-diaminocyclobutane[10,37] (2.03 g., 8.53 mmoles) was heated with 5 ml. of 37% formalin and 50 ml. of 90% formic acid on a steam bath for 12 hr.; the solution was then neutralized and extracted with petroleum ether. The petroleum ether solution was dried and the solvent was removed to yield 2.20 g. of crude product (88%), which after sublimation at 115–120° and 1 mm. and recrystallization from methanol–water gave 1.65 g. (66%) of compound IV in the form of white crystals, m.p. 120–122°.

Anal. Calcd. for $C_{20}H_{26}N_2$: C, 81.58; H, 8.90; N, 9.52; mol. wt., 294. Found: C, 81.76; H, 8.70; N, 10.09; mol. wt., 267, 302 (Rast micro method).

(B) From 1,3-Diphenyl-2,4-diisocyanatocyclobutane (II).—The total diisocyanate II from the Curtius rearrangement of 15.0 g. (45.0 mmoles) of truxillic acid chloride and sodium azide was dissolved in 200 ml. of formic acid, and 60 ml. of formalin solution was added. The solution was heated on the steam bath for 40 hr. and worked up by the procedure given in method A to yield 6.05 g. (20.6 mmoles, 46%) of the tetramethyldiamine IV.

Compound IV was recrystallized from hexane to give light feathery crystals, m.p. 121.7–122.2°. When the solution was allowed to evaporate very slowly, the compound was deposited in the form of large octahedra. The infrared spectrum contains an interesting absorption band at 3.62 μ, apparently characteristic of the dimethylamino group (β-phenylethyldimethylamine has a peak at the same position). The n.m.r. spectrum in $CDCl_3$ shows a complex aromatic signal centered at 2.5 τ (10 protons), a sharp singlet for the dimethylamino groups at 8.18 τ (12 protons), and a complex group of twelve peaks with a center of symmetry at 6.63 τ (4 protons)—an A_2B_2 pattern for the protons on the cyclobutane ring.

Attempted Amine Oxide Pyrolysis.—1,3-Diphenyl-2,4-bis-(dimethylamino)-cyclobutane (IV, 1.20 g., 4.08 mmoles) was dissolved in 20 ml. of glacial acetic acid and 2.5 ml. of 36% hydrogen peroxide was added. After 24 hr. at 25°, 30 mg. of palladium black was added to destroy the excess peroxide. The mixture was filtered and the solution was freeze dried. The residue was extracted with chloroform to yield 1.32 g. of an amorphous solid.

The picrate of this material was prepared in, and recrystallized from, ethanol; m.p. 188–189°.

Anal. Calcd. for $C_{32}H_{32}N_8O_{16}$: C, 48.98; H, 4.11. Found: C, 48.39; H, 3.95.

The amine oxide was pyrolyzed at 0.002 mm. pressure and at temperatures up to 130°. Only a few mg. of dimethylhydroxylamine was collected in the liquid nitrogen-cooled traps. The sublimate was dissolved in ether and the solution was treated with dilute hydrochloric acid. Evaporation of the ether yielded 0.3 g. of a complex oil which showed several carbonyl bands in the infrared. This pyrolysis reaction was not pursued further.

1,3-Diphenyl-2,4-bis-(dimethylamino)-cyclobutane Dimethiodide (V).—1,3-Diphenyl-2,4-bis-(dimethylamino)-cyclobutane (IV, 1.40 g., 4.76 mmoles) was dissolved in 150 ml. of methanol and 7.5 ml. (0.12 mole) of methyl iodide was added. The solution was allowed to stand at room temperature under nitrogen in the dark for 38 hr. On removing the methanol and methyl iodide, there remained 2.9 g. of a slightly yellow crystalline material, which on shaking with cold acetone yielded 2.13 g. (77%) of the salt in the form of white crystals, m.p. 215–216° (evacuated capillary), m.p. unchanged on recrystallization from aqueous methanol.

Anal. Calcd. for $C_{22}H_{32}N_2I_2$: C, 45.68; H, 5.58; N, 4.84; I, 43.89. Found: C, 45.65; H, 5.84; N, 5.04; I, 44.10.

