-oil at room temperature and had infrared and proton magnetic resonance spectra consistent with a compound of this structure.

O,O'-Dibenzoyldihydroxyphenylmethane (19i) was synthesized using a procedure identical with that of 19j with comparable yields, m.p. 61.5–62.5°, lit.[8] m.p. 62–63°.

The Reaction of the Cyclooctatetraenyl Dianion with *gem*-Dihalides. The Addition of Alkyl Carbenes to Cyclooctatetraene
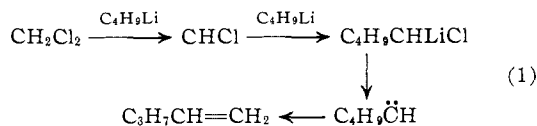
By Thomas J. Katz and Peter J. Garratt

Dipotassium or dilithium cyclooctatetraenide reacts with 1,1-dichloroethane to yield *syn*-9-methylbicyclo-[6.1.0]nonatriene (II) and with 1,1,1-trichloroethane to yield 9-chloro-9-methylbicyclo[6.1.0]nonatriene. A mixture of cyclooctatetraene and methylene chloride reacts with methyllithium containing lithium iodide to give II in low yield and with methyllithium containing lithium bromide to give some II, but mainly *syn*- and *anti*-9-chlorobicyclo[6.1.0]nonatriene (Ia and b). (The predominant *syn* isomer, Ia, is isolated.)

Introduction

Mixtures of methylene chloride, methyl- or *n*-butyllithium in ether, and any of a number of olefins react to form chlorocyclopropanes,[1] apparently through the intermediate divalent carbon species[2] chlorocarbene, which adds to the olefin to yield the observed product. Accompanying this reaction is a side reaction in which *n*-butyllithium, for example, combines with methylene chloride to yield 1-pentene, apparently through the intermediacy of an alkyl carbene (eq. 1).[3]

$$CH_2Cl_2 \xrightarrow{C_4H_9Li} CHCl \xrightarrow{C_4H_9Li} C_4H_9CHLiCl$$
$$C_3H_7CH{=}CH_2 \longleftarrow C_4H_9\ddot{C}H \tag{1}$$

However, one product normally not observed is the alkylcyclopropane that would form if the alkylcarbene added to the olefin. Presumably this reaction cannot compete with others that the alkylcarbenes might undergo, such as intramolecular rearrangement to yield olefins or internal insertion to yield cyclopropanes. It is observed that olefins and, cyclopropanes form in numerous reactions that appear to proceed through the intermediacy of alkylcarbenes[2]— the reaction of alkyllithiums with methylene chloride,[3] the thermal decomposition of salts of toluenesulfonylhydrazones,[4] the thermolysis or photolysis of diazoalkanes,[5] the dehydrohalogenation of alkyl halides,[6] and the reduction of *gem*-dihalides[7]— in a reaction that is rapid, for the lifetime of ethylidene formed in the vapor-phase photolysis

of diazoethane is very short.[5b] Two exceptional reactions of methylene chloride and methyllithium are with benzene, which yields 1-methylcycloheptatriene,[8] and with dimethylacetylene, which yields trimethylcyclopropene,[9] but these undoubtedly proceed through the formation of the expected chlorocarbene adducts, followed by their dissociation to the tropylium and dimethylcyclopropenium cations, which, in turn, are alkylated by the methyllithium. There are some cases reported in which alkylcarbenes undergo intermolecular reaction. These include reactions of ethylidene in the vapor phase, even with propylene, to yield some dimethylcyclopropanes (but not with *cis*- or *trans*-2-butene to yield trimethylcyclopropanes)[5b] and in ether solution with phenylsilane to yield phenylethylsilane.[10] Another reaction that may be of this kind, reported after the completion of our work, is that of styrene with methylene chloride and methyllithium, which yields 1-phenyl-2-methylcyclopropane.[11]

Considering these results, the reaction of cyclooctatetraene with methylene chloride and methyllithium is surprising. The 9-chlorobicyclo[6.1.0]nonatriene (Ia or b), the expected product of the reaction, was sought as an intermediate for the synthesis of the cyclononatetraenyl anion,[12,13] but initial experiments yielded none of this material. Instead, there was discovered in low yield (*ca.* 3%) *syn*-9-methylbicyclo[6.1.0]nonatriene (II). This reaction and the reaction of dipotassium cyclooctatetraenide with *gem*-dihalides, a more felicitous procedure for adding alkylcarbene fragments to cyclooctatetraene, are reported below.

