a stirred $0.05\ M$ hydrochloric acid solution. The cathode was a platinum wire. The finished electrode was stored in 50% aqueous ethanol saturated with potassium chloride and silver chloride.

The cell consisted of a jacketed beaker of 100-ml. capacity with a Bakelite top. Three holes accommodated two glass and the silver–silver chloride electrodes. An inlet part for nitrogen (saturated with the solvent) and two smaller holes for the burets were also available. Water from a constant temperature bath was circulated through the jacket. The solution was stirred magnetically. Grunwald's procedure[19] was used without important modification. The results are summarized in Table I.

Kirkwood–Westheimer Calculations. Table III.—The distance from the removable proton to the midpoint of the dipole was assessed for the case with the dipole oriented along the 1,4-axis from conventional values for bond distances. Where several atoms were involved in the group moment aligned along that axis, *e.g.*, nitro, the midpoint of the dipole was taken as the midpoint of the projected bond distances along the same axis. For other substituents, *e.g.*, hydroxy, with the group dipole not coincident with the 1,4-axis, the distance was taken to the midpoint of the projected dipole on the molecular axis. Effective dielectric constants were derived from the published tables of Westheimer, Jones, and Lad.[50] The volume of the cavity was determined by Traube's rule for the Kirkwood–Westheimer ellipsoidal model and by the assignment of d (the distance from the midpoint of the dipole to the edge of the cavity) as 1.5 Å. for the Tanford modification.[8] The results for the Tanford elliptical model, not presented in Table III, are in poorer agreement with experiment as previously found.[8]

Table V.—A two-point charge model was employed. The cavity was assigned the same dimensions as the Tanford sphere to allow a direct comparison between the two approaches. The charges were positioned at the carbon and bromine nuclei and assigned as μ/l where l is the bond length.

Table VI.—Unfortunately D_E for dipole substituents has not been ascertained for substituents not oriented on the principal axis of the molecule and the two-point charge form of the Kirkwood–Westheimer equation cannot be factored to provide D_E. To estimate the parameter, $\log (K/K_i)$ was calculated for each acid from the two-point charge formulation. In each case the center of the parent hydrocarbon was taken as the center of the cavity and the radius of the cavity assigned as the sum of the distances from the origin to the ionizable proton and an additional 1.5 Å. With this definition of the radius and the knowledge of the other angles and distances as defined by the structure, the value of $\log (K/K_i)$ was calculated. Using the result for $\log (K/K_i)$ eq. 3 was solved for D_E. D_E and $\log (K/K_i)$ for 4-bromobicyclo[2.2.2]octane-1-carboxylic acid are 4.2 and 0.65, respectively.

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(50) F. H. Westheimer, W. A. Jones, and R. A. Lad, *J. Chem. Phys.*, **10**, 478 (1942).

[Contribution from the Department of Chemistry, Columbia University, New York, New York 10027]

Reactions of the Cyclooctatetraenyl Dianion with *gem*-Dihalides. The Preparation of Derivatives of Bicyclo[6.1.0]nonatriene. Synthesis of the Cyclononatetraenyl Anion

By Thomas J. Katz and Peter J. Garratt

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The reactions of dipotassium or dilithium cyclooctatetraenide in tetrahydrofuran (THF) with methylene chloride, chloroform, carbon tetrachloride, and dichloromethyl methyl ether yield bicyclo[6.1.0]nonatriene and its *anti*-9-chloro, 9,9-dichloro, and *anti*-9-methoxy derivatives. *anti*-9-Chlorobicyclo[6.1.0]nonatriene is thermally rearranged at 70° to 1-chloro-8,9-dihydroindene. The former reacts with lithium in THF to yield lithium cyclononatetraenide. Similarly, *anti*-9-methoxybicyclo[6.1.0]nonatriene with potassium in THF gives potassium cyclononatetraenide. Some physical properties and chemical reactions of the cyclononatetraenyl anion are presented.

Introduction

Although the familiar cyclically conjugated hydrocarbon molecules and ions[1] are those with six unsaturation electrons, derivatives of the two-electron cyclopropenium ion,[1] of the ten-electron cyclooctatetraenyl dianion[2] and cyclononatetraenyl anion,[3,4] and of macrocyclic hydrocarbons with 12, 14, 16, 18, 20, 24, and 30 unsaturation electrons[5] have recently been synthesized. The ten-electron compounds are a challenge since medium-sized rings are expected to oppose in a number of ways the formation of an aromatic system. If the rings were of the planar all-*cis* conformation, bond angles would be severely strained; if some of the bonds were *trans*, nonbonded atoms would clash in the center.[6]

In either case the skeletal strain could be relieved by a distortion from planarity,[7] which would, however, interfere with the cyclic conjugation of the unsaturation electrons, or by a valence tautomerization,[8] which would interrupt conjugation completely.

Despite these obstacles, the cyclooctatetraenyl dianion[2] and cyclononatetraenyl anion[3,4] are aromatic. Cyclodecapentaene, however, is reported to be unstable with respect to its valence tautomer, *cis*-9,10-dihydronaphthalene,[9] but a related dihydronaphthalene[10] is reported to valence tautomerize spontaneously to the corresponding cyclodecapentaene derivative.

The cyclononatetraenyl anion was synthesized by Katz and Garratt by the procedure outlined in eq. 1.[3] The details of this synthesis are reported below. A similar synthesis of the anion was achieved independently by LaLancette and Benson.[4]

Results

The Synthesis of Derivatives of Bicyclo[6.1.0]nonatriene.—A few derivatives of bicyclo[6.1.0]nonatriene are known. The first reported was 9-carboethoxybicyclo[6.1.0]nonatriene (IIa), prepared by the

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(1) (a) "Non-Benzenoid Aromatic Compounds," D. Ginsberg, Ed., Interscience Publishers, Inc., New York, N. Y., 1959; (b) M. E. Vol'pin *Russ. Chem. Rev.*, **29**, 129 (1960).

(2) (a) T. J. Katz, *J. Am. Chem. Soc.*, **82**, 3784 (1960); (b) H. P. Fritz and H. Keller, *Chem. Ber.*, **95**, 158 (1962).

(3) T. J. Katz and P. J. Garratt, *J. Am. Chem. Soc.*, **85**, 2852 (1963).

(4) E. A. LaLancette and R. E. Benson, *ibid.*, **85**, 2853 (1963).

(5) F. Sondheimer, "Congress Lectures Presented at the XIXth International Congress of Pure and Applied Chemistry," Butterworths, London, 1963; see also, V. Boekelheide and J. B. Phillips, *J. Am. Chem. Soc.*, **85**, 1545 (1963).

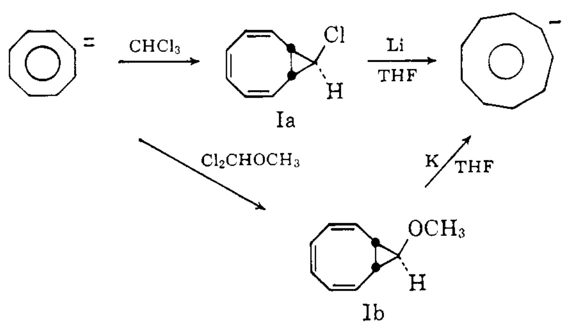
(6) K. Mislow, *J. Chem. Phys.*, **20**, 1489 (1952).

(7) Cyclooctatetraene is nonplanar (*cf.* R. A. Raphael, Chapter VIII in ref. 1a).

(8) E. Vogel, *Angew. Chem. Intern. Ed. Engl.*, **2**, 1 (1963).

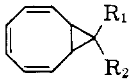
(9) E. E. van Tamelen and B. Pappas, *J. Am. Chem. Soc.*, **85**, 3296 (1963). See also J. J. Bloomfield and W. T. Quinlin, *ibid.*, **86**, 2738 (1964).

(10) E. Vogel and H. D. Roth, *Angew. Chem.*, **76**, 145 (1964). See also W. S. Johnson, J. D. Bass, and K. L. Williamson, *Tetrahedron*, **19**, 861 (1963).



