dried over magnesium sulfate. Preparative glpc (20 ft × ³/₈ in., 20% silicone nitrile on Chromosorb P, 60–80 mesh; isothermal at 150°) was used to collect the remaining product. Its infrared and nmr spectra were superimposable on those of an authentic sample of 13 prepared by an independent synthesis described below.

Preparation of Cyclohex-3-en-1-yltrimethyltin (13). To 0.43 g (17 g-atoms) of magnesium turnings in 50 ml of anhydrous ether was added, dropwise, over a period of 5 min, 2.8 g (17 mmoles) of 4-bromocyclohexene-1[24] dissolved in 10 ml of ether. The solution was stirred for 0.5 hr, and then 3.4 g (17 mmoles) of trimethyltin chloride was added over a 10-min period. The mixture was refluxed for 8 hr and then hydrolyzed with a saturated ammonium chloride solution. The ether layer was separated, washed five times with water, and dried over magnesium sulfate. The ether was removed on a rotary evaporator and the product purified by preparative glpc (20 ft × ³/₈ in., 20% silicone nitrile on Chromo-

sorb P, 60–80 mesh, isothermally at 150°, flow rate 200 cc/min) to give 1.0 g (24%) of product.

Preparation of Cyclooct-2-en-1-yltrimethyltin (14). Amalgamated magnesium (3.04 g, 0.125 g-atom) was placed into a flask with 150 ml of ether. To this was added 1 ml of ethylene bromide which reacted rapidly. This was followed by a solution of 3-bromocyclooctene[25] (5.0 g; 25 mmoles) and trimethyltin chloride (10.0 g; 50 mmoles) in 10 ml of ether. After the addition was completed (1.5 hr), the reaction mixture was refluxed for 1 hr, cooled, and filtered, and the residue was washed well with dry ether. To remove excess trimethyltin chloride, the ether solution was washed with a saturated potassium fluoride–water solution, followed by water. The organic layer was dried, concentrated, and distilled to give hexamethylditin (1.47 g, 4.0 mmoles) and cyclooct-2-en-1-yltrimethyltin (2.16 g, 8.0 mmoles; 32%), bp 63.5–68.5° (0.25 mm).

(24) C. A. Grob and W. Baumann, *Helv. Chim. Acta*, **38**, 594 (1955).

(25) A. C. Cope and L. L. Ester, Jr., *J. Am. Chem. Soc.*, **72**, 1129 (1950).

Acylation of Cyclooctatetraene Dianion and the Chemistry of Its Products

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Abstract: Cyclooctatetraene dianion (I) reacts as a 1,2- and a 1,4-dicarbanionic reagent with various acyl halides. Thus I and acetyl chloride give 3,5,7,9-dodecatetraene-2,11-dione (III), *syn*-9-acetoxy-9-methylbicyclo[4.2.1]-nonatriene (V), *syn*-9-hydroxy-9-methylbicyclo[4.2.1]nonatriene (IV), and *syn*-9-acetoxy-9-methylbicyclo[6.1.0]-nonatriene (VI). Benzoyl chloride and I yield *trans,cis,cis,trans*-1,10-diphenyl-2,4,6,8-decatetraene-1,10-dione (XIV) and *syn*-9-benzoyloxy-9-phenylbicyclo[4.2.1]nonatriene (XV); similar products (XIX and XX) are obtained from *p*-bromobenzoyl chloride and I. The lactone XXV of 9-(2-carboxyphenyl)-9-hydroxybicyclo-[6.1.0]nonatriene is obtained from I and phthaloyl chloride. The structures of these products are proven by combination of chemical degradation and synthesis. Pyrolysis of the bicyclo[4.2.1]nonatrienes (V and XV) gives 2-substituted indenes; the bicyclo[6.1.0]nonatriene (VI) yields 3-methylindene. The mechanisms of these pyrolyses are discussed.

One of the important developments of modern structural theory has been the demonstration of the existence[2a,b] and aromatic character[2b,3] of the cyclooctatetraene dianion (I). That I is planar and

I

possesses a delocalized π-electron system has been firmly established[3] and provides a dramatic confirmation of the Hückel rule.

There has been little systematic investigation, however, of the chemistry of the cyclooctatetraene dianion (I). Reppe and his colleagues, in their original work on cyclooctatetraene, report that cyclooctatetraene forms a dilithium derivative which gives on carbonation a dicarboxylic acid assigned the structure 2,5,7-cyclooctatriene-1,4-dicarboxylic acid.[2a] Cope and Hochstein prepared dilithium and disodium derivatives of

cyclooctatetraene; these yield mixtures of 1,3,5- and 1,3,6-cyclooctatrienes on treatment with proton sources.[4]

Alkylation and acylation of cyclooctatetraene dianion (I) were initially described by Azatyan and coworkers.[5,6] Reactions of I with methyl, allyl, and benzyl halides give disubstituted cyclooctatrienes as high-boiling material. Acylation with acetyl chloride is said to yield diacetylcyclooctatriene, a viscous product; benzoyl chloride forms a solid dibenzoylcyclooctatriene, mp 123°.[5,6] The positions of the substituents in all of these products were not specified in the above studies.