Ia   Ib   II
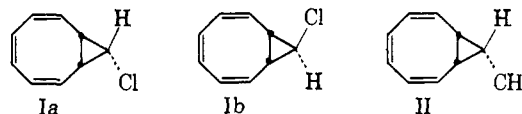
(1) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **82**, 5723 (1960).

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

(3) G. L. Closs, *J. Am. Chem. Soc.*, **84**, 809 (1962).

(4) (a) L. Friedman and H. Schechter, *ibid.*, **81**, 5512 (1959); **82**, 1002 (1960); (b) J. W. Powell and M. C. Whiting, *Tetrahedron*, **7**, 305 (1959).

(5) (a) H. M. Frey and I. D. R. Stevens, *J. Am. Chem. Soc.*, **84**, 2647 (1962); (b) H. M. Frey, *Chem. Ind.* (London), 218 (1962).

(6) (a) W. Kirmse and W. von E. Doering, *Tetrahedron*, **11**, 266 (1960); (b) L. Friedman and J. G. Berger, *J. Am. Chem. Soc.*, **83**, 492, 500 (1961); (c) P. S. Skell and A. P. Krapcho, *ibid.*, **83**, 754 (1961).

(7) (a) W. Kirmse, *Angew. Chem.*, **74**, 183 (1962); (b) W. R. Moore, H. R. Ward, and R. F. Merritt, *J. Am. Chem. Soc.*, **83**, 2019 (1961); W. R. Moore and H. R. Ward, *J. Org. Chem.*, **25**, 2073 (1960); (c) W. T. Miller and C. S. Y. Kim, *ibid.*, **81**, 5008 (1959).

(8) G. L. Closs and L. E. Closs, *Tetrahedron Letters*, **No. 10**, 38 (1960).

(9) G. L. Closs and W. A. Böll, *J. Am. Chem. Soc.*, **85**, 3796 (1963).

(10) K. A. W. Kramer and A. N. Wright, *Tetrahedron Letters*, **No. 24**, 1095 (1962).

(11) W. L. Dilling, *J. Org. Chem.*, **29**, 960 (1964).

(12) (a) T. J. Katz and P. J. Garratt, *J. Am. Chem. Soc.*, **85**, 2852 (1963); (b) E. A. LaLancette and R. E. Benson, *ibid.*, **85**, 2853 (1963).

(13) T. J. Katz and P. J. Garratt, *ibid.*, in press.

Results

The reaction product of cyclooctatetraene, methylene chloride, and methyllithium in ether, a liquid, b.p. 53° at 4.5 mm., is a hydrocarbon, $C_{10}H_{12}$. Its ultraviolet spectrum, λ_{max}^{EtOH} 252 mμ (log ϵ 3.71), is characteristic of bicyclo[6.1.0]nonatrienes[14]; its n.m.r. spectrum (Fig. 1) consists of two multiplets of equal intensity around τ 4.2 and 8.8,[16] and its infrared spectrum shows absorption bands at 2962, 2870, 1442, and 1385 cm.$^{-1}$, characteristic of compounds with C-methyl groups.[17] Ozonolysis of the compound yields cis-3-methyl-1-cis-2-cyclopropanedicarboxylic acid.[18] These data prove that the hydrocarbon is syn-9-methylbicyclo[6.1.0]nonatriene.