Attempted Preparation of 1,3-Diphenyl-2,4-bis-(dimethylamino)-cyclobutane Monomethiodide.—A solution of methyl iodide (1.42 g., 0.01 mole) in 40 ml. of benzene was added to a solution of the tetramethyldiamine IV (2.94 g., 0.01 mole) in 60 ml. of benzene and the resulting solution was allowed to stand in the dark at 25°; an oily precipitate formed within 30 min. After 18 hr., the supernatant phase was decanted and the solvent was removed *in vacuo*. The crystalline residue was extracted with hot pentane and the extract was evaporated to give 1.93 g. (6.6 mmoles, 66%) of unreacted starting material (infrared identification). Treatment of the insoluble oil with base did not yield 1,3-diphenyl-4-(dimethylamino)-cyclobutene.

1,3-Diphenyl-4-dimethylaminocyclobutene Methochloride (VIb).—A sample of dimethiodide V (2.116 g., 3.66 mmoles) was dissolved in 100 ml. of an ethanol–water mixture (1:1) and the solution was stirred with thoroughly washed, moist silver oxide prepared from 3.6 g. (21 mmoles) of silver nitrate and excess base.

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(30) M. H. Goodrow and T. L. Jacobs, Abstracts, 133rd National Meeting of the American Chemical Society, San Francisco, Calif., April, 1958, p. 78 N.

(31) Attempts to prepare this compound have apparently led to dimeric substances: T. L. Jacobs and M. H. Goodrow, *J. Org. Chem.*, **23**, 1653 (1958); W. Herz and E. Lewis, *ibid.*, **23**, 1646 (1958).

(32) Private communication from Professor G. F. Woods.

(33) Reaction of V with diethylamide ion in the presence of the diphenylisobenzofuran led to an interesting substitution and rearrangement of the isobenzofuran to 9-phenyl-10-diethylaminoanthracene. This reaction can be formulated as a nucleophilic addition followed by ring closure through an *o*-position of one phenyl group; the reaction seems to be a general one for strong bases.

(34) Y. Kitahara, M. C. Caserio, F. Scardiglia, and J. D. Roberts, *J. Am. Chem. Soc.*, **82**, 3109 (1960).

(35) Personal communication from Professor J. D. Roberts.

(36) Analyses were determined by the Galbraith Microanalytical Laboratories, Knoxville, Tenn. Melting points are uncalibrated. Infrared spectra were determined with a Perkin–Elmer Model 21 spectrometer, ultraviolet spectra with a Cary Model 11 spectrometer, and n.m.r. spectra with a Varian Associates A-60 spectrometer.

(37) This compound was also synthesized by a modification of the method reported in ref. 10. The bis-isocyanate II from 0.90 g. (2.68 mmoles) of truxillyl chloride was treated with benzyl alcohol in chloroform and the mixture was refluxed for several hours. On evaporation, the crude benzyl carbamate (1.1 g.) was obtained. This was hydrogenated in 50 ml. of a mixture of ethyl acetate and acetic acid (3/1) over palladium-on-carbon at 30 lb. of pressure. The product was the diamine III (75%).

The solution was stirred under nitrogen in a flask equipped with a sintered glass filter disk. After 20 hr., the solution was filtered and the filtrate and washings were titrated to a phenolphthalein end point with standard HCl (4.10 mmoles required). Freeze drying of this solution yielded 1.13 g. of a clear, colorless glass which could not be obtained crystalline from chloroform, alcohol, etc. The glass was dissolved in 5 ml. of purified dimethylformamide and filtered from a small insoluble residue. The solution, evaporated to 3 ml. and cooled, yielded 0.30 g. of white crystals, m.p. 195–196.5°. The ultraviolet spectrum showed λ_{max} 243 mμ (log ϵ 4.21) in close agreement with the absorption developed by basic solutions of V. The n.m.r. spectrum contained a broad band at 2.74 τ (phenyl hydrogens), a broad band at 3.49 τ (vinyl hydrogen), a doublet centered at 3.77 τ (ring hydrogen, J = 4.5 c.p.s.), a doublet centered at 5.34 τ (ring benzylic hydrogen, J = 4.5 c.p.s.), and a sharp singlet at 6.80 τ (N-methyl groups). These peaks were present in a weight ratio of approximately 10:1:1:1:9. The presence of small peaks at 6.55 and 7.12 τ suggests that small amounts of other compounds, including VII, possibly, were present.