(1)

addition of ethyl diazoacetate to cyclooctatetraene,[11-14] and its transformation products, the corresponding acid IIb,[11] hydrazide,[12] carbinol,[12] and diphenylcarbinol.[15] Subsequently, the parent hydrocarbon, bi-



IIa, $R_1 = H, R_2 = CO_2Et$
b, $R_1 = H, R_2 = CO_2H$
c, $R_1 = H, R_2 = H$
d, $R_1 = Cl, R_2 = Cl$
e, $R_1 = Br, R_2 = Br$
f, $R_1 = H, R = Cl$
g, $R_1 = H, R_2 = CH_3$
h, $R_1 = Cl, R_2 = CH_3$
i, $R_1 = OAc, R_2 = CH_3$

cyclo[6.1.0]nonatriene (IIc), was made by the reaction of cyclooctatetraene with the Simmons-Smith reagent[16] or with diazomethane-cuprous chloride[17]; the dichloride IId and dibromide IIe were made by the reaction of cyclooctatetraene with chloroform or bromoform and base.[16]

The reactions presumably proceed by forming divalent carbon species, which add to the cyclooctatetraene molecule.[18] It was expected, therefore, that 9-chlorobicyclo[6.1.0]nonatriene (IIf) would also be easily preparable upon the reaction of cyclooctatetraene with methylene chloride and methyllithium according to the procedure for the addition of chlorocarbene to olefins developed by Closs and Closs.[19] Initial attempts to effect this reaction led, however, to the unexpected product *syn*-9-methylbicyclo[6.1.0]nonatriene (IIg).[20] Only later was it determined that if the methyllithium used contained lithium bromide rather than lithium iodide, the desired product IIf could indeed be obtained.[4,20]

However, a new method for preparing derivatives of bicyclo[6.1.0]nonatriene was discovered—the reaction of alkali cyclooctatetraenides with *gem*-dihalides.[3] The preparation of Ia, Ib, IIc, and IId by this procedure is described below. The preparation of IIg and IIh is reported elsewhere.[20] (A similar reaction, that of alkali cyclooctatetraenides with acid chlorides, was found by Cantrell and Shechter to give the bicyclo[6.1.0]nonatriene derivative IIi.[21])

As shown in eq. 1, dipotassium cyclooctatetraenide in tetrahydrofuran (THF) when added to cold chloroform gives in 52% yield *anti*-9-chlorobicyclo[6.1.0]nonatriene (Ia), a liquid isolable by distillation at low temperatures (b.p. 26–27° at 0.1 mm.). The compound was identified by its analysis, its ultraviolet spectrum (Table I) characteristic of bicyclo[6.1.0]nonatrienes, its n.m.r. spectrum (Fig. 1), and by its chemical reactions discussed below. The n.m.r. spectrum consists of two groups of lines, the olefinic proton resonances, a multiplet at τ 4.1 of relative intensity 6, and the cyclopropyl proton resonances, a coupled (J = 4 c.p.s.) triplet at τ 7.54 of relative intensity 1, and doublet at τ 8.14 of relative intensity 2.

TABLE I

ULTRAVIOLET SPECTRA OF BICYCLO[6.1.0]NONATRIENES

Compd.	λ_{max}, mμ	log ε	Solvent	Ref.
IIc	247	3.69	EtOH	
IIc	245	3.59		17
IIg (*syn*)	252	3.71	EtOH	20
IIa	244	3.56		13[a]
IIb	249	3.61	EtOH	26
IId	243	3.46	EtOH	
Ia	248	3.57	EtOH	
IIf (*syn*)	250	3.48	EtOH	20
Ib	255	3.69	EtOH	
IIh	249	3.61	EtOH	20
IIi	247	3.61	MeOH	21

[a] The methyl ester is reported to have λ_{max} 242 mμ (log ε 3.63).

Similarly, dipotassium cyclooctatetraenide in THF reacts with methylene chloride at room temperature to yield bicyclo[6.1.0]nonatriene (IIc) and with carbon tetrachloride at −20 to −30° in a very vigorous reaction to yield 9,9-dichlorobicyclo[6.1.0]nonatriene (IId).[22] With dichloromethyl methyl ether it gives *anti*-9-methoxybicyclo[6.1.0]nonatriene (Ib) in up to 49% yield. These compounds were identified by their analyses and by their spectroscopic properties. As can be seen in Table I, the bicyclo[6.1.0]nonatriene chromophore is characterized by an absorption maximum in the ultraviolet at 248 ± 3 mμ. The n.m.r. spectra of the bicyclo[6.1.0]nonatrienes (Fig. 1) all show olefinic resonances of appropriate relative intensity at about τ 4.1. The cyclopropyl resonances each appear to be of the form required by the substitution pattern. Moreover, IIc exhibits infrared absorption at 3076 and 1020 cm.$^{-1}$, and 1.64 μ, characteristic of cyclopropanes with unsubstituted methylene groups.[23-25]

The appearance in the n.m.r. spectra of Ia and Ib (Fig. 1) of only one triplet and one doublet attributed to the cyclopropyl proton resonances shows that of the two possible epimers of 9-chloro- and 9-methoxybicyclo[6.1.0]nonatriene that might result from the reaction of dipotassium cyclooctatetraenide with chloroform and with dichloromethyl methyl ether, one is predominantly formed. The magnitude of the splitting constant, 4 c.p.s. in both cases, indicates that these are the *anti* isomers.[27,28] To determine whether the kind

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(11) S. Akiyoshi and T. Matsuda, *J. Am. Chem. Soc.*, **77**, 2476 (1955).

(12) D. D. Phillips, *ibid.*, **77**, 5179 (1955).

(13) K. F. Bangert and V. Boekelheide, *ibid.*, **86**, 905 (1964).

(14) G. J. Fonken and W. Moran, *Chem. Ind.* (London), 1841 (1963).

(15) K. F. Bangert and V. Boekelheide, *J. Am. Chem. Soc.*, **86**, 1159 (1964).

(16) E. Vogel, *Angew. Chem.*, **73**, 548 (1961).

(17) E. Vogel, W. Wiedemann, H. Kiefer, and W. F. Harrison, *Tetrahedron Letters*, **No. 11**, 673 (1963).

(18) J. Hine, "Divalent Carbon," The Ronald Press Co., New York, N. Y., 1964.

(19) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **82**, 5723 (1960).

(20) T. J. Katz and P. J. Garratt, *ibid.*, **86**, 4876 (1964).

(21) T. S. Cantrell and H. Schechter, *ibid.*, **85**, 3300 (1963).

(22) Some *anti*-9-chlorobicyclo[6.1.0]nonatriene was also formed.

(23) L. J. Bellamy, "Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 17, 29.

(24) (a) W. H. Washburn and M. J. Mahoney, *J. Am. Chem. Soc.*, **80**, 504 (1958); (b) P. G. Gassman, *Chem. Ind.* (London), 740 (1962); (c) J. Meinwald, A. Lewis, and P. G. Gassman, *J. Am. Chem. Soc.*, **84**, 977 (1962).

(25) The *anti*-9-chlorobicyclo[6.1.0]nonatriene also exhibits a low wave length maximum in the near infrared, at 1.68 μ (*cf.* ref. 4). However, *anti*-9-methoxybicyclo[6.1.0]nonatriene and *syn*-9-methylbicyclo[6.1.0]nonatriene do not show any distinct maxima below the main absorption at 1.7 μ.[26]

(26) P. J. Garratt, Dissertation, Columbia University, 1964.

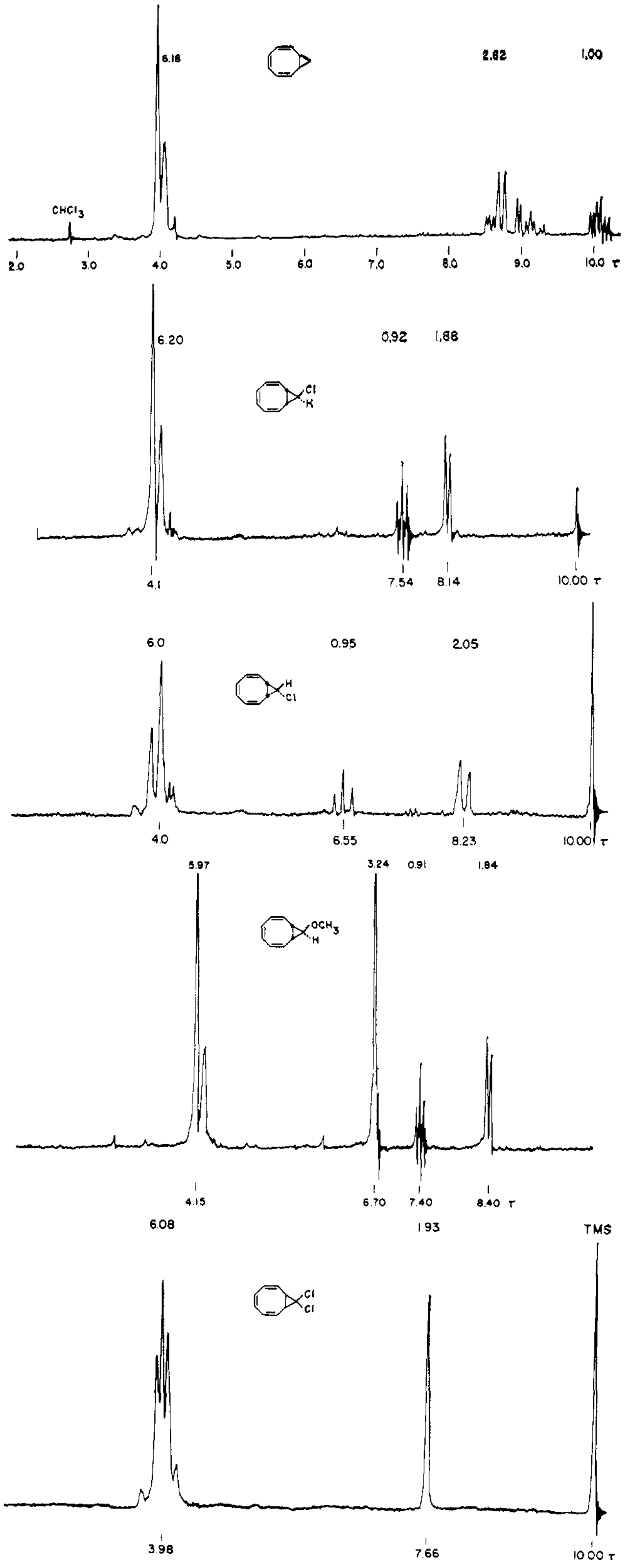


Fig. 1.—N.m.r. spectra of bicyclo[6.1.0]nonatriene derivatives at a frequency of 60 Mc. Spectra of IIc and d were determined neat, and spectra of Ia, its *syn* isomer, and Ib in carbon tetrachloride solution. TMS was the internal standard except in the case of IIc, for which a trace of chloroform was used. Above each peak its relative intensity is given.

of alkali metal cyclooctatetraenide used affects the nature of the product, dilithium (rather than potassium) cyclooctatetraenide in THF was added to chloroform. The reaction proceeded with exceptional vigor, even at −78°, and gave 9-chlorobicyclo[6.1.0]nonatriene in 19% yield. The only isomer found, however, was the one of *anti* stereochemistry (Ia).