To test whether the hydrocarbon appears as a result of a sequence of reactions in which the expected 9-chlorobicyclo[6.1.0]nonatriene forms initially and is alkylated subsequently, anti-9-chlorobicyclo[6.1.0]nonatriene, prepared in another way,[12a,13] was treated with methyllithium to determine whether 9-methylbicyclo[6.1.0]nonatriene would form. None of this hydrocarbon could, however, be isolated from the largely polymeric reaction product. The possibility that 9-chlorobicyclo[6.1.0]nonatriene forms and then reacts with methyllithium to give lithium cyclononatetraenide[12,13] and methyl chloride,[19] which in turn combine to yield the observed 9-methylbicyclo[6.1.0]nonatriene, was also considered, but rejected when it was found that potassium cyclononatetraenide in tetrahydrofuran (THF) fails to react with methyl chloride. The improbability of this sequence accounting for the observed product is also suggested by the observation that with other electrophiles the cyclononatetraenyl anion reacts to yield derivatives, not of bicyclo[6.1.0]nonatriene, but of 8,9-dihydroindene. Thus it reacts with water to yield 8,9-dihydroindene,[12a,13] with· carbon dioxide to yield 1-carboxy-8,9-dihydroindene, and with methyl iodide to yield 1-methyl-8,9-dihydroindene.[13]

The implication remains that the 9-methylbicyclo[6.1.0]nonatriene may form by the addition of ethylidene to cyclooctatetraene. The possibility of preparing the hydrocarbon from cyclooctatetraene and ethylidene generated in another way was, therefore, investigated. Bicyclo[6.1.0]nonatriene and its 9-chloro and 9,9-dichloro derivatives are formed when dipotassium or dilithium cyclooctatetraenide is combined, respectively, with methylene chloride, chloroform, and carbon tetrachloride,[12a,13] a reaction that possibly occurs by the initial formation and then combination of cyclooctatetraene and a divalent carbon species. It was the feasibility of similarly preparing 9-methylbicyclo[6.1.0]-
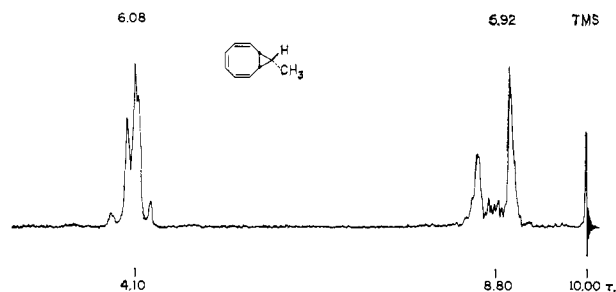
(14) Bicyclo[6.1.0]nonatrienes have ultraviolet maxima at 248 ± 3 mμ (log ϵ ca. 3.6).[12a,13,15]

(15) (a) K. F. Bangert and V. Boekelheide, J. Am. Chem. Soc., 86, 905 (1964); (b) E. Vogel, W. Wiedemann, H. Kiefer, and W. F. Harrison, Tetrahedron Letters, No. 11, 673 (1963); cf. E. Vogel, Angew. Chem., 73, 548 (1961); (c) T. S. Cantrell and H. S. Shechter, J. Am. Chem. Soc., 85, 3300 (1963).

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

(17) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden–Day, Inc., San Francisco, Calif., 1962.

(18) (a) M. G. Ettlinger, S. H. Harper, and F. Kennedy, J. Chem. Soc., 922 (1957); (b) M. G. Ettlinger and F. Kennedy, Chem. Ind. (London), 891 (1957).

(19) D. E. Applequist and D. F. O'Brien, J. Am. Chem. Soc., 85, 743 (1963); cf. G. L. Closs and G. M. Schwartz, ibid., 82, 5729 (1960).

Fig. 1.—N.m.r. spectrum of II in CCl_4; TMS is the internal standard. Above each peak its integrated intensity is given.

nonatriene from dilithium cyclooctatetraenide[20] and 1,1-dichloroethane which was, therefore, examined (eq. 2, R = H).

$$\text{(eq. 2)}$$
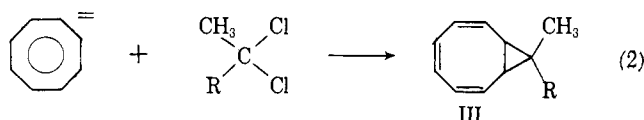
The reaction occurs readily at −30°, and the 9-methylbicyclo[6.1.0]nonatriene is isolated in 20% yield. Only one such substance could be identified, the syn isomer II, identical with that formed from cyclooctatetraene, methylene chloride, and methyllithium.