This material was recrystallized in the following way. Ether was added to a solution in dimethylformamide until a distinct turbidity was observed. Within a few seconds, a small amount of flocculent material separated and this was removed by filtration. After a few minutes, heavy needles of compound VIb crystallized out of the reaction mixture. These were dried at room temperature under high vacuum to yield *ca.* 0.2 g. of compound VIb, m.p. 195.5–196.5° dec., λ_{max} 243 mμ (log ϵ 4.23).

Anal. Calcd. for $C_{19}H_{22}NCl$: C, 76.11; H, 7.40; N, 4.67; Cl, 11.82. Found: C, 76.22; H, 7.60; N, 4.32; Cl, 11.59.

Recrystallization of compound VIb from a mixture of chloroform and ether yielded a stable complex of the compound and chloroform; m.p. 195–195.5° dec. The infrared spectrum of the complex contain bands at 7.98, 12.9, and 13.45 μ which can be attributed to chloroform.

Anal. Calcd. for $C_{19}H_{22}NCl\cdot CHCl_3$: C, 57.30; H, 5.53; N, 3.34. Found: C, 58.18; H, 5.64; N, 4.00.

This sample was heated to 90° at 0.02 mm. for 4 hr. to yield brownish crystals analyzing for 59.45% C and 6.12% H. Recrystallization from dimethylformamide–ether then yielded chloroform-free material.

The Reaction of Dimethiodide V with Aqueous Base. (A) With Hydroxide.—Dimethiodide V (36 mg., 0.062 mmole) was dissolved in 10 ml. of methanol–water (8:1) and treated with an excess of freshly prepared silver oxide. After the mixture was stirred for 30 min., the reaction was essentially over; the ultraviolet spectrum showed λ_{max} 242 mμ (log ϵ 4.25). After 15 hr.; the spectrum showed λ_{max} 242 mμ (log ϵ 4.27).

(B) **With Ammonia as the Base.**—Dimethiodide V (0.100 g., 0.173 mmole) was dissolved in 15 ml. of ethanol–water (1:2) and 1.7 mmoles of ammonia was added. Several ultraviolet spectra were taken of this solution as it stood at room temperature. A peak developed after 24 hr. at room temperature, λ_{max} 242 mμ (log ϵ 4.08). After an additional 2 hr. at 69°, λ_{max} was 242 mμ (log ϵ 4.29). The solution was then reduced to dryness and attempts were made to crystallize the clear yellow oil which remained (mixed with crystalline ammonium iodide). The oil, however, failed to crystallize.

Due to the presence of iodide ion, λ_{max} 226 mμ, log ϵ 4.1, the peak at 242 mμ was not sharp but appeared as a pronounced shoulder on the iodide peak. Because of this, the log ϵ values obtained are not strictly accurate.

(C) **With Acetate Ion as the Base.**—Dimethiodide V (50 mg., 0.087 mmole) was dissolved in methanol–water and treated with an excess of silver acetate. A series of spectra was taken over a period of several days, which showed the slow development of a peak at 242 mμ. Pyrolysis of the diacetate obtained by short exposure of the dimethiodide to silver acetate yielded only 15% trimethylamine and a small amount of a complex oil.

(D) **Recovery of Trimethylamine.**—Dimethiodide V (0.282 g., 0.488 mmole) was dissolved in 2 ml. of ethanol and 17.3 ml. of 0.028 *N* sodium hydroxide (0.484 mmole) was added. Nitrogen (oxygen-free) was passed through the solution using a medium-porosity "candle." After 6.5 hr. at room temperature, 0.44 mmole (91%) of trimethylamine had been trapped by passing the nitrogen through a standard acid solution *via* a similar sintered-glass candle.

The Hofmann Elimination of Dimethiodide V.—A solution of dimethiodide V (0.375 g., 0.65 mmole) in 20 ml. of ethanol–water (1:1) under nitrogen was treated with silver oxide (prepared from 0.50 g., 2.96 mmoles, of silver nitrate and excess base and washed five times with distilled water). After 3 hr., the colorless solution was filtered and the solution was freeze dried in the bottom of a small sublimator to yield 0.190 g. of a yellow oil (calcd. for the cyclobutenyltrimethylammonium hydroxide (VIc), 0.183 g.). The oil was gradually heated to 165° at a pressure of 5 × 10^{-3} mm. Fractions were taken as the oil was heated; the sublimate in each case, however, contained a number of carbonyl-containing compounds and no pure material could be isolated.