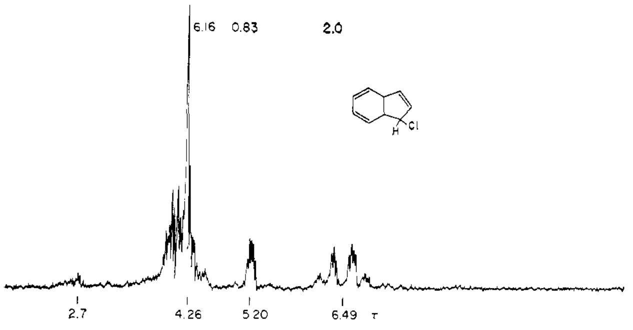
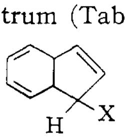


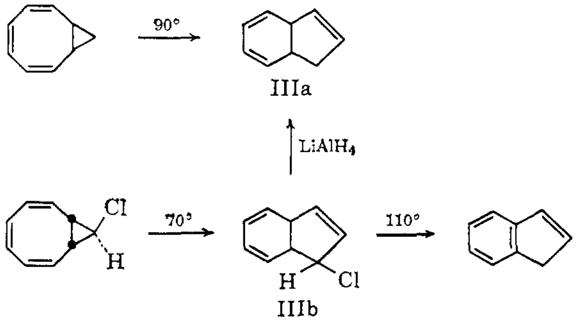
Fig. 2.—N.m.r. spectrum of IIIb in carbon tetrachloride at 60 Mc. Intensities are given above each peak.

Reactions of Bicyclo[6.1.0]nonatrienes (*Cf.* Chart I).—Heating bicyclo[6.1.0]nonatriene (IId) at 90° for 12 hr., as previously described,[16,17] converts it largely into 8,9-dihydroindene (IIIa), which was characterized by its ultraviolet spectrum (Table II), its n.m.r. spectrum (two multiplets, around τ 4.4 and 7, of relative intensity 6:4), and the melting point of its maleic anhydride adduct (m.p. 142°, reported[29] 144°). A tetracyanoethylene adduct of IIIa was also prepared (m.p. 231–231.5°) and characterized by its analysis, its infrared spectrum, and the absence of an absorption maximum in the ultraviolet above 230 mμ. The tetracyanoethylene adduct of bicyclo[6.1.0]nonatriene was also prepared, and proved to be different from the adduct of 8,9-dihydroindene. It melted at 141–141.5°, its infrared spectrum was different, and in the ultraviolet it showed an inflection at 230 mμ.



IIIa, X = H
b, X = Cl
c, X = D
d, X = OCH_3
e, X = CO_2H
f, X = CH_3
g, X = CO_2Et

CHART I



Similarly, *anti*-9-chlorobicyclo[6.1.0]nonatriene (Ia) after heating at 70° for 4 hr. was converted into 1-chloro-8,9-dihydroindene (IIIb), identified by its analysis, its ultraviolet spectrum (Table II), its n.m.r. spectrum (Fig. 2), and by lithium aluminum hydride reduc-

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(27) (a) G. L. Closs, R. A. Moss, and J. J. Coyle, *J. Am. Chem. Soc.*, **84**, 4985 (1962); (b) J. D. Graham and M. T. Rogers, *ibid.*, **84**, 2249 (1962); (c) D. J. Patel, M. E. H. Howden, and J. D. Roberts, *ibid.*, **85**, 3218 (1963).

(28) See also (a) U. Schöllkopf and W. Pitteroff, *Chem. Ber.*, **97**, 636 (1964); (b) U. Schöllkopf, A. Lerch, and J. Paust, *ibid.*, **96**, 2266 (1963); (c) U. Schöllkopf and G. S. Lehman, *Tetrahedron Letters*, 165 (1962); (d) U. Schöllkopf and H. Küppers, *ibid.*, 105 (1963); (e) D. Seyferth, H. Yamazaki, and D. L. Allesten, *J. Org. Chem.*, **28**, 703 (1963).

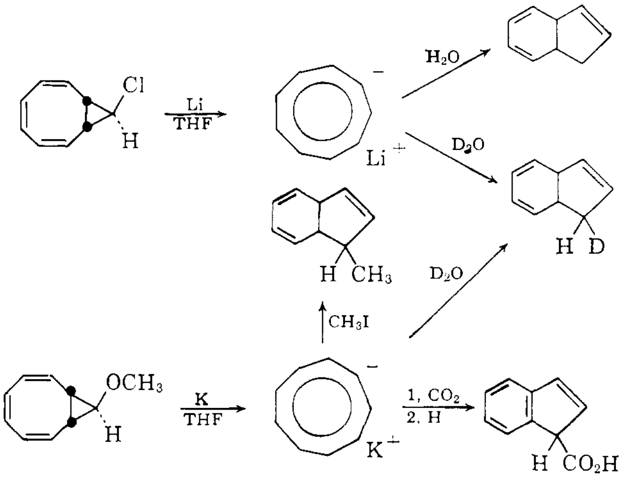
(29) K. Alder and F. H. Flock, *Chem. Ber.*, **87**, 1916 (1954).

tion, which yielded 8,9-dihydroindene (IIIa), identical with that prepared by heating bicyclo[6.1.0]nonatriene (IId). Compound IIIb was further characterized by its infrared spectrum and by the formation of a tetracyanoethylene adduct (m.p. 222°). Interestingly, the same 1-chloro-8,9-dihydroindene was formed when *syn*-9-chlorobicyclo[6.1.0]nonatriene was heated to 70°. When IIIb was heated to a somewhat higher temperature, 110°, for 6 hr., it dehydrohalogenated to give indene, identified by its ultraviolet and n.m.r. spectra.

anti-9-Methoxybicyclo[6.1.0]nonatriene (Ib) also undergoes thermal decomposition when heated at 70° for 20 hr. The n.m.r. spectrum of a sample from the reaction is very complex—it exhibits three resonances in the region characteristic of methoxyl groups—and the product has not yet been further identified. However, 1-methoxy-8,9-dihydroindene (IIId) has been prepared by the methanolysis of 1-chloro-8,9-dihydroindene (IIIb).

The Preparation of the Cyclononatetraenyl Anion (*Cf.* Chart II).—Lithium cyclononatetaenide was prepared in THF solution by the reaction of *anti*-9-chlorobicyclo[6.1.0]nonatriene (Ia) with lithium metal. The experiment can be monitored by observing the n.m.r. spectrum of the reaction mixture, which shows, besides the resonances of the solvent and starting material, a new singlet at τ 3, which increases in intensity as the resonances of the starting material fade. After complete reaction, besides the solvent resonances at τ 6.37 and 8.21, only a single peak, at τ 3.1, is observed. In completely deuterated THF this is the only intense peak, implying that no resonances had been obscured by the solvent. The small peaks attributed to the trace amounts of protonated THF present in the solvent were used to calibrate the chemical shift of the lithium cyclononatetraenide resonance.

CHART II



Similarly, potassium cyclononatetraenide was prepared in THF solution by the reaction of *anti*-9-methoxybicyclo[6.1.0]nonatriene with potassium metal.[30] The n.m.r. spectrum of this material in deuterated THF exhibits a single sharp resonance at τ 2.96 (Fig. 3).

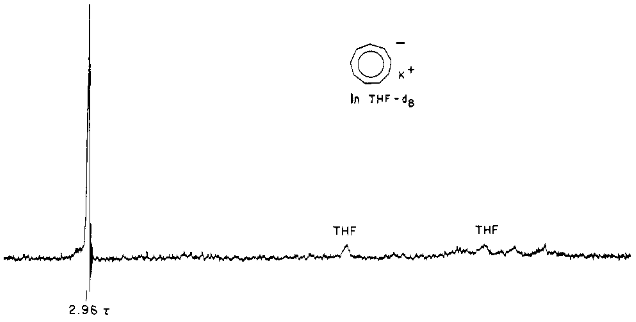


Fig. 3.—N.m.r. spectrum of potassium cyclononatetraenide in deuterated THF. The chemical shift was measured relative to the small peaks attributed to traces of protonated THF.