Unexpected was the discovery that the reaction of cyclooctatetraene with methylene chloride and methyllithium takes a completely different course if the source of one of the reagents, the solution of methyllithium in ether, is changed. Although the 9-methylbicyclo[6.1.0]nonatriene is the only isolable product if the methyllithiuum in ether used is prepared from methyl iodide and lithium metal following the usual laboratory procedure,[21] when the commercially available reagent[22] is used, the isolable reaction product consists, instead, largely of an approximately 4:1 mixture of syn- (Ia) and anti-9-chlorobicyclo[6.1.0]nonatrienes[12b] (Ib), accompanied by small amounts of syn-9-methylbicyclo[6.1.0]nonatriene (II).[13] This difference probably arises because the former "methyllithium" contains an equivalent amount of lithium iodide, whereas the latter contains an equivalent of lithium bromide.

The syn-9-chlorobicyclo[6.1.0]nonatriene (Ia) could be isolated by distillation in essentially pure form (contaminated by only small amounts of the anti isomer) from the reaction product of which it is the major component. It was identified by its ultraviolet spectrum (λ_{max}^{EtOH} 250 mμ, log ϵ 3.48), and its n.m.r. spectrum. The latter shows a multiplet at τ 4.0 attributed to the olefinic protons, and a coupled triplet at 6.55 and doublet at 8.23 (J = 7 c.p.s.) attributed to the cyclopropyl protons. The gross features of the n.m.r. spectra of the syn and anti[12a,13] isomers are similar, but the chemical shifts of the cyclopropyl resonances, especially of the triplet, and the splitting constants, J, are different. It was the magnitude of the splitting constants (7 and 4 c.p.s.) that was used to assign the stereochemistry to these two isomers.[12,13]

To discover whether salts of the cyclooctatetraenyl dianion react with other gem-dihalides to yield the cyclooctatetraene adducts of alkylcarbenes, the reaction of dipotassium cyclooctatetraenide with 1,1,1-trichloro-

(20) T. J. Katz, ibid., 82, 3784, 3785 (1960).

(21) H. Gilman, E. A. Zoellner, and W. M. Selby, ibid., 55, 1252 (1933).
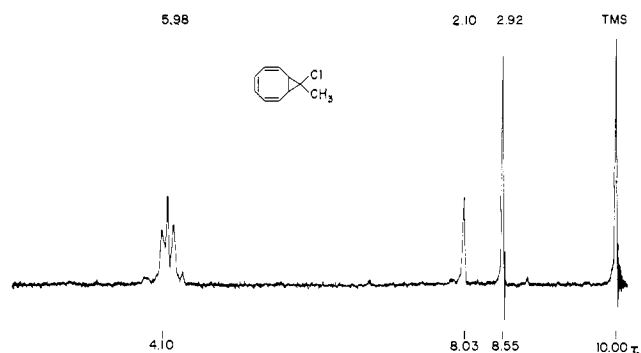
(22) Lithium Corp. of America.

Fig. 2.—N.m.r. spectrum of III (R = Cl) in CCl₄; TMS is the internal standard. Above each peak its integrated intensity is given.

ethane was studied. Indeed, 9-chloro-9-methylbicyclo-[6.1.0]nonatriene is formed (eq. 2, R = Cl). The compound was identified by its analysis, its ultraviolet spectrum (λ_{max}^{EtOH} 249 mμ, log ϵ 3.61), characteristic of bicyclo[6.1.0]nonatrienes,[14] and its n.m.r. spectrum (Fig. 2).[16] The latter consists of three groups of lines of relative intensity 5.98, 2.10, and 2.92, a multiplet attributed to the olefinic protons at τ 4.1, a singlet attributed to the cyclopropyl protons at τ 8.03, and a singlet attributed to the methyl protons at τ 8.55. The simplicity of the n.m.r. spectrum and the homogeneity exhibited by the material when it is subjected to vapor phase chromatography imply that only one of the two possible epimers is present.