Condensation of cyclooctatetraene dianion (I) with acetone, methyl ethyl ketone, benzophenone, benzaldehyde, and cyclohexanone is reported to yield the respective 7,8-bis(α-hydroxyalkyl)-1,3,5-cyclooctatrienes; dehydration of these diols to tetrahydrofuran derivatives is described.[6,7] The product of reaction of cyclooctatetraene dianion with benzophenone is assigned the structure 7,8-bis(α-hydroxybenzhydryl)-1,3,5-cyclooctatriene.[8]

(1) (a) Abstracted in part from the Ph.D. dissertation of T. S. Cantrell, The Ohio State University, Columbus, Ohio, 1964. (b) National Science Foundation Cooperative Fellow, 1961–1962 and 1963–1964. National Science Foundation Graduate Fellow, 1962–1963.

(2) (a) W. Reppe, O. Schlichting, K. Klager, and T. Toepel, *Ann.*, **560**, 1 (1948); (b) T. J. Katz, *J. Am. Chem. Soc.*, **82**, 3784, 3785 (1960); (c) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, Chapter 10.

(3) (a) T. J. Katz, W. H. Reinmuth, and D. E. Smith, *J. Am. Chem. Soc.*, **84**, 802 (1962); (b) H. L. Strauss, T. J. Katz, and G. K. Fraenkel, *ibid.*, **85**, 2360 (1963); (c) H. Keller and H. P. Fritz, *Z. Naturforsch.*, **16b**, 234 (1961); (d) H. P. Fritz and H. Keller, *Ber.*, **95**, 158 (1962).

(4) A. C. Cope and F. A. Hochstein, *J. Am. Chem. Soc.*, **72**, 2515 (1950).

(5) V. D. Azatyan, *Dokl. Akad. Nauk SSSR*, **98**, 403 (1954).

(6) V. D. Azatyan and R. S. Gyuli-Kevkhyan, *Dokl. Akad. Nauk Arm. SSR*, **20**, 81 (1955).

(7) V. D. Azatyan and R. S. Gyuli-Kevkhyan, *Izv. Akad. Nauk Arm. SSR, Otd. Khim. Nauk*, **14**, 451 (1961); *Chem. Abstr.*, **58**, 3327 (1963).

As a result of these reports, I appears to behave as a simple diorganometallic reagent (Ia and Ib) in its reac-

Ia   **Ib**
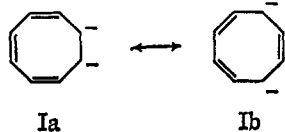
tions, yielding disubstituted 1,3,5- and 1,3,6-cycloocta-trienes. The structural assignments in much of this work reported,[5-8] however, are based on limited evidence, apparently on intuition alone, in some cases; the stereochemistries of the substituents have neither been determined nor discussed. In addition, the physical properties reported for the products make it likely that mixtures rather than pure compounds were obtained in many instances.

In view of these facts and because of the likelihood of finding unusual or novel transformations which might enliven the chemistry of the parent hydrocarbon, it seemed worthwhile to investigate the reactions of I under well-defined conditions. The reactions of I with acyl halides have now been reinvestigated and found to give linear products and a series of bicyclic compounds resulting from unusual intramolecular alkylation[9] rather than the diacylcyclooctatrienes previously described.[5-7] The details of this study of reactions of I with acetyl chloride, benzoyl chloride, p-bromobenzoyl chloride, and phthaloyl chloride are presently described. Very recently, displacement reactions of I with dichlorophenylphosphine and with methyl iodide were reported.[10] These elegant studies complement those described in this and the following paper.