Lithium cyclononatetraenide in THF reacts with water to give 8,9-dihydroindene (IIIa), identical with an authentic sample, and with deuterium oxide to give 1-deuterio-8,9-dihydroindene (IIIc). The infrared spectrum of the deuterated hydrocarbon shows a C–D stretch at 2180 cm.$^{-1}$,[31] and its n.m.r. spectrum shows a decrease, compared to the undeuterated material, of the number of allylic protons (relative to the olefinic protons) from four to three. Three samples of the deuterated material subjected to falling drop analysis were found to be enriched in deuterium by 9.40, 9.60, and 9.38 atom %—the expected enrichment for C_9H_9D is 10 atom %—and mass spectrometric analyses carried out on two samples showed that 97.0 and 92.4% of the 8,9-dihydroindene was monodeuterated.[32] Falling drop analysis of the 1-deuterio-8,9-dihydroindene formed by quenching a solution of *potassium* cyclononatetraenide in THF with deuterium oxide similarly showed a 9.46 atom % excess of deuterium.

Potassium cyclononatetraenide in THF reacts with carbon dioxide to give 1-carboxy-8,9-dihydroindene (IIIe), m.p. 51–52°, identified by its analysis and ultraviolet spectrum (Table II). A maleic anhydride adduct of this material was prepared, and its melting point (m.p. 210–211°) and mixture melting point showed it to be identical with the maleic anhydride adduct of the oily 1-carboxy-8,9-dihydroindene formed by hydrolysis of the thermal rearrangement product of 9-carbethoxybicyclo[6.1.0]nonatriene.[13,33]

TABLE II

ULTRAVIOLET SPECTRA OF 8,9-DIHYDROINDENES

Compd.	λ_{max}, mμ	log ϵ	Solvent	Ref.
IIIa	262	3.57	EtOH	
	270	3.51		
IIIb	262	3.52	EtOH	
	270	3.44		
IIId	261	3.64	EtOH	
	270	3.59		
IIIe	262	3.51	EtOH	
	270	3.49		
IIIg	252	3.56		13
	261	3.66		
	282	3.35		

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[30] *Cf.* K. Ziegler and B. Schnell, *Ann.*, **437**, 227 (1924); K. Ziegler and H. Dislich, *Chem. Ber.*, **90**, 1107 (1957).

[31] K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p. 63.

[32] We thank Dr. P. D. Caeser and Dr. F. Hochgesang of the Socony Mobil Oil Co., Paulsboro, N. J., for these analyses.

[33] (a) We are grateful to Professor Boekelheide for a sample of this adduct. In our laboratory the melting point of the sample was 210–211°, slightly higher than reported (204.5–206.5°).[13] (b) The melting point of the 1-carboxy-8,9-dihydroindene is, however, much lower than that of the 1-carboxy-8,9-dihydroindene (m.p. 103–105°) formed by thermal rearrange-

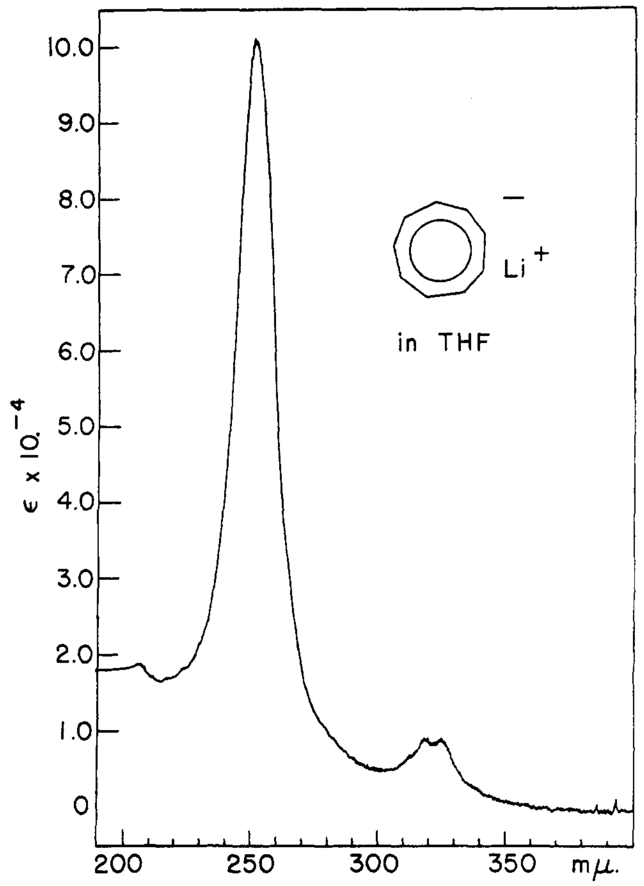

Fig. 4.—Ultraviolet spectrum of lithium cyclononatetraenide in THF

Potassium cyclononatetraenide in THF does not react with methyl chloride, but does with methyl iodide, to yield 1-methyl-8,9-dihydroindene (IIIf), identified by its analysis, ultraviolet spectrum (Table II), and n.m.r. spectrum.

The ultraviolet spectrum of lithium cyclononatetraenide in THF (Fig. 4) exhibits maxima at 251 (log ϵ 5.0), 319 (3.9), and 324 mμ (3.9). Potassium cyclononatetraenide in THF has a similar spectrum. Maxima appear at 249 (log ϵ 5.0), 314 (4.0), and 320 mμ (4.0).

Discussion

It is possible that the reactions of alkali metal cyclooctatetraenides with *gem*-dihalides, yielding derivatives of bicyclo[6.1.0]nonatriene, form cyclooctatetraene and divalent carbon species, which then combine.[20] In the reaction of dipotassium cyclooctatetraenide with chloroform, yielding *anti*-9-chlorobicyclo[6.1.0]nonatriene,[34] the implication would be that cyclooctatetraene and chlorocarbene are intermediates that unite, but a problem posed by this mechanism is that the reaction of cyclooctatetraene with methylene chloride and methyllithium (made from methyl bromide) in ether, which also produces 9-chlorobicyclo[6.1.0]nonatriene, presumably by the union of the same intermediates, gives a product of different stereochemistry.[4,20] The latter is a mixture of *syn* and *anti* isomers, the former predominating by about 4:1. (A mixture of *syn* and *anti* isomers, the former predominating, appears to be the kind of product usually obtained when chlorocarbene is added to olefins by the Closs method.[27,28]) If the reaction of dipotassium cyclooctatetraenide with chloroform proceeded by way of the carbene, this difference could still be accounted for if chlorocarbene were not free but complexed by the alkali halide, as has previously been suggested,[35] since the complex formed from dipotassium cyclooctatetraenide and chloroform might be different from that formed from methylene chloride and methyllithium. However, one hypothesis tested—that the difference is due to the different alkali metal cation present in the two reaction mixtures—is untenable, for lithium cyclooctatetraenide in THF also reacts with chloroform to yield only *anti*-9-chlorobicyclo[6.1.0]nonatriene.

Assignment of the stereochemistry to the two isomers of 9-chlorobicyclo[6.1.0]nonatriene is based upon the observation (Fig. 1) that the separation between individual lines of the triplet and doublet is 4 c.p.s. in the n.m.r. spectrum of one isomer and 7 c.p.s. in the spectrum of the other. The former splitting is that expected for the *anti* isomer, whereas the latter is that expected for the *syn* isomer.[27] The characterization of both epimers makes it unlikely that the stereochemistry has been misassigned. In the case of 9-methoxybicyclo[6.1.0]nonatriene only one isomer has been prepared, but the 4 c.p.s. splitting of its A_2X cyclopropyl proton resonances indicates that it possesses the *anti* stereochemistry.

The thermal rearrangement of *anti*-9-chlorobicyclo[6.1.0]nonatriene to 1-chloro-8,9-dihydroindene (Ib) follows the pattern established by Vogel[16] for rearrangement of bicyclo[6.1.0]nonatriene and 9,9-dichlorobicyclo[6.1.0]nonatriene, and later found also for the isomerization of 9-carbethoxy-,[13,14] 9-carbomethoxy-,[17] and 9-carboxybicyclo[6.1.0]nonatriene.[14] The possibility that thermal rearrangement of *syn*-9-chlorobicyclo[6.1.0]nonatriene might yield an epimer of IIIb was examined, but the product is the same.

The n.m.r. spectrum of the cyclononatetraenyl anion is of special interest with regard to theories of chemical shifts in n.m.r. spectroscopy since the ion is one of a small group of hydrocarbon molecules or ions in which the charge density associated with each carbon atom is known independent of arbitrary assumptions. The n.m.r. spectra of better known members of this series—the cyclopentadienyl anion, benzene, and the tropylium ion—have indicated that their proton chemical shifts are proportional to their charge densities, and the proportionality constant has been variously evaluated as -10,[36] -10.7,[37] and -9.3[38] p.p.m. per unit charge. The assumption is made that other effects are minor; that is, were it not for the difference in charge density, the proton chemical shifts would be the same. However, small corrections based on theories of ring currents have usually been applied to account for expected differential effects of the π-electron ring current in the different size rings. Whatever

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ment of the 9-carboxybicyclo[6.1.0]nonatriene made by saponification of the ethyl ester of the latter.[14]

(34) The n.m.r. spectrum of the reaction product indicates that a trace (<5%) of the *syn* isomer is present.

(35) (a) W. T. Miller, Jr., and D. M. Whalen, *J. Am. Chem. Soc.*, **86**, 2089 (1964); (b) G. L. Closs and J. J. Coyle, *ibid.*, **84**, 4350 (1962); (c) G. L. Closs and L. E. Closs, *Angew. Chem.*, **74**, 431 (1962).

(36) G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Am. Chem. Soc.*, **82**, 5846 (1960).