Discussion

These are the only known reactions of utility in synthesis in which alkylcarbene fragments add to an olefin.[23] The following data suggest that the reactions of alkali cyclooctatetraenides with gem-dihalides proceed by a path in which the dipotassium cyclooctatetraenide reduces the dihalo compound to a species, possibly, although not necessarily, divalent, which adds to the cyclooctatetraene fragment rather than by a path of direct displacement. Methylene chloride is unreactive toward SN2 displacement,[25,26] and replacement of its hydrogens by either methyl or chlorine is expected to have a further deactivating effect.[25] Moreover, with alkali metals or organolithium compounds gem-dihalides do undergo reactions that appear to proceed through the divalent reduction product of the gem-dihalide.[7,24] Furthermore, dipotassium cyclooctatetraenide is a good reducing agent,[27] and reacts with another electrophile, the trimethylpyrylium cation, not by alkylating it, but by reducing it.[28] Lastly, the

reactivity of dipotassium cyclooctatetraenide toward gem-dihalides increases from methylene chloride to chloroform to carbon tetrachloride in opposition to expectation based on a mechanism of direct displacement, but as might be expected if the initial step were reduction of the alkyl halide.

The formation of syn-9-methylbicyclo[6.1.0]nonatriene (III) from cyclooctatetraene, methylene chloride, and methyllithium (containing lithium iodide) and from dilithium cyclooctatetraenide and 1,1-dichloroethane may take place through mechanisms that are similar in that the same carbene species formed in different ways (by eq. 1 and by reduction of the gem-dihalide) adds to cyclooctatetraene.[29]

Two aspects of the reactions are not clearly analyzed. One is the role of the alkali halide in the reaction of cyclooctatetraene, and possibly other olefins, with methylene chloride and methyllithium. The products change markedly depending upon which halide is present in the methyllithium reagent,[30] suggesting, as does other evidence based on the difference in reactivity of the same carbene generated by decomposition of a diazo compound and by dehydrohalogenation,[31] that carbenes are complexed by alkali halides.[32] The effect may, however, be much less fundamental. One of the methyllithium reagents may destroy 9-chlorobicyclo-[6.1.0]nonatriene more rapidly than the other.

Unexplained also is what determines the stereochemistry of the product. The syn isomer of 9-methylbicyclo[6.1.0]nonatriene is the only one isolated from either of the two ways of adding the methyl carbene fragment to cyclooctatetraene although this isomer is presumably more sterically hindered and less stable than its anti epimer. syn isomers are often[33,34] found to be the major (although not usually exclusive) products of carbene addition reactions, and even in the vapor phase photochemical reaction of diazoethane with propylene, the cis-1,2-dimethylcyclopropane predominates over the trans isomer.[5b,33a] Cyclooctatetraene follows this precedent in yielding mainly syn-9-chlorobicyclo[6.1.0]nonatriene (Ia) as the major product of its reaction with methylene chloride and methyllithium (containing lithium bromide), but it appears to do just the opposite in the reaction of dipotassium or dilithium cyclooctatetraenide in THF with chloroform; mainly the anti epimer Ib results.[12a,13] Stereospecificity is also exhibited in the formation of 9-chloro-9-methylbicyclo[6.1.0]nonatriene (III, R = Cl) from dipotassium cyclooctatetraenide and 1,1,1-trichloroethane for whichever isomer forms appears to be homogeneous.