Results

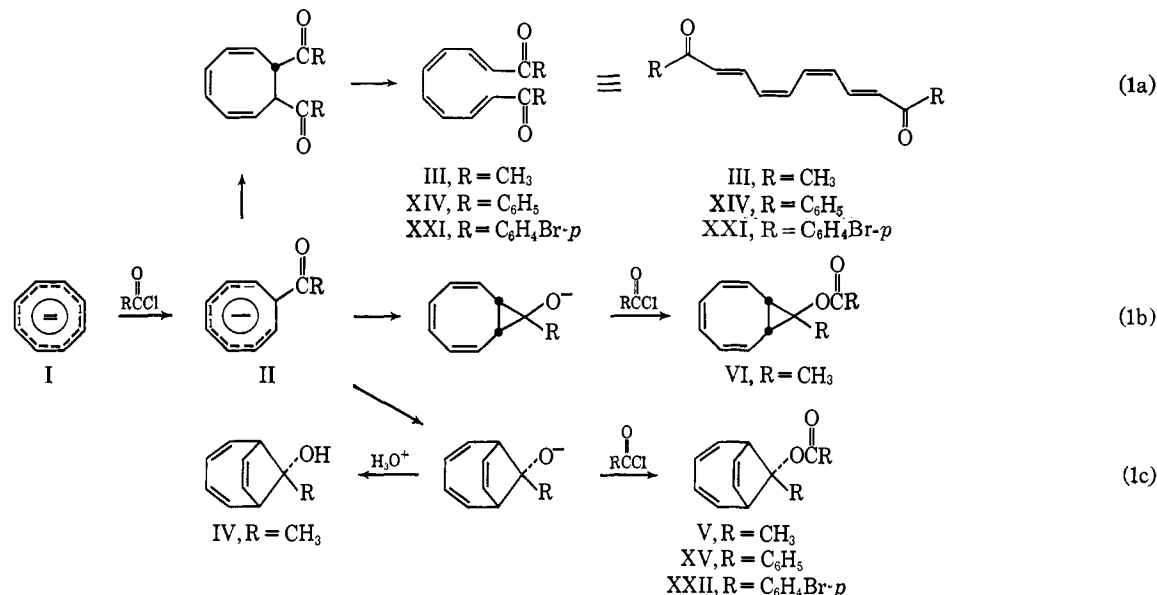Dilithium cyclooctatetraenide (I) is prepared by reaction of ethereal cyclooctatetraene with lithium

methylbicyclo[4.2.1]nona-2,4,7-triene (V, 12–13%), and syn-9-acetoxy-9-methylbicyclo[6.1.0]nona-2,4,6-triene (VI, 19–22%).

Compound III is obtained as yellow leaflets, mp 110°. Its structure can be initially assigned on the basis of its infrared (strong bands at 5.96 and 6.29 μ; conjugated ketone and C=C double bond), ultraviolet (λ_{max} 343, 265, and 211 mμ (ϵ 52,000, 9000, and 10,500), and nuclear magnetic resonance (nmr; multiplets at τ 2.2–3.9, eight acyclic vinyl hydrogens; singlet at τ 7.37, six methyl hydrogens) spectra. Confirmation of the gross structure of III is provided by its hydrogenation to a saturated diketone which is identical with 2,11-dodecanedione prepared from sebacoyl chloride and dimethylcadmium.[12]

Compound III is converted when heated above its melting point, or better, by treatment with a trace of acid in chloroform, to an isomer, VII, yellow needles, mp 137–138°. Compound VII exhibits λ_{max} 346 and 362 mμ (ϵ 63,000 and 65,000) and a strong infrared band at 9.98 μ (trans double bond). From these data and from the methods of formation, it is probable that III and VII differ only in the geometry about one or more of their double bonds.

Formation of III likely involves initial diacylation of I to 7,8-diacetyl-1,3,5-cyclooctatriene, which undergoes valence isomerization to the totally conjugated tetraene, III, as in eq 1a. Ample precedent exists for ring opening of 1,3,5-cyclooctatrienes bearing electron-withdrawing substituents on C-7 and C-8.[13] This process reflects the strain in the disubstituted cyclooctatriene and the stabilization resulting by formation of a fully conjugated product.

Compound III is assigned the trans,cis,cis,trans structure, as arising from the intermediate 7,8-diacetyl-

$$\text{(1a)}$$

III, R = CH₃
XIV, R = C₆H₅
XXI, R = C₆H₄Br-p

III, R = CH₃
XIV, R = C₆H₅
XXI, R = C₆H₄Br-p

$$\text{(1b)}$$

I   **II**   VI, R = CH₃

$$\text{(1c)}$$

IV, R = CH₃

V, R = CH₃
XV, R = C₆H₅
XXII, R = C₆H₄Br-p

under helium. Addition of I in ether to excess acetyl chloride in ether at 0° gives, after hydrolysis and work-up (eq 1), trans,cis,cis,trans-3,5,7,9-dodecatetraene-2,11-dione (III, 7–8%), syn-9-hydroxy-9-methylbicyclo-[4.2.1]nona-2,4,7-triene (IV, 18–19%),[11] syn-9-acetoxy-9-

1,3,5-cyclooctatriene by valence tautomerism; the isomer VII is believed to possess the all-trans stereochemistry shown. The nmr spectrum of III exhibits a

(11) There is, as yet, no official method for designating the stereochemistry of bicyclic compounds in which all three bridges are of different lengths. The convention adopted here uses the longer of the two bridges not bearing the substituent in question as the reference point; a substituent cis to that bridge is designated syn.