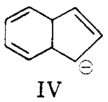
(37) T. Schaeffer and W. G. Schneider, *Can. J. Chem.*, **41**, 966 (1963).

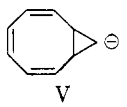
(38) B. P. Dailey, A. Gawer, and W. C. Neikam, *Discussions Faraday Soc.*, **34**, 18 (1962).

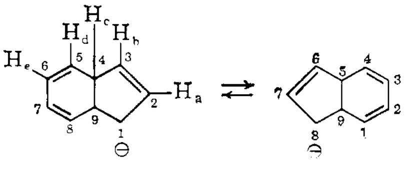
effects changes in hybridization have upon chemical shift have been neglected.

Significantly, the chemical shifts of the ten-π-electron systems—the cyclooctatetraenyl dianion and the cyclononatetraenyl anion—also support this theory. Thus, it is assumed, as in the six-π-electron systems, that were it not for the difference in charge density associated with each carbon atom in the two ions, their chemical shifts would be the same. A correction for the differential effects of ring currents can be applied, but appears to be insignificant.[39] The question is whether the difference in the chemical shifts is $a(^1/_4 - {}^1/_9)$, where a is the proportionality constant that relates charge density and chemical shift, previously evaluated as *ca.* -10 p.p.m./unit charge (see above), and $-^1/_4$ and $-^1/_9$ are the charge densities per carbon in the two ions. The calculated difference is thus 1.4 p.p.m., and the observed chemical shifts are τ 4.3 for the cyclooctatetraenyl dianion and *ca.* τ 3.0[2a] for the cyclononatetraenyl anion, an excellent agreement. A similar proportionality between carbon-13 chemical shifts and charge density is supported by the C^{13} n.m.r. spectrum of the cyclononatetraenyl anion.[4]

The proton n.m.r. spectrum of the cyclononatetraenyl anion is inconsistent with the hypothesis that the anion has the structure IV or V, for these would be expected to have complicated spectra. The spectrum also appears to exclude the possibility that the anion is a rapidly interconverting mixture of valence tautomers of IV or V, *e.g.*

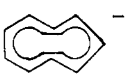

IV


V



If this interconversion were sufficiently rapid, the spectrum would show only one line, but the chemical shift would not be τ 3.0. In the case of IV it would be about $^1/_9(2H_a + 2H_d + 2H_c + 2H_b + H_a) = \tau$ 5.9, where H_c, H_d, and H_e are the chemical shifts of the corresponding protons in 8,9-dihydroindene (τ 6.9 for H_c and *ca.* 4.4 for H_d and H_e) and H_a and H_b are the chemical shifts of the corresponding protons in allyllithium ($H_a = \tau$ 3.4, $H_b = \tau$ 7.6).[41] In the case of a rapidly interconverting mixture of isomers of V, the proton resonance signal should appear at even higher field.

The n.m.r. spectrum of the cyclononatetraenyl anion also excludes VI as a possible structure for the ion, for the large chemical shift expected of protons inside and outside the ring and their strong coupling should lead to a complex spectrum, unlike that observed.


VI

Experimental[42]

Preparation of Bicyclo[6.1.0]nonatriene.—Potassium cyclooctatetraenide[20] (0.10 mole) in THF was added slowly with stirring over a period of 60 min. to methylene chloride (250 ml.), under nitrogen at room temperature. After completion of addition, the mixture was stirred for 8 hr., and then ethanol (15 ml.) was added to destroy any transferred potassium. Water was added to dissolve the precipitated potassium chloride, the layers were separated, and the aqueous layer was washed with ether (2 × 50 ml.). The combined organic layers were extracted with water (3 × 200 ml.) and saturated sodium chloride solution (2 × 200 ml.) and then dried over magnesium sulfate. The solvent was removed under reduced pressure, and the residue distilled: fraction I, b.p. 31–47° (8.0 mm.), 0.6 g.; fraction II, b.p. 47–51° (8.0 mm.), 6.1 g.

Fraction II was redistilled, and bicyclo[6.1.0]nonatriene, b.p. 51° (7.0 mm.), 5.7 g., 45%, was obtained; λ_{max}^{EtOH} 247 mμ (log ϵ 3.69); ν 3076, 1020 cm.$^{-1}$ (cyclopropyl hydrogens); n.m.r.: 4.15 (multiplet, 6.18 H), 8.6 (multiplet, 2.82 H), 9.8 τ (multiplet 1.00 H).

Anal. Calcd. for C_9H_{10}: C, 91.47; H, 8.53. Found: C, 91.74, 91.79; H, 8.28, 8.36.

Preparation of Tetracyanoethylene Adduct of Bicyclo[6.1.0]nonatriene.—Bicyclo[6.1.0]nonatriene (0.116 g., 0.001 mole) was dissolved in THF (0.5 ml.) and added to a solution of tetracyanoethylene (0.26 g., 0.001 mole) in THF (0.5 ml.).[43] A red color developed and the solution was warmed on a steam bath and then allowed to stand for 30 min. The solvent was removed; a deep green liquid remained, which solidified on cooling. This solid was extracted with hot carbon tetrachloride, the extracts were decolorized with Norit, and the product recrystallized from carbon tetrachloride. A white solid (0.109 g., 44%), m.p. 141–141.5°, was obtained; λ_{max}^{EtOH} 230 mμ (log ϵ 3.41) (shoulder on end absorption,) ν (KBr) 2280 cm.$^{-1}$ (C≡N).

Anal. Calcd. for $C_{15}H_{10}N_4$: C, 73.15; H, 4.09; N, 22.75. Found: C, 73.30; H, 4.26; N, 22.60.

Preparation of *anti*-9-Chlorobicyclo[6.1.0]nonatriene.—Potassium cyclooctatetraenide (0.29 mole) in THF was added, under an atmosphere of nitrogen, to vigorously stirred chloroform (250 ml.) at $-10°$ over a period of 90 min. After completion of the addition, the flask was allowed to warm to room temperature and was stirred further for 2 hr. After addition of a little ethanol, sufficient water was added to dissolve the precipitated potassium chloride. The aqueous layer was separated and washed with ether (2 × 50 ml.). The combined organic layers were washed with water (2 × 100 ml.) and saturated sodium chloride solution (2 × 50 ml.) and dried over anhydrous magnesium sulfate. The solvents were removed under reduced pressure at temperatures below 40°, and the residue was distilled. After removing some cyclooctatetraene, a fraction was collected, b.p. 28–32° (0.3 mm.). This was redistilled, and *anti*-9-chlorobicyclo[6.1.0]nonatriene, b.p. 28° (0.2 mm.), 19.9 g., 45%, was obtained; λ_{max}^{EtOH} 248 mμ (log ϵ 3.57); n.m.r.: 4.1 (multiplet, 6.20 H), 7.54 (A, triplet, 0.92 H), 8.14 τ (B, doublet, 1.88 H), J_{AB} 4 c.p.s.

Anal. Calcd. for C_9H_9Cl: C, 70.82; H, 5.94; Cl, 23.23. Found: C, 71.06; H, 6.06; Cl, 23.42.

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[39] In the point-dipole approximation,[37,40] with the assumption that the ring current effect in benzene is 1.5 p.p.m. and all carbon–carbon bond lengths are the same as in benzene, the difference in the chemical shifts of the two ions attributable to ring current effects could be

$$20\left[\frac{(2.04)^2}{(3.13)^3} - \frac{(1.83)^2}{(2.92)^3}\right] = 0.02 \text{ p.p.m.}$$

[40] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 180 ff.

[41] C. S. Johnson, M. A. Wiener, J. S. Waugh, and D. Seyferth, *J. Am. Chem. Soc.*, **83**, 1306 (1961).

[42] N.m.r. spectra were determined with a Varian Associates A-60 spectrometer, on neat samples or with carbon tetrachloride as solvent, unless stated otherwise, and with tetramethylsilane as an internal standard. Ultraviolet spectra were determined with a Cary 14 spectrophotometer in 95% ethanol unless stated otherwise. Infrared spectra were determined with a Perkin–Elmer 421 spectrophotometer with chloroform as the solvent, unless stated otherwise. Near-infrared spectra were determined on a Cary 14 spectrophotometer in 1-cm. quartz cells as 5% solutions in carbon tetrachloride. Melting points were taken on a Thomas Hoover melting point apparatus, and are uncorrected. Vapor phase chromatography was carried out on a modified Perkin–Elmer 154 L with thermistor detector. Tetrahydrofuran was dried over potassium hydroxide pellets and distilled from lithium aluminum hydride.

[43] W. J. Middleton, R. E. Heckett, E. L. Little, and C. G. Krespan, *J. Am. Chem. Soc.*, **80**, 2783 (1958).

Preparation of 9-Methoxybicyclo[6.1.0]nonatriene.—Potassium cyclooctatetraenide (0.21 mole) in THF was added to 224 g. of vigorously stirred dichloromethyl methyl ether[44] under nitrogen at 0° over a period of 90 min. After completion of addition, the mixture was allowed to warm to room temperature and was then stirred for 12 hr. The mixture was added to a vigorously stirred slurry of sodium bicarbonate (360 g.) in water (500 ml.). After completion of the addition, the mixture was stirred for a further 30 min. until effervescence had ceased. The mixture was extracted with ether (5 × 250 ml.), and the ethereal extracts were washed with saturated sodium chloride solution (2 × 250 ml.). The extracts were dried over sodium sulfate, the solvent was removed under reduced pressure, and the residue distilled *in vacuo*. 9-Methoxybicyclo[6.1.0]nonatriene was obtained, b.p. 54–56° (1.1 mm.), 8.1 g. (27%), $\lambda_{\max}^{\mathrm{EtOH}}$ 255 mμ (log ϵ 3.69); n.m.r.: 4.2 multiplet (6.00 H), 6.70 singlet (3.31 H), and a coupled triplet (A) 7.40 (0.82 H) and doublet (B) 8.40 τ (1.79 H), J_{AB} 4 c.p.s.