(23) (a) Photolysis of mixtures of diazoethane and propylene in the vapor phase yields traces of cis- and trans-dimethylcyclopropane.[5b] (b) The reaction of styrene with methylene chloride and methyllithium might be of this kind.[11] (c) A preliminary communication suggests that a mixture of alkyl-substituted gem-dihalides and olefins might react with lithium in THF to give alkylcyclopropanes, but no examples of this reaction have been reported [cf. O. M. Nefedov, A. A. Ivashenko, M. N. Manakov, B. I. Shiryaev, and A. D. Petrov, Bull. Acad. Sci. USSR (English Trans.), 343 (1962)]. (d) Cyclopropylidenes appear more stable to internal rearrangement than other alkylcarbenes, for they have been trapped by olefins.[7b,24]

(24) W. M. Jones, M. H. Grasley and D. G. Baarda, J. Am. Chem. Soc., 86, 912 (1964).

(25) J. Hine, C. H. Thomas, and S. J. Ehrenson ibid., 77, 3886 (1955); J. Hine, S. J. Ehrenson, and W. H. Bader, Jr., ibid., 78, 2282 (1956).

(26) Even a primary alkyl halide, 1-chloropentane, does not react appreciably with n-butyllithium in ether at −30° during the course of an hour.[3]

(27) T. J. Katz, W. H. Reinmuth, and D. E. Smith, J. Am. Chem. Soc., 84, 802 (1962).

(28) K. Conrow and P. C. Radlick, J. Org. Chem., 26, 2260 (1961).

(29) Phenylcarbene appears to form from phenyllithium and methylene chloride and to be trapped by olefins to yield phenylcyclopropanes (O. M. Nefedov, V. I. Shiryaev, and A. D. Petrov, Zh. Obshch. Khim., 32, 662 (1962); Chem. Abstr., 57, 14,971g (1962).

(30) The methyllithium used by Dilling[11] also was made from methyl iodide.

(31) (a) G. L. Closs and J. J. Coyle, J. Am. Chem. Soc., 84, 4350 (1962); (b) G. L. Closs and L. E. Closs, Angew. Chem., 74, 431 (1962).

(32) W. T. Miller, Jr., and D. M. Whalen, J. Am. Chem. Soc., 86, 2090 (1964).

(33) (a) G. L. Closs, R. A. Moss, and J. J. Coyle, ibid., 84, 4985 (1962); (b) U. Schöllkopf and H. Küppers, Tetrahedron Letters, 105 (1963); (c) U. Schöllkopf and G. S. Lehman, ibid., No. 4, 165 (1962), and G. S. Lehman, Dissertation, University of Heidelberg, 1963, quoted in ref. 33d, footnote 25, and ref. 34, footnote 12; (d) U. Schöllkopf, A. Lerch, and J. Paust, Chem. Ber., 96, 2266 (1963).

(34) syn isomers are not always the major products of carbene additions. Cf. ref. 33d, and U. Schöllkopf and W. Pitteroff, Chem. Ber., 97, 636 (1964).

Experimental

The Perkin–Elmer Model 154 vapor fractometer with thermistor detector was used for all analytical and preparative vapor phase chromatograms. Ultraviolet spectra were determined in 1-cm. quartz cells using the Cary Model 14 spectrophotometer; n.m.r. spectra were determined with tetramethylsilane as the internal standard using the Varian A-60 spectrometer.

syn-9-Methylbicyclo[6.1.0]nonatriene (II). A. From Cyclooctatetraene, Methyllithium (Containing Lithium Iodide), and Methylene Chloride.—Methyllithium in ether, prepared from methyl iodide and lithium[21] (330 ml., 1 N total base titer) was added over a period of 150 min. to a rapidly stirred solution of methylene chloride (57 g., 0.67 mole) and cyclooctatetraene (104 g., 1 mole) maintained at $-10°$ in a nitrogen atmosphere.[1] The mixture was stirred further for 60 min. at $-10°$. Water was added to dissolve the precipitated lithium chloride, the layers were separated, and the aqueous phase was extracted with methylene chloride (three 50-ml. portions). The organic phases were combined, dried (Na$_2$SO$_4$), and distilled at reduced pressure. After methylene chloride and cyclooctatetraene, a fraction, b.p. 44–48° at 5 mm., was collected (1.29 g., 3%). Preparative vapor phase chromatography (v.p.c.) on di-n-decyl phthalate (20% on firebrick, 0.25 in. × 6 ft. column, 138°, 15 p.s.i. He carrier) yielded two components, the major one (80%) identified as syn-9-methylbicyclo[6.1.0]nonatriene.