(12) J. Cason, J. Am. Chem. Soc., 68, 2078 (1946).

(13) (a) A. C. Cope and D. J. Marshall, ibid., 75, 3208 (1953); (b) H. Hover, Tetrahedron Letters, 256 (1962).

(8) G. Wittig and D. Wittenberg, Ann., 606, 1 (1957).

(9) The preliminary results of this investigation have been reported by T. S. Cantrell and H. Shechter, J. Am. Chem. Soc., 85, 3300 (1963).

(10) (a) T. J. Katz, C. R. Nicholson, and C. A. Reilly, ibid., 88, 3832 (1966); (b) D. A. Bak and K. Conrow, J. Org. Chem., 31, 3958 (1966).
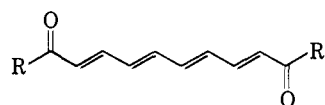
VII, R = CH₃
XVI, R = C₆H₅

pair of doublets at τ 2.38 (J = 15.2 and J' = 11.8 cps) whose chemical shift is indicative of vinyl hydrogens β to a carbonyl group, and a sharp doublet at τ 3.76 (J = 15.2 cps) for the hydrogens α to the carbonyls. The coupling constants of the β-hydrogens are characteristic for vinyl hydrogens *trans* to each other and for vinyl hydrogens on adjacent double bonds, respectively.[14] Clearly, then, the two outer double bonds of III are *trans*. Of the remaining signals in the spectrum of III, a pair of doublets centered at τ 3.05 (J = 7.8 and J' = 2.3 cps) is assigned to the hydrogens δ to the carbonyl groups. The coupling constants are typical *cis*-olefinic and 1,3-coupling constants, respectively; thus the central double bonds are assigned the *cis* stereochemistry.

In the spectrum of the isomeric tetraene VII, resonance of the β-hydrogens appears at τ 2.85 (J = 16.4 and J' = 11.2 cps), and the doublet due to the α-hydrogens occurs at τ 3.52 (J = 16.4 cps). The coupling constants observed thus indicate that the double bonds adjacent to the carbonyl groups of VII still possess *trans* stereochemistry. The γ- and δ-hydrogen signals are complex multiplets at τ 3.3–3.8; the coupling constants could not be determined, but it is apparent from the change in the splitting pattern that the central double bonds have undergone isomerization and are, therefore, *trans*. These stereochemical assignments are supported by the means of transformation of III to VII (heat or acid) and by the ultraviolet spectra of the two compounds. A discussion of the significance of the ultraviolet spectra is deferred until later.

According to the rules governing the stereochemistry of electrocyclic reactions,[15] thermal opening of a cyclooctatriene to a linear octatetraene is a *conrotatory* process, and hence the precursor of III, with its *trans* terminal double bonds, is predicted to be the cyclooctatriene with the acetyl groups *trans*, as in eq 1a. This assignment is speculative at present since the electrocyclic rules have been experimentally confirmed only for C-4 and C-6 cases, and may not hold for the cyclooctatriene–octatetraene system. Conjugated C-4 and C-6 systems can become planar or nearly planar without undue difficulty. A planar or nearly planar C-8 system will involve severe steric strain, and the orbital symmetry relationships may not be obeyed because of the lack of overlap.

The bicyclic alcohol IV, bp 36–37° (0.6 mm), is characterized as such as a result of its analytical and spectral properties [infrared bands at 2.80 and 8.55 μ, indicative of O–H and C–O stretching, respectively; λ_{max} 260 mμ (ϵ 6100)]. Hydrogenation of IV (eq 2) yields the saturated bicyclic alcohol IX, mp 53–54°. From its analysis and spectra [infrared bands at 5.75 and 8.00 μ, indicative of saturated esters; λ_{max} 265, 256, and 219 mμ

(14) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Inc., London, 1959, p 85.

(15) R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 395 (1965).