The Hofmann Elimination of Dimethiodide V with Potassium *t*-Butoxide as the Base.—Potassium (0.78 g., 0.019 mole) was added to 90 ml. of *t*-butyl alcohol freshly distilled from sodium. The potassium was completely reacted after 4 hr. at room temperature. Dimethiodide V (5.19 g., 9.0 mmoles), which had been extracted with acetone, dried at 80–90° and 0.5 mm. for 1 hr., and finally powdered in a mortar, was added to the solution of potassium *t*-butoxide in a 3-necked flask equipped with stirrer and condenser and well protected from moisture. The solution was stirred rapidly and heated slowly to reflux. After 5 min. at reflux, the solution was blood-red in color. The color deepened for the next 30 min., then remained a very dark red. The solution was refluxed for a total of 5.75 hr.; it was then cooled and the *t*-butyl alcohol was removed at the water pump. The residue was extracted with 20 ml. of benzene and this solution was diluted to 500 ml. with petroleum ether, b.p. 60–70°. This solution was placed on a column of 320 g. of alumina (14 × 1.25 in.) packed in petroleum ether, and the material was eluted: Fraction 1, 1200 ml. of 4% benzene in petr. ether yielded 0.71 g. of eluent (white solid); 2, 500 ml. of 10% benzene in petr. ether yielded 0.00 g. of eluent; 3, 500 ml. of 25% benzene in petr. ether yielded 0.55 g. of eluent (yellow solid); 4, 300 ml. of 15% ether in petr. ether yielded 0.00 g. of eluent; 5, 300 ml. of 30% ether in petr. ether yielded 0.063 g. of eluent (yellow oil); 6, 450 ml. of 60% ether in petr. ether yielded 0.19 g. of eluent (yellow oil); 7, 300 ml. of 100% methanol in petr. ether yielded 0.23 g. of eluent (yellow oil).

Fraction 1 on recrystallization from ethanol (95%) yielded 0.63 g. (1.54 mmoles, 34%) of 1,3,5,7-tetraphenylcyclooctatetraene (VIII) in the form of white needles, m.p. 192–193° (see Table I for physical data).

Anal. Calcd. for $C_{32}H_{24}$: C, 94.08; H, 5.92; mol. wt., 408. Found: C, 94.02; H, 6.20; mol. wt., 402 (Signer–Barger method).

Fraction 3, on recrystallization from ethanol, yielded 0.44 g. (1.08 mmoles, 24%) of 1,2,4,7-tetraphenylcyclooctatetraene (IX) in the form of yellow needles, m.p. 133–134° (see Table I for physical data).

Anal. Calcd. for $C_{32}H_{24}$: C, 94.08; H, 5.92; mol. wt., 408. Found: C, 94.00; H, 5.90; mol. wt., 463 (Rast micro method).

The yields for this reaction were somewhat variable; in particular at lower concentrations of reactants, the yields fell markedly. Dimethiodide V (0.86 mmole) in 100 ml. of *t*-butyl alcohol yielded only 0.008 g. (5%) of cyclooctatetraene VIII and none of the cyclooctatetraene IX. In runs on a larger scale,[17] three compounds which analyzed for $C_{20}H_{22}O$, $C_{36}H_{34}O$, and $C_{48}H_{36}$ were obtained in addition to the two cyclooctatetraenes.

The reaction of dimethiodide V with potassium *t*-butoxide was also carried out in the presence of diphenylacetylene, anthracene, and 2,3-dimethylbutadiene. The principal products in each case were the two cyclooctatetraenes. In the butadiene reaction, though, a crystalline solid (m.p. 289°) was obtained in addition; this, however, did not contain the dimethylbutadiene moiety.

Anal. Calcd. for $(C_{16}H_{12})_n$: C, 94.08; H, 5.92. Found: C, 94.10, 93.96; H, 6.02, 5.91.

Both cyclooctatetraenes reacted slowly with perbenzoic acid in benzene at 5°. Cyclooctatetraene VIII reacted with 1.58 moles of perbenzoic acid in 16 days, whereas cyclooctatetraene IX reacted with 1.03 moles in 5 days (suitable blanks were run in each case).