Anal. Calcd. for C$_{10}$H$_{12}$: C, 90.84; H, 9.15. Found: C, 91.01; H, 9.05.

B. From Dilithium Cyclooctatetraenide and 1,1-Dichloroethane.—Lithium (4.0 g., 0.57 mole) was added in small pieces to dry tetrahydrofuran (THF, 250 ml., freshly distilled from LiAlH$_4$) at $-78°$ in a nitrogen atmosphere. Cyclooctatetraene (26 g., 0.25 mole) was added, the mixture stirred vigorously for 24 hr., allowed to warm to 0°, and stirred at this temperature for 24 hr. and then at room temperature for 24 hr.

The deep green solution of lithium cyclooctatetraenide in THF was added over a 1-hr. period to vigorously stirred cold ($-30°$) 1,1-dichloroethane (250 ml.) under N$_2$. After further stirring for 1 hr. at $-30°$, the mixture was allowed to warm to room temperature and stirred for 8 hr. more. Water (250 ml.) was added, a solid residue filtered, and the filtrate was extracted with ether (six 500-ml. portions). The combined organic layers were washed with water (150 ml.) and saturated sodium chloride and then dried (MgSO$_4$). The solvent was removed at reduced pressure and the residue distilled to yield 7.07 g. (20%) of 9-methylbicyclo[6.1.0]nonatriene, b.p. 35° at 0.8 mm.

The samples of the hydrocarbon made by procedure A and B above have identical n.m.r. spectra.

Ozonolysis of syn-9-Methylbicyclo[6.1.0]nonatriene.—The procedure of Winstein and Sonnenberg was used.[35] An oxygen stream containing ozone was passed through a solution of II (0.40 g., 3 mmoles) in glacial acetic acid (8 ml.) and acetic anhydride (4 ml.) at 0° until the effluent gas reacted with KI solution and for 10 min. thereafter. Hydrogen peroxide (2 ml., 30% Merck) and water (12 ml.) were added and the mixture was refluxed for 16 hr. Some of the water was boiled away and the sample was evaporated to dryness *in vacuo*. The pale brown liquid residue that solidified on cooling was recrystallized from benzene to yield 0.195 g. (47%) of the diacid. A sample recrystallized from ethyl acetate (a better solvent for this than benzene), m.p. 130–130.5°, was identical in m.p., mixture m.p., infrared, and n.m.r. (in D$_2$O) with a sample of cis-3-methyl-1-cis-2-cyclopropanedicarboxylic acid, prepared from Feist acid.[18]

Attempted Reaction of Potassium Cyclononatetraenide with Methyl Chloride.—Gaseous methyl chloride was bubbled for 45 min. through a rapidly stirred solution of potassium cyclononatetraenide (0.06 mole)[12a,13] prepared under N$_2$ in 120 ml. of THF at 17°. The mixture was stirred at room temperature for 15 hr., methyl chloride added for another 45 min., and stirred further for 6 hr. Water was added (exothermic!) and the mixture cooled and extracted with ether (3 × 75 ml.). The organic layers were washed with water (2 × 50 ml.) and satu-

rated sodium chloride solution (50 ml.), dried over MgSO$_4$, and the solvent was removed under reduced pressure. Distillation yielded 2.7 g. (39%) of 8,9-dihydroindene,[12a,13] b.p. 32–33° at 2 mm.

Reaction of Methyllithium with anti-9-Chlorobicyclo[6.1.0]nonatriene.—To Ib (1.48 g., 0.01 mole) in ether (0.5 ml.) at $-50°$, methyllithium in ether[22] (10 ml., 1.94 N, 0.0194 mole) was slowly added while stirring in a nitrogen atmosphere. A purple color developed. The solution was stirred at $-50°$ for 1 hr., allowed to warm to room temperature for 1 hr., cooled to $-20°$, and quenched with water. Extraction with ether (three 20-ml. portions) yielded, after drying (MgSO$_4$) and removal of solvent, only undistillable material. The reaction, when carried out using THF (10 ml.) in place of ether and adding the methyllithium at $-10°$, yielded a similar result.