Anal. Calcd. for $C_{10}H_{12}O$: C, 81.09; H, 8.11. Found: C, 80.89; H, 8.18.

When potassium cyclooctatetraenide (0.25 mole) was added to dichloromethyl methyl ether (58 g., 0.5 mole) in THF (250 ml.), the reaction could be carried out at room temperature. The reaction mixture was then added to sodium bicarbonate in water and worked up as previously described. 9-Methoxybicyclo[6.1.0]nonatriene was obtained in 49% yield (18.2 g.).[45]

Preparation of 9,9-Dichlorobicyclo[6.1.0]nonatriene.—Potassium cyclooctatetraenide (0.167 mole) was added over a 90-min. period to vigorously stirred carbon tetrachloride (250 ml.) at −30° under nitrogen. The dark mixture was allowed to warm to room temperature and was stirred for 12 hr. Sufficient water was then added to dissolve the precipitated potassium chloride. The mixture was extracted with ether (3 × 100 ml.). The organic layers were washed with water (3 × 100 ml.) and saturated sodium chloride solution (1 × 100 ml.) and dried over magnesium sulfate. The solvent was removed at reduced pressure and the residue was distilled. Three fractions were obtained. The first (b.p. 28–29° (0.05 mm.)) was 9-chlorobicyclo[6.1.0]nonatriene; the second (b.p. 29–31° (0.05 mm.)), a mixture of this compound and 9,9-dichlorobicyclo[6.1.0]nonatriene; and the major fraction (b.p. 31° (0.05 mm.)), 6.1 g., 19%, 9,9-dichlorobicyclo[6.1.0]nonatriene. This latter compound was identical with an authentic sample (ultraviolet, infrared, n.m.r.).[16]

Reaction of Lithium Cyclooctatetraenide with Chloroform.—Lithium (4.0 g., 0.57 g.-atom) was added in small pieces to dry THF (300 ml.) at −78° under nitrogen. Cyclooctatetraene (28 g., 0.27 mole) was added, the mixture was stirred vigorously for 4 hr., allowed to come to 0°, and then stirred further at this temperature for 24 hr. and at room temperature for 24 hr. The deep green solution of lithium cyclooctatetraenide was added slowly to vigorously stirred chloroform (300 ml.) at −78° under nitrogen, whereupon an extremely exothermic reaction occurred. The dark mixture was stirred and allowed to warm slowly to room temperature. Sufficient water was added to dissolve the precipitated lithium chloride, the organic layer was separated, and the aqueous layer was washed with ether (3 × 100 ml.). The combined organic layers were washed with water (2 × 100 ml.) and saturated sodium chloride solution (2 × 50 ml.) and were dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure at temperatures below 40°, and the residue was distilled. *anti*-9-Chlorobicyclo[6.1.0]nonatriene (7.2 g., 19%) was obtained.

Conversion of Bicyclo[6.1.0]nonatriene to 8,9-Dihydroindene.[16]—Bicyclo[6.1.0]nonatriene (1.15 g., 0.01 mole) sealed in an evacuated tube, was immersed in an oil bath at 90° for 24 hr. The product was distilled (b.p. 51–52° (18 mm.)) and chromatographed in the vapor phase on a di-*n*-decyl phthalate column (6 ft., 115°, 15 p.s.i. helium). Three peaks were observed, and the major component (80–90%), 8,9-dihydroindene, b.p. 46° (11 mm.), 0.81 g. (70%), was collected; $\lambda_{\max}^{\mathrm{EtOH}}$ 262 (log ϵ 3.57), 271 mμ (3.51); n.m.r.: 4.4 (multiplet, 5.8 H), 7.1 τ (multiplet, 4.2 H). The maleic anhydride adduct, prepared by the method of Alder and Flock,[29] melted at 142° (lit. 144°).

Preparation of Tetracyanoethylene Adduct of 8,9-Dihydroindene.—Crude 8,9-dihydroindene (0.252 g., 0.0021 mole) obtained by rearrangement of bicyclo[6.1.0]nonatriene was dissolved in THF (1 ml.) and added to tetracyanoethylene (0.267 g., 0.0021 mole) dissolved in THF (2 ml.),[43] An exothermic reaction occurred, and the solution turned red. After cooling, the solution was allowed to stand for 5 hr., and the solvent was removed at reduced pressure. The solid residue was extracted with benzene and decolorized with Norit. On cooling, the white adduct crystallized (0.234 g., 45%, m.p. 231–231.5°). The ultraviolet spectrum showed no absorption maximum above 230 mμ; ν (KBr) 2260 cm.$^{-1}$ ($C\equiv N$).

Anal. Calcd. for $C_{15}H_{10}N_4$: C, 73.15; H, 4.09; N, 22.75. Found: C, 72.90; H, 4.21; N, 22.93.

Conversion of *anti*-9-Chlorobicyclo[6.1.0]nonatriene into 1-Chloro-8,9-dihydroindene.—9-Chlorobicyclo[6.1.0]nonatriene (2.12 g., 0.0014 mole) was heated under nitrogen for 3 hr. at 70°. The product was distilled, and 1-chloro-8,9-dihydroindene, b.p. 60–61° (3.0 mm.), 1.82 g., 86%, was obtained; $\lambda_{\max}^{\mathrm{EtOH}}$ 262 (log ϵ 3.52), 270 (3.44); n.m.r.: 4.2 (multiplet, 6.16 H), 5.20 (multiplet, 0.83 H), 6.49 τ (multiplet, 1.99 H).

Anal. Calcd. for C_9H_9Cl: C, 70.82; H, 5.94; Cl, 23.23. Found: C, 71.03; H, 6.01; Cl, 23.24.

Conversion of 1-Chloro-8,9-dihydroindene into Indene.—1-Chloro-8,9-dihydroindene (1.87 g., 0.012 mole) was heated under nitrogen for 4 hr. in an oil bath at 110°. The product was distilled (b.p. 80° (1 mm.)) and identified as indene; $\lambda_{\max}^{\mathrm{EtOH}}$ 250 mμ (log ϵ 3.75) (indene, $\lambda_{\max}^{\mathrm{EtOH}}$ 250 mμ (log ϵ 4.0)), n^{21}_{D} 1.5689 (indene, n^{20}_{D} 1.5711); n.m.r.: 3.27 (multiplet, 4.00 H), 3.75 (multiplet, 0.97 H), 4.13 (multiplet, 0.90 H), 7.13 τ (triplet, 2.06 H).

Tetracyanoethylene Adduct of 1-Chloro-8,9-dihydroindene.—1-Chloro-8,9-dihydroindene (1.5 g., 0.01 mole) was added to a solution of sublimed tetracyanoethylene (1.28 g., 0.01 mole) in THF (8 ml.). An exothermic reaction occurred and the solution was cooled in ice–water. The red solution was allowed to stand at room temperature for 30 min., and the solvent was removed at reduced pressure. The residue was washed with benzene (100 ml.). The filtrate was reduced in volume and a second crop collected. The combined crystalline material was recrystallized from 95% ethanol to yield a white crystalline adduct, m.p. 222° (2.35 g., 84%). The ultraviolet spectrum showed no absorption maximum above 230 mμ; ν (KBr) 2280 cm.$^{-1}$ ($C\equiv N$).

Anal. Calcd. for $C_{16}H_9N_4Cl$: C, 64.18; H, 3.23; N, 19.96; Cl, 12.63. Found: C, 64.01; H, 3.43; N, 20.15; Cl, 12.44.

Reduction of 1-Chloro-8,9-dihydroindene to 8,9-Dihydroindene.—1-Chloro-8,9-dihydroindene (1.55 g., 0.01 mole), dissolved in 10 ml. of dry ether, was added from a dropping funnel to a stirred suspension of lithium aluminum hydride (0.4 g., 0.01 mole) in 15 ml. of dry ether at such a rate that gentle refluxing occurred.[46] After completion of addition, the mixture was stirred for 10 min., and then water was added cautiously to the mixture at 0°. Potassium sodium tartrate (50 ml., 20%) was added. The ether extracts (2 × 20 ml.) were combined and dried over anhydrous magnesium sulfate. The ether was removed, and the residue was distilled at reduced pressure. 8,9-Dihydroindene (b.p. 46° (11 mm.)), 0.42 g., 36%, was obtained, identical in some respects (ultraviolet, infrared, n.m.r.; maleic anhydride adduct, m.p., m.m.p. 141.5°) with that obtained from thermal rearrangement of bicyclo[6.1.0]nonatriene.