The ozonolysis of cyclooctatetraene VIII on a small scale in ethyl acetate at −60° (followed by hydrogenation over Pd) yielded only benzoic acid and an oil from which no pure compound could be isolated. The results with cyclooctatetraene IX were essentially the same except that a small amount of a crystalline substance with a carbonyl band at 6.0 μ in the infrared was isolated.

Attempts to form adducts of cyclooctatetraene VIII with maleic anhydride, with acetylenedicarboxylic acid dimethyl ester, and with tetracyanoethylene were unsuccessful. In each case, starting material and a red oil were obtained.

Hydrogenation of 1,3,5,7-Tetraphenylcyclooctatetraene (VIII).—The cyclooctatetraene (5.19 mg., 0.013 mmole) was added to a mixture of 4 cc. of ethyl acetate and 40 mg. of prereduced platinum oxide in a microhydrogenation flask. After 6 hr., the hydrogenation was complete. The sample required 1.06 cc. of hydrogen at STP (0.047 mmole); this is a ratio of 3.72 moles of hydrogen per mole of hydrocarbon.

Hydrogenation of 1,2,4,7-Tetraphenylcyclooctatetraene (IX).—Cyclooctatetraene IX (12.4 mg., 0.0304 mmole) was added to an equilibrated system of 5 ml. of ethyl acetate, 0.2 ml. of acetic acid, and 80 mg. of platinum black in a microhydrogenation flask. After 50 min., a sharp break occurred in the hydrogenation rate. A total of 2.82 cc. of hydrogen at STP had been absorbed; this represents 4.14 moles of hydrogen per mole of hydrocarbon.

The Hofmann Elimination of Dimethiodide V with Lithium Diethylamide as the Base.—Diethylamine (6 ml.) was distilled from potassium into a dry 100-ml. flask swept with dry oxygen-free nitrogen. The dimethiodide V (4.75 g., 8.2 mmoles), dried 3 hr. at 85° and 0.01 mm., was added and the flask was evacuated at the oil pump while being cooled in a Dry Ice–acetone bath. Dry oxygen-free nitrogen was admitted and a solution of 32.5 mmoles of butyllithium in 50 ml. of ether was added quickly. The solution, now at 0°, turned a dark red color. Stirring at 0° under N_2 was continued for 22 hr., at which time the solution was black in color. Methanol (30 ml.) was added and the solution was reduced to dryness at 20° at the water pump. The residue was extracted with several portions of benzene totaling 300 ml. and the benzene solution was extracted with dilute HCl, then washed with water. The dried benzene solution, which contained 1.45 g. of a reddish oil, was evaporated onto 10 g. of alumina and this material was added to the top of a column of 100 g. of alumina in hexane. Elution was carried out with pentane containing increasing amounts of ether. The cyclooctadienes were eluted with mixtures containing 1.5 to 5% ether. The fractions were placed in the deep freeze at −20°, and after 1 day the supernatants were decanted from the white heavy needles of tricyclooctadiene X which had formed (290 mg.). The mother liquids were evaporated to dryness at 20° and the residues were dissolved in a minimum of chloroform. Ethanol (95%) was added and the solutions were cooled to give second crops of compound X. The total recovery of tricyclooctadiene X was 345 mg. (0.845 mmole, 20.6%), m.p. 183–185° (the melting points varied with the rate of heating).

Anal. Calcd. for $C_{32}H_{24}$: C, 94.08; H, 5.92. Found: C, 93.87; H, 5.98.

Concentration of the mother liquids then yielded (with more difficulty) tricyclooctadiene XI (140 mg., 0.343 mmole, 8.4%) in the form of white crystals, m.p. 124–128° dec.

Anal. Calcd. for $C_{32}H_{24}$: C, 94.08; H, 5.92. Found: C, 93.69; H, 5.89.

In addition, runs carried out in furan yielded up to 22% of tricyclooctadiene X. The reaction of potassium *t*-butoxide with dimethiodide V at room temperature also yielded the tricyclooctadienes, but the yields were lower.