(2)

IV, R = CH₃

Xa

HO R

IX, R = CH₃
XVIII, R = C₆H₅

V, R = CH₃
XV, R = C₆H₅

Xb
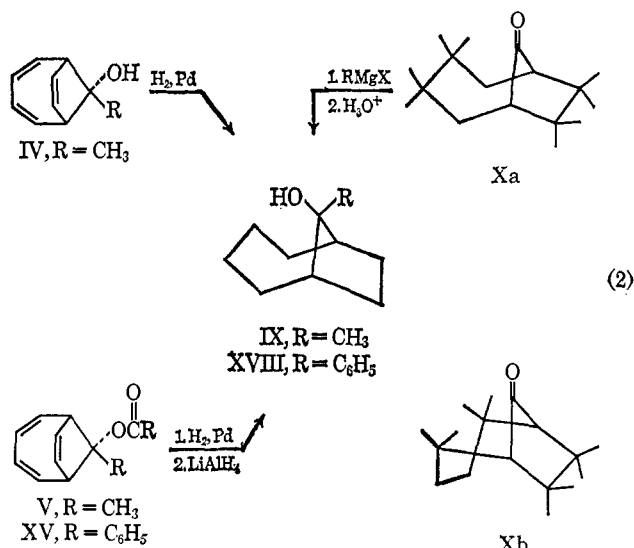
(ϵ 3600, 3750, and 3200)] V is a bicyclic acetate. Hydrogenation of V, followed by cleavage of the saturated acetate VIII with lithium aluminum hydride, results in the saturated alcohol IX (eq 2). Thus V is the acetate of IV.

That IV and V are bicyclo[4.2.1]nonatrienes rather than bicyclo[6.1.0]nonatrienes is proven by unambiguous synthesis of the mutual transformation product, the saturated alcohol IX. Reaction of bicyclo[4.2.1]-nonan-9-one[16] (X) with methylmagnesium iodide results in *syn*-9-hydroxy-9-methylbicyclo[4.2.1]nonane (76%), identical melting point and mixture melting point; superimposable infrared spectra with IX obtained by reduction of IV and V (eq 2). A second alcohol (presumably isomeric) is also obtained, but the quantity available precluded complete characterization.

The stereochemistry of the hydroxyl group in IX is assigned as *syn* to the four-carbon bridge on the basis that, in both the quasi-chair (Xa) and quasi-tub (Xb) conformations of X, the side of the carbonyl group facing the two-carbon bridge is considerably less hindered than the side facing the four-carbon bridge. Approach of a reagent from the side of the carbonyl *syn* to the four-carbon bridge is blocked by the hydrogens on the β-carbons of the quasi-chair structure, Xa, and by the hydrogens on the α-carbons of the quasi-tub conformation, Xb (see eq 2). Thus, attack of the Grignard reagent should occur predominantly from the side of the carbonyl group *syn* to the two-carbon bridge to give IX. It is highly unlikely that epimerization occurs in reduction of IV to IX and, therefore, the stereochemistries of IV and V are formulated with the oxygen function *syn* to the four-carbon bridge.

Formation of IV and V from I and acetyl chloride can be envisaged as proceeding *via* the path in eq 1b; the intermediate monoacetyl monoanion II undergoes intramolecular reaction at C-4 of the eight-membered ring to give the bicyclic alkoxide ion indicated. Reaction of the alkoxide intermediate with acetyl chloride yields the acetate V or, with water, the corresponding alcohol IV. In the transition state for intramolecular alkylation of monoanion III (eq 3), the stereochemistry of the alkoxy group must be as shown, with the methyl group *syn* to the two-carbon bridge. Such a
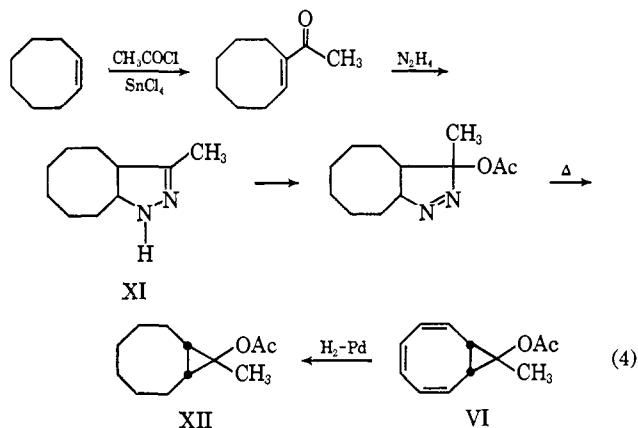
(16) C. D. Gutsche and T. D. Smith, *ibid.*, **82**, 4067 (1960).
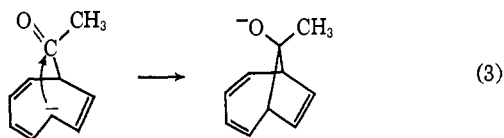
result is predicted on the basis of the greater effective size of a methyl group than of alkoxide. The sequence shown (eq 3) would be expected to occur more rapidly than that leading to the epimeric alkoxide, since less steric interference will be encountered.