Preparation of 1-Methoxy-8,9-dihydroindene.—1-Chloro-8,9-dihydroindene (5.0 g., 0.033 mole) was added to a stirred solution of 3 g. of sodium bicarbonate in 30 ml. of methanol.[47] The mixture was stirred and refluxed for 30 min. Gas was evolved and a solid precipitated. Sufficient water was added to dissolve the solid, and the solution was extracted with ether (4 × 30 ml.). The ethereal extracts were washed with saturated sodium chloride solution (1 × 50 ml.) and dried over anhydrous magnesium sulfate. The solvent was removed and the residue distilled at reduced pressure. 1-Methoxy-8,9-dihydroindene (b.p. 64–65° (2.3 mm.)), 3.27 g., 68%, was obtained; $\lambda_{\max}^{\mathrm{EtOH}}$ 261 (log ϵ 3.64), 270 mμ (3.59); n.m.r.: 4.3 (6.02 H), 5.72 (0.96 H), 6.75 τ (5.04 H).

Anal. Calcd. for $C_{10}H_{12}O$: C, 81.09; H, 8.11. Found: C, 81.03; H, 8.14.

Thermal Rearrangement of 9-Methoxybicyclo[6.1.0]nonatriene.—9-Methoxybicyclo[6.1.0]nonatriene (1.06 g., 0.007 mole) was heated under nitrogen for 20 hr. at 70°. Samples were examined at intervals by n.m.r. spectroscopy, and the disappearance of the parent spectrum and the appearance of a new complex spectrum was observed. At least three methoxy peaks were apparent and the complex mixture was not examined further.

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(44) A. Reide, H. Gross, and E. Hoft, *Chem. Ber.*, **93**, 88 (1960).

(45) This modification was carried out by Mr. E. Faeder.

(46) R. F. Nystrom and W. G. Brown, *J. Am. Chem. Soc.*, **70**, 3738 (1948).

(47) M. Charon, *Bull. soc. chim. France*, **7**, 86 (1910).

Preparation of the Cyclononatetraenyl Anion. (i) **The Reaction of Lithium with 9-Chlorobicyclo[6.1.0]nonatriene.**—To a U-tube containing a magnetic stirring bar and fitted with a coarse sintered disk and n.m.r. tube on one limb and a Ŧ 19/38 joint on the other 9-chlorobicyclo[6.1.0]nonatriene (0.126 g., 0.0008 mole) was introduced. Lithium (0.060 g., 0.009 g.-atom) was added in freshly cut pieces, and care was taken that these did not come in contact with the chloro compound. The tube was cooled to −190° and evacuated on a vacuum manifold; THF (1 ml.), distilled from potassium anthracenide, was transferred into the evacuated tube, which was then sealed. The mixture was warmed to −78° and then stirred and allowed to come slowly to room temperature. A deep magenta color developed, which slowly discharged, and the mixture became dark brown. After 12 hr. the mixture was filtered through the sintered disk into the n.m.r. tube, which was then sealed. As some solid had passed through the filter, the inverted n.m.r. tube was centrifuged and the solid collected at the sealed end. The n.m.r. spectrum revealed, besides the solvent peaks, one sharp resonance signal at 3.1 τ.

(ii) **The Reaction of Potassium with 9-Methoxybicyclo[6.1.0]nonatriene.**—9-Methoxybicyclo[6.1.0]nonatriene (0.116 g., 0.0008 mole) was introduced into a U-tube identical with that described in the previous section, and potassium (0.189 g., 0.0047 g.-atom) was added in freshly cut pieces. THF (1 ml.), distilled from potassium anthracenide, was then transferred through the vacuum manifold, and the sample was treated as described previously for lithium cyclononatetraenide (i). The n.m.r. spectrum revealed, besides the solvent peaks, a single sharp resonance at 2.9 τ.

Both these experiments were repeated a number of times, and fully deuterated THF was also used as the solvent. The n.m.r. spectra in the deuterated solvent showed only one sharp resonance besides the small protonated tetrahydrofuran peaks. The latter were the correct distance apart and were used to determine the chemical shift.[48]

Reaction of Lithium Cyclononatetraenide with Water.—9-Chlorobicyclo[6.1.0]nonatriene (1.39 g., 0.009 mole) was added to lithium (0.44 g., 0.06 g.-atom) in dry THF (5 ml.) at −78° under a nitrogen atmosphere. The mixture was stirred for 3 hr. at −78°, allowed to warm to 0°, and stirred further for 1 hr. A pH 7 buffer (75 ml. prepared from 50 ml. of 1 *M* potassium dihydrogen phosphate and 30 ml. of 1 *M* sodium hydroxide made up to 100 ml. with distilled water) was added with vigorous agitation; a white precipitate formed. The mixture was extracted with pentane (4 × 25 ml.), and the organic extracts were washed with water (1 × 25 ml.) and dried over anhydrous magnesium sulfate. Removal of the pentane left a pale yellow oil (0.73 g.), which, after vacuum distillation and vapor phase chromatography on a di-*n*-decyl phthalate column (6 ft., 114°, 15 p.s.i. helium), gave 8,9-dihydroindene (0.33 g. (32%)), identical with an authentic sample (infrared, ultraviolet, n.m.r., tetracyanoethylene adduct m.p. 229–230°, mixture m.p.) prepared by rearrangement of bicyclo[6.1.0]nonatriene.

Reaction of Potassium Cyclononatetraenide with Water.—This was carried out as described in the preceding paragraph, except that the anion was prepared from 9-methoxybicyclo[6.1.0]nonatriene (1.08 g., 0.0073 mole) and potassium (0.94 g., 0.024 mole). 8,9-Dihydroindene (0.233 g., 27%) was obtained.

Reaction of Lithium Cyclononatetraenide with Deuterium Oxide.—9-Chlorobicyclo[6.1.0]nonatriene (1.42 g., 0.0093 mole) was introduced into a U-tube that had a sintered disk and a side arm tube with a break seal on one limb and a Ŧ 19/38 joint on the other. Lithium (0.48 g., 0.07 g.-atom) was added to the tube (care being taken to prevent mixing) and THF (5 ml.) was transferred through a vacuum manifold. The tube was sealed and the contents stirred at −78° and allowed to warm slowly to room temperature. The stirring was continued for 12 hr., and the mixture was then filtered through the sintered disk. The side arm tube was evacuated through a serum cap, and deuterium oxide (25 ml.) introduced into it. The break seal was destroyed, and the anion quenched with the deuterium oxide. The mixture was extracted with pentane (3 × 40 ml.) and the organic layer washed with water (2 × 50 ml.) and dried over anhydrous magnesium sulfate. The solvent was removed, and the yellow oil (0.57 g.) was distilled. The distillate was chromatographed in the vapor phase on a di-*n*-decyl phthalate column (6 ft., 114°, 15 p.s.i. helium), and 1-deuterio-8,9-dihydroindene (0.260 g. (24%)) was obtained, ν 2180 cm.$^{-1}$ (C–D); n.m.r.: 4.4 (multiplet, 5.8 H), 7.1 τ (multiplet, 3.2 H).

Deuterium analysis was carried out on three samples prepared in this way,[49] and two of these samples were subjected to mass spectrometric analysis[32]: I, 9.40 atom % excess deuterium. II, 9.60 atom % excess deuterium: C_9H_9D 97%, C_9H_7D 0.9%,[50] C_9H_{10} 2.0%, $C_9H_8D_2$ 0.1%. III, 9.38 atom % excess deuterium: C_9H_9D 92.4%, C_9H_7D 5.1%,[50] C_9H_{10} 2.1%, $C_9H_8D_2$ 0.4%.

Reaction of Potassium Cyclononatetraenide with Deuterium Oxide.—The reaction was carried out as described in the preceding paragraph, except that the anion was prepared from 9-methoxybicyclo[6.1.0]nonatriene (1.08 g., 0.0077 mole) and potassium (0.94 g., 0.024 g.-atom). The 1-deuterio-8,9-dihydroindene (0.233 g. (27%)) was enriched with 9.46 atom % excess of deuterium.[49]

Reaction of Potassium Cyclononatetraenide with Methyl Iodide.—Potassium cyclononatetraenide (0.037 mole) in THF (100 ml.) was added to vigorously stirred methyl iodide (100 ml.) at −10° over a period of 1 hr. The mixture turned pale yellow and a precipitate formed. After completion of addition, the mixture was allowed to warm to room temperature and was stirred for a further 2 hr. Sufficient water was then added to dissolve the precipitated salt, and the layers were separated. The aqueous layer was washed with ether (3 × 50 ml.), and the combined organic layers were dried over anhydrous magnesium sulfate. After the solvent was removed, the residue was distilled and a fraction, b.p. 41–46° (1.6 mm.) (1.83 g., 38%), was obtained; v.p.c. (*n*-didecyl phthalate, 3 ft., 110°, 10 p.s.i. He) showed 2 major and 3 minor components. The major component (> 50%) was collected and shown to be 1-methyl-8,9-dihydroindene; $\lambda_{\max}^{\mathrm{EtOH}}$ 263 (log ϵ 3.76), 270 mμ (3.68); n.m.r.: 4.2 (multiplet, 5.80 H), 6.90 (broad multiplet 2.94 H), 8.9 τ (multiplet, 3.26 H).

Anal. Calcd. for $C_{10}H_{12}$: C, 90.84; H, 9.15. Found: C, 90.85; H, 9.00.

The other major component was collected and identified (n.m.r., ultraviolet, infrared) as 8,9-dihydroindene.