9-Chloro-9-methylbicyclo[6.1.0]nonatriene.—Dipotassium cyclooctatetraenide (0.25 mole) in THF (ca. 250 ml.) was added slowly under a nitrogen atmosphere to 200 ml. of rapidly stirred 1,1,1-trichloroethane at $-10°$. After completion of addition, the mixture was stirred at $-10°$ for 2 hr. and further for 15 hr. at room temperature. Water was added to dissolve the precipitated salts, and the layers separated. The aqueous layer was washed with ether (four 150-ml. portions), and the combined organic layers were washed with water (150 ml.) and saturated brine (100 ml.), and dried (MgSO$_4$). The solvents and product were distilled at reduced pressure. A fraction b.p. 29–30° (0.1 mm.) was collected (20.1 g.). Redistillation afforded little further purification, but v.p.c. on a column of SE-30 coated on firebrick (0.25 in. × 3 ft., 120°, 15 p.s.i. He carrier) showed three main peaks. A sample of 500 mg. was purified preparatively by injecting 50 μl. at a time. The component with the largest retention time was collected (210 mg.), rechromatographed, and identified as 9-chloro-9-methylbicyclo[6.1.0]nonatriene.

Anal. Calcd. for C$_{10}$H$_{11}$Cl: C, 72.07; H, 6.65; Cl, 21.28. Found: C, 72.40, 72.08; H, 6.76, 6.94; Cl, 21.12, 20.98.

Reaction of Methyllithium (Containing LiBr) with Methylene Chloride and Cyclooctatetraene.—Methyllithium (180 ml., 1.9 N in ether, 0.34 mole)[22] was added over a period of 150 min. to a rapidly stirred solution of methylene chloride (57 g., 0.67 mole) and cyclooctatetraene (90 g., 0.86 mole) at $-10°$ under a nitrogen atmosphere. After completion of the addition, the mixture was stirred for a further 60 min. at $-10°$, and then allowed to come to room temperature. Water was added to dissolve the precipitated lithium chloride, the organic layers were separated, the aqueous layer was extracted with ether (four 100-ml. portions), and the combined organic layers were dried over MgSO$_4$. The solvent and most of the excess cyclooctatetraene were removed at reduced pressure, and the residue was distilled. Two fractions were collected: fraction 1, b.p. 28–30° at 0.2 mm. (1.2 g.), and fraction 2, b.p. 31° at 0.15 mm. (4.7 g.).

Fraction 1 on v.p.c. (di-n-decyl phthalate on firebrick, (0.25 × 6 ft., 144°, 25 p.s.i. He) gave an unidentified minor component followed by a mixture of indene[36] and syn-9-methylbicyclo-[6.1.0]nonatriene (II). The latter two were separated by v.p.c. on Carbowax 1000 on firebrick (0.25 in. × 6 ft., 100°, 15 p.s.i. He) and identified by spectral comparison with authentic samples.

Fraction 2 was identified by its n.m.r. spectrum as a mixture of syn- and anti-9-chlorobicyclo[6.1.0]nonatrienes (Ia and b) in a ratio of ca. 4:1.[12b] The syn isomer Ia, essentially pure (1.8 g.), was isolated by redistillation, b.p. 31° at 0.10 mm. Its n.m.r. spectrum shows a multiplet at τ 4.0, a triplet (A) at 6.55, and doublet (B) at 8.23 of relative intensity 6.00:0.95:2.05, with $J_{AB} = 7$ c.p.s. Its ultraviolet spectrum in ethanol shows λ_{max} 250 mμ (log ε 3.48).

(35) S. Winstein and J. Sonnenberg, *J. Am. Chem. Soc.*, **83**, 3235 (1961).

(36) Indene is formed from the thermal rearrangement and dehydrohalogenation of 9-chlorobicyclo[6.1.0]nonatriene.[12a,13]