Compound VI, *syn*-9-acetoxy-9-methylbicyclo[6.1.0]-nona-2,4,6-triene, mp 53.5–54°, is a bicyclic acetate isomeric with V [analytical data, infrared bands at 5.76, 8.08, and 8.21 μ, indicative of an ester group; λ_{max} 247 mμ, (ϵ 4100)]. That VI is not a bicyclo-[4.2.1]nonatriene epimeric with V at C-9 is suggested by nmr signals of their bridgehead hydrogens. The spectrum of V displays, among other signals, a complex multiplet at τ 6.77 attributable only to the bridgehead hydrogens. The chemical shift is consistent with the magnetic environment of such hydrogens. The nmr spectrum of VI is similar to that of V in other respects, but shows a narrow multiplet at τ 8.24 rather than a broad multiplet at τ 6.77. Hydrogens on cyclopropanes are shielded by a small ring-current effect[17] and show signals at considerably higher field than do those on larger rings. The bridgehead hydrogen signal of VI at high field suggests that the product is a bicyclo-[6.1.0]nonatriene. Its ultraviolet spectrum, which differs from that of V and closely resembles that of known bicyclo[6.1.0]nonatrienes,[18] support this supposition.

Conclusive proof that VI has the structure assigned is provided by unambiguous synthesis (eq 4) of 9-acetoxy-9-methylbicyclo[6.1.0]nonane (XII), the hydrogenation product of VI. The synthesis involves reaction of cyclooctene and acetyl chloride catalyzed by stannic chloride to give the desired 1-acetylcyclooctene and an unidentified saturated ketone in a 2:1 ratio. Separation is effected by fractional crystallization of the semicarbazones of the mixture of ketones, followed by regeneration of the desired ketone and distillation. 3-Methyl-4,5-hexamethylene-2-pyrazoline (XI) is obtained by reaction of 1-acetylcyclooctene with hydrazine. The 2-pyrazoline reacts with lead tetraacetate to give 3-acetoxy-3-methyl-4,5-hexamethylene-1-pyrazoline.[19] Pyrolysis of the crude product and sepa-

(3)

(4)

ration of the resulting mixture by gas chromatography yield a component which has a retention time and infrared absorption identical with that of XII prepared by hydrogenation of VI. The gross structure of VI is as shown.

Compound VI is thus derivable (eq 5) by ring closure of the monoacetyl monoanion II at C-2 of the eight-membered ring; the intermediate bicyclic alkoxide is then acetylated by the available acetyl chloride. No direct evidence is available for the stereochemistries of VI and XII; however, by analogy with the process involved in formation of V, the acetoxyl groups in VI and XII are probably *syn* to the eight-membered ring.

(5)

Reaction of VI occurs readily with N-phenylmaleimide to give an adduct XIII, mp 213–214°, which is formulated with the imide moiety *syn* to the double

XIII
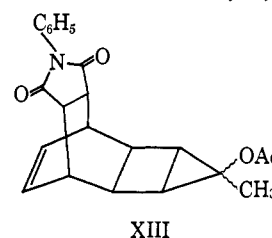
bond in the product, in accordance with the rule of maximum accumulation of overlap.[20] Pyrolysis of VI at 150° gives 3-methylindene and acetic acid (eq 6).

(6)
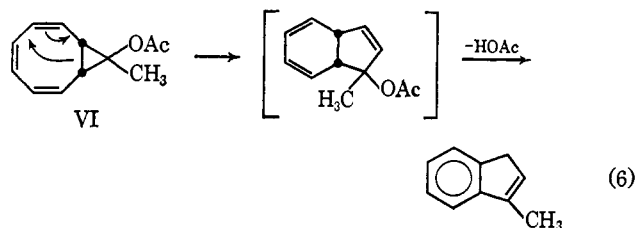
Apparently these products result from elimination of acetic acid from the expected 1-acetoxy-1-methyl-8,9-dihydroindene followed by prototropic rearrangement; pyrolyses of other bicyclo[6.1.0]nonatriene derivatives are reported to yield 8,9-dihydroindenes.[21]

The behavior of aromatic acid chlorides with I has been investigated.[22] Thus reactions of excess benzoyl chloride in ether with dilithium cyclooctatetraenide (I) in ether at 0° give after hydrolysis *trans,cis,cis,trans*-1,10-diphenyl-2,4,6,8-decatetraene-1,10-dione (XIV, 6–7%) and *syn*-9-benzoyloxy-9-phenylbicyclo[4.2.1]-nona-2,4,7-triene (XV, 58–62%) as identifiable products.