The cyclooctadienes isomerized cleanly to the corresponding cyclooctatetraenes in both liquid and solid phases. Dispersed in KBr, the half-life at room temperature for the conversion of X to VIII was less than 1 week, whereas the half-life for XI → IX was about 10 weeks. The rates in solution were considerably faster; the half-life for the isomerization of X in methylene chloride at 25° was about 12 hr. These changes could be followed easily in the infrared. In addition, powder patterns of the four compounds proved to be quite different, and the rate could be followed by this method as well.

Attempts to react the tricyclooctadienes (X and XI) with phenyl azide at 25° were unsuccessful. In each case, the corresponding cyclooctatetraene was isolated.

The Reaction of Dimethiodide V with Lithium Diethylamide in Furan.—Butyllithium (15 ml. of an ether solution, 14 mmoles) was added to a solution of diethylamine (2.96 g., 40 mmoles, distilled from potassium) in 35 ml. of furan (distilled from potassium). The mixture was added to 0.7 g. (1.22 mmoles) of the dimethiodide V under nitrogen, and the mixture, which became very dark in color, was stirred at −5° for 1 day and then at 25° for 40 min. A mixture of D_2O and ether was added and the product was quickly worked up at 0° as outlined above to give 0.22 g. of a red oil plus some crystalline material. The total product was chromatographed on alumina. The 1% ether eluate yielded an oil which crystallized slowly in the refrigerator. It was sublimed at 50° and 0.01 mm. and recrystallized from 95% alcohol to give needles, m.p. 89–92°, which decomposed on standing at room temperature. The ultraviolet spectrum showed two maxima: 314 mμ (log ε 4.60) and 334 mμ (log ε 4.41).

Anal. Calcd. for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 93.40; H, 6.55.

The remaining fractions yielded only the tricyclooctadienes X (22% yield) and XI, although in one case, a 3% yield of 1,3,5-triphenylbenzene was isolated in addition.[29] The infrared spectrum of compound X was superimposable on that of an authentic sample; *i.e.*, the compound did not contain deuterium. No evidence was obtained for a furan adduct.

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Ring Inversion in Cycloheptatriene

BY F. A. L. ANET

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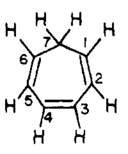
The n.m.r. spectrum of tropilidene is temperature dependent below about −120°. At −150°, the methylene protons give rise to two chemically shifted bands and thus the molecule is nonplanar. The activation energy for the inversion process is 6.3 kcal./mole.

Introduction

Although tropilidene is known[1] to have the 1,3,5-cycloheptatriene (I) rather than the norcaradiene structure, the planarity or nonplanarity of the seven-membered ring has been in dispute. A planar structure with appreciable aromatic character was suggested[2] as a result of theoretical speculations. Infrared and Raman spectral measurements[3] were interpreted on the basis of the planar structure, but these did not rule out completely the possibility of C-7 being slightly out of plane of the remaining carbon atoms. A recent X-ray determination[4] of the structure of the *p*-bromophenacyl ester of 7,7-dimethylcycloheptatriene-3-carboxylic acid showed that the seven-membered ring exists, in this compound at least, in a boat conformation, with C-7 and C-3–C-4 at distances of 0.63 and 0.48 Å., respectively, from the plane of C-1–C-2–C-5–C-6. The boat structure has also received support from the observation[5] of 1,5-transannular hydrogen shift in cycloheptatriene.



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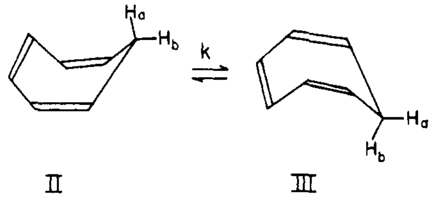

II III

The n.m.r. spectrum of tropilidene can be interpreted on the basis either of a planar structure or of a rapidly inverting nonplanar structure. In either case, the two methylene protons would appear equivalent, as is indeed observed.[1,6]

In a very recent paper, which appeared after completion of our own work, Conrow, *et al.*,[7] made the interesting observation that the 7,7-dimethyl groups of 2-*t*-butyl-3,7,7-trimethyltropilidene (Ia) were nonequivalent at low temperatures (*e.g.*, −100°). This

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(4) A. Tulinsky and R. F. Davis, *Tetrahedron Letters*, 839 (1962).

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