Preparation of 1-Carboxy-8,9-dihydroindene.—9-Methoxybicyclo[6.1.0]nonatriene (1.49 g., 0.011 mole) was added to potassium (1.0 g., 0.025 g.-atom) in THF (20 ml.) at −78° under nitrogen atmosphere. The mixture was stirred for 2 hr. at −78° and then allowed to warm slowly to room temperature and stirred for a further 12 hr. Dry carbon dioxide was bubbled through the stirred mixture for 30 min.; *t*-butyl alcohol was then added to destroy the excess potassium, and sufficient water was added to dissolve the precipitate that had formed. The solution was extracted with ether (3 × 50 ml.), and the organic layer was washed with water (1 × 50 ml.). The combined aqueous layers were acidified with 6 *N* hydrochloric acid and extracted with ether (4 × 50 ml.). The ethereal extract was dried over anhydrous magnesium sulfate. The ether was removed under reduced pressure, and the solid which remained (0.59 g.) was sublimed to yield 0.47 g. of 1-carboxy-8,9-dihydroindene (30%, m.p. 51–52°); $\lambda_{\max}^{\mathrm{EtOH}}$ 262 (log ϵ 3.51), 270 mμ (3.49); ν 1740 cm.$^{-1}$ (C=O).

Anal. Calcd. for $C_{10}H_{10}O_2$: C, 74.05; H, 6.22. Found: C, 73.92; H, 6.28.

The maleic anhydride adduct, prepared by the method of Bangert and Boekelheide[15] and recrystallized from ethyl acetate, melted at 210–211°. Comparison with an authentic sample[33] showed they were identical (m.p., m.m.p. 210–211°, infrared).

Ultraviolet Spectrum of the Cyclononatetraenyl Anion. (i) **Prepared from Lithium Cyclononatetraenide.**—9-Chlorobicyclo[6.1.0]nonatriene (2 μl., 0.0231 g., 0.00015 mole) was introduced into a U-tube fitted on one limb with a sintered disk and 0.1-mm. quartz cell attached with picene to the U-tube through a Ŧ 14/10 joint and on the other with a Ŧ 19/38 joint. Lithium (0.141 g., 0.02 g.-atom) was added; THF (15 ml.) was transferred through a vacuum manifold, the evacuated tube sealed, the mixture stirred, and the ultraviolet spectrum examined at intervals. The maxi-

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[48] The THF peaks appear at τ 6.37 and 8.21 (G. V. D. Tiers, "Characteristic Nuclear Magnetic Resonance (NMR) 'Shielding Values' (Spectral Positions) for Hydrogen in Organic Structures," Central Research Lab., Minnesota Mining and Manufacturing Co., St. Paul 6, Minn., 1958).

[49] Falling drop analyses were performed by J. Nemeth, Urbana, Ill.

[50] The deuterated indene may be an impurity in the 9-chloro[6.1.0]-nonatriene, or it may arise in the mass spectrometer. The latter appears more reasonable as indene is easily separated from 8,9-dihydroindene on the di-*n*-decyl phthalate column used for chromatography.

mum extinction was reached after 36 hr., and after 96 hr. the extinction began to decrease, probably owing to air leaking into the sample; $\lambda_{\max}^{\mathrm{THF}}$ 251 (log ε 5.0), 319 (3.7), 322 mμ (3.7).

(ii) **Preparared from Potassium Cyclononatetraenide.**—The anion was prepared from 9-methoxybicyclo[6.1.0]nonatriene (2 μl. 0.0204 g., 0.000146 mole) and potassium (0.63 g., 0.016 g.-atom) in 15 ml. of THF in the apparatus described in the preceding paragraph. Early spectra had a peak at 272 mμ (log ε 4.3) that later disappeared as the 249 mμ absorption increased in intensity. The maximum extinction of the 249 mμ absorption was reached after 62 hr.; $\lambda_{\max}^{\mathrm{THF}}$ 249 (log ε 5.0), 314 (ε 4.0), 320 mμ (4.0).

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Thermal and Photosensitized Dimerizations of Cyclohexadiene

By Donald Valentine,[1a] Nicholas J. Turro, Jr.,[1b] and George S. Hammond

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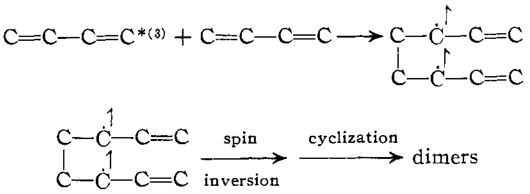
Photosensitized dimerization of 1,3-cyclohexadiene gives 90% yields of *trans-cis-trans*-tricyclo[6.4.0.0^{2,7}]-dodeca-3,11-diene (**3**), the corresponding *cis-cis-cis*-isomer (**4**), and *exo*-dicyclohexadiene (**2**) in 3:1:1 ratios. Traces of *endo*-dicyclohexadiene (**1**) are also formed. Thermal dimerization of cyclohexadiene gives only **1** and **2** in 4:1 ratio. Novel interconversions of the dimers have been studied. At high temperature **3** and **4** both rearrange to yield, respectively, **1** and **2**. At and below room temperature, however, **1** and **2** revert slowly to **3** and **4** by what is believed to be a surface-catalyzed path.

Introduction

Photosensitized dimerizations have been reported for butadiene, isoprene, cyclopentadiene, and several related systems.[2-5] The mechanism of these reactions is believed to involve four steps

$$\underset{\text{(sensitizer)}}{\mathrm{S}} \xrightarrow{h\nu} \underset{\substack{\text{(excited singlet)}\\ \text{sensitizer}}}{\mathrm{S}^{*(1)}} \longrightarrow \underset{\substack{\text{(triplet)}\\ \text{sensitizer}}}{\mathrm{S}^{*(3)}}$$

$$\mathrm{S}^{*(3)} + \mathrm{C{=}C{-}C{=}C} \longrightarrow \mathrm{S} + \mathrm{C{=}C{-}C{=}C}^{*(3)}$$



$$\mathrm{C{=}C{-}C{=}C}^{*(3)} + \mathrm{C{=}C{-}C{=}C} \longrightarrow \begin{array}{l} \mathrm{C{-}\overset{\upharpoonright}{\dot{C}}{-}C{=}C} \\ \ | \qquad \upharpoonright \\ \mathrm{C{-}\dot{C}{-}C{=}C} \end{array}$$

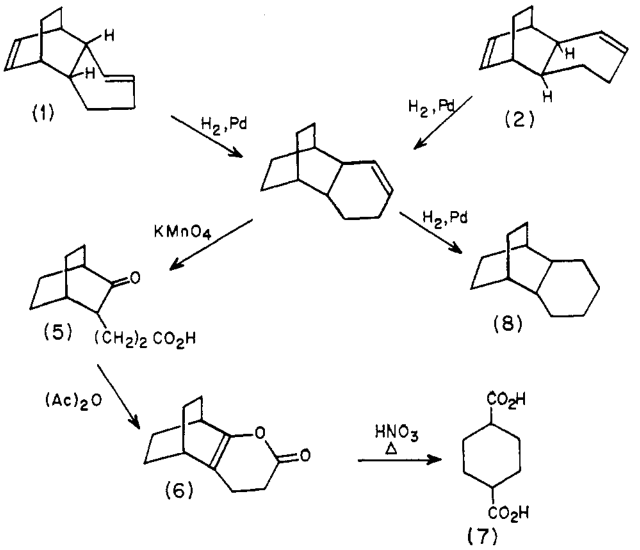
$$\begin{array}{l} \mathrm{C{-}\overset{\upharpoonleft}{\dot{C}}{-}C{=}C} \\ \ | \qquad \upharpoonleft \\ \mathrm{C{-}\dot{C}{-}C{=}C} \end{array} \xrightarrow[\text{inversion}]{\text{spin}} \xrightarrow{\text{cyclization}} \text{dimers}$$

Generally the products of photosensitized and thermal dimerizations of conjugated dienes are different and, at least in the case of cyclopentadiene,[3] the processes appear to proceed through different intermediates. This has been adduced as evidence[3] against a recent formulation of Diels–Alder intermediates as biradicals.[6]

We present here a study of the thermal and photosensitized dimerizations of 1,3-cyclohexadiene. Novel low temperature rearrangements of the dimers are described.

Results and Discussion

Alder and Stein reported isolation of a single product from the thermal dimerization of 1,3-cyclohexadiene at 200°.[7] The structure of the dimer was shown to be either **1** or **2** by the following chemical evidence



The dimerization was repeated and analysis of the products by vapor phase chromatography using Apiezon J columns showed two dimers in a 4:1 ratio. Since the analytical procedure of Alder and Stein could not have shown that **1** and **2** were different compounds because of the initial hydrogenation step, it was suspected that the two dimers observed were **1** and **2**. Hydrogenation of the dimers separately lead to the same saturated hydrocarbon, tricyclo[6.2.2.0^{2,7}]dodecane (**8**), confirming that the dimers are the *endo-exo* isomer pair **1** and **2**.

The major thermal dimer has b.p. 226° (746 mm.), $n^{20}\mathrm{D}$ 1.5250. Its n.m.r. spectrum in carbon tetrachloride consists of a quintet centered at τ 4.04, a broad region with maximum at τ 4.58, and broad partially resolved bands from τ 7.61 to 9.00. The relative areas of the three groups are 2:2:12. The

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