The tetraene XIV is initially characterizable from its infrared (strong bands at 6.04 and 6.29 μ; doubly conjugated carbonyl) and ultraviolet [$\lambda_{max}^{CH_3OH}$ 378, 271, and 248 mμ (ϵ 47,000, 9500, and 11,000)] spectra. Its gross structure is confirmed by its hydrogenation to 1,10-di-
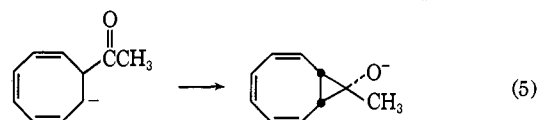
(17) For an explanation of this phenomenon, see K. Wiberg and B. J. Nist, *J. Am. Chem. Soc.*, **83**, 1226 (1961).

(18) Several such derivatives have been reported to have λ_{max} 245–248 mμ; see ref 10 and E. Vogel, *Angew. Chem.*, **73**, 548 (1961).

(19) (a) This synthesis involves adaptation of the method of Freeman for preparing cyclopropyl acetates: (b) J. P. Freeman, *J. Org. Chem.*, **28**, 885 (1963); (c) J. P. Freeman, *ibid.*, **29**, 3375 (1964).

(20) J. G. Martin and R. K. Hill, *Chem. Rev.*, **61**, 537 (1961).

(21) (a) E. Vogel, W. Wiedemann, H. Kiefer, and W. F. Harrison, *Tetrahedron Letters*, 673 (1963); (b) K. F. Bangert and V. F. Boekelheide, *J. Am. Chem. Soc.*, **86**, 905 (1964); (c) T. J. Katz and P. J. Garratt, *ibid.*, **86**, 4876, 5194 (1964).

(22) Treatment of I with propionyl chloride yields products analogous to III–VI.

phenyldecane-1,10-dione, identical with that prepared by aluminum chloride catalyzed reaction of sebacoyl chloride and benzene.[23]

Compound XIV, yellow needles, mp 172°, is converted in a few seconds at its melting point or better, in chloroform containing a trace of acid, to an isomer, XVI, yellow needles, mp 200°. Compound XVI exhibits an infrared band at 10.1 μ characteristic of *trans* double bonds and shows λ_{max}^{EtOAc} 385, 370, and 348 mμ (ϵ 66,000, 69,000, and 10,000). It is likely from these data that XIV and XVI differ only in the geometry of one or more of their double bonds.

As a result of extensive studies of carotenes and α,ω-diphenylpolyenes, the following empirical generalizations have been made concerning the ultraviolet absorption of polyenes:[24] (1) the long-wavelength absorption band in the electronic spectra of the all-*trans* compounds shows definite fine structure: at least two, and usually three, distinct maxima are present. The long-wavelength band in the spectra of compounds containing one or more *cis* double bonds is a smooth curve and is somewhat less intense than that of the all-*trans* compounds. (2) The all-*trans* compounds exhibit only one other band, one of comparatively low intensity and located in the 200–250-mμ region. The *cis* compounds possess a second weak band at intermediate wavelengths (250–300 mμ). (3) The *cis* compounds are isomerized to the all *trans* by heating, whereas the reverse transformation does not take place.

It thus seems clear, in view of the observed stability relationship between XIV and XVI, and because of the details indicated above concerning the ultraviolet spectra of the two compounds, that the thermally stable isomer XVI possesses the all-*trans* structure and the isomer melting at 172° has one or more *cis* double bonds. The low solubilities of XIV and XVI preclude determination of their nmr spectra. There is thus no direct evidence available for the number and location of the *cis* double bonds in XIV; from its method of formation and by analogy with III, the *trans,cis,cis,trans* structure indicated for XIV appears probable.

The bicyclic benzoate XV has strong infrared bands at 5.83 and 7.76 μ (benzoate); the ultraviolet spectrum displays absorption maxima at 266, 258, and 224 mμ (ϵ 2900, 3050, and 11,800). Its melting point (123–124°) corresponds to that reported for "dibenzoylcyclooctatriene."[5] The structure of XV is probable in the same manner as that of the methyl analog, V. Hydrogenation of XV (eq 2) yields the saturated benzoate, XVII, which is cleaved with lithium aluminum hydride to *syn*-9-hydroxy-9-phenylbicyclo[4.2.1]nonane (XVIII). The product obtained is identical with that from reaction of bicyclo[4.2.1]nonan-9-one (X) with phenylmagnesium bromide and subsequent hydrolysis (eq 2). The stereochemistry at C-9 in these compounds is assigned, with the oxygen *syn* to the four-carbon bridge, by arguments similar to those used for IV and V.

The reactions of dipotassium cyclooctatetraenide and benzoyl chloride in tetrahydrofuran have been briefly investigated and found to yield *trans*-1,10-dibenzoyloxy-1,10-diphenyldeca-1,3,5,7,9-pentaene (XX, very small amounts) along with XIV (38%) and unidentified

(23) V. Auger, *Ann. Chim.*, [6] 22, 363 (1891).
(24) L. Zechmeister and J. H. Pinckard, *J. Am. Chem. Soc.*, 76, 4144 (1954), and references to earlier work given therein.
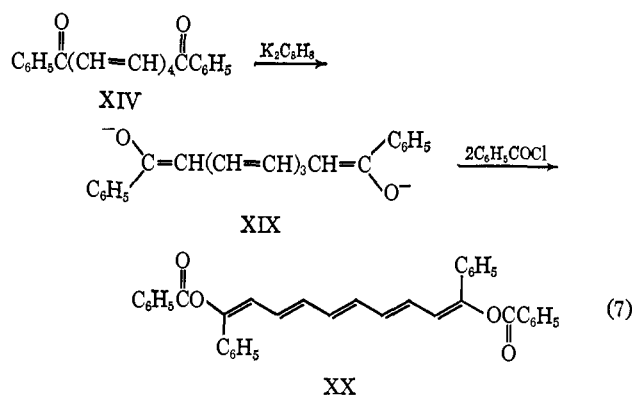
products. The identification of XX rests on its infrared absorption [strong bands at 5.84, 8.11 (benzoate ester), and 10.10 μ (*trans* double bond)] and, in particular, its ultraviolet spectrum [λ_{max} 424, 403, and 387 mμ (ϵ 66,000, 68,000, and 46,000)].[25]

The formation of XX appears to involve reduction of XIV, as in eq 7, by electron transfer from dipotassium cyclooctatetraenide, followed by benzoylation of the enediolate dianion XIX. Further examples involving electron transfer from cyclooctatetraene dianion have been observed in this laboratory and will be described in future publications.

Reaction of I with *p*-bromobenzoyl chloride results in 1,10-bis(*p*-bromobenzoyl)-2,4,6,8-decatetraene-1,10-dione (XXI, eq 1a) and *syn*-9-*p*-bromobenzoyloxy-9-*p*-bromophenylbicyclo[4.2.1]nonatriene (XXII, eq 1c). The structures of XXI and XXII are assignable simply from their chemical and spectral properties. The ultraviolet spectrum of the tetraene XXI [λ_{max} 388 mμ (ϵ 45,000)] is quite similar to that of the analogous tetraene XIV, except that the long-wavelength band is shifted 10 mμ to longer wavelength. It is probable that XXI has *trans,cis,cis,trans* stereochemistry. The bicyclic *p*-bromobenzoate XXII is a bicyclo[4.2.1]-nonatriene since the nmr signal of its bridgehead hydrogens at τ 6.22 is comparable to that (τ 6.16) of XV.

The ultraviolet spectra of the bicyclo[4.2.1]nonatrienes (λ_{max} 258–266 mμ) obtained in this and in other work[26] are of interest. Such nonatrienes can be regarded as 1,3,6-cyclooctatrienes with a methylene bridge across C-5 and C-8; however, they exhibit well-defined absorption bands at wavelengths close to that for 1,3,5-cyclooctatrienes.[4] Known 1,3,6-cyclooctatrienes and 1,3-cyclooctadienes possess no well-defined ultraviolet absorption maximum, but only end absorption or, at most, a shoulder in the 240–250-mμ region.[4,27] The lack of absorption of the cyclooctatrienes and cyclooctadienes becomes apparent from models; the diene chromophore is badly skewed and cannot assume a planar configuration without severe strain. Similar absorption behavior has been reported for other skewed diene chromophores.[28]

An explanation for the spectra of bicyclo[4.2.1]-nona-2,4,7-trienes is also clear from models. Bicyclo-[4.2.1]nonatriene is seriously strained; indeed, a Dreiding model can be constructed only by bending

(25) K. Hausser, R. Kuhn, and E. Smakula, *Z. Physik. Chem.*, 29B, 384 (1935).
(26) L. G. Cannell, *Tetrahedron Letters*, 5947 (1966).
(27) J. L. Kice and T. S. Cantrell, *J. Am. Chem. Soc.*, 85, 2298 (1963).
(28) A. Blomquist and A. Goldstein, *ibid.*, 77, 998 (1955); E. E. van Tamelen, S. Levin, G. Brenner, J. Wolinsky, and P. Aldrich, *ibid.*, 81, 1666 (1959).

XXIIIa   XXIIIb
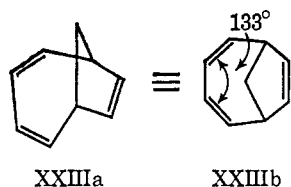
certain bonds past the point of no return. The least strained configuration is one (XXIIIb) in which the diene chromophore is planar, with an angle between the C-2, C-3, and the C-3, C-4 double bonds of *ca.* 133°. On the basis of the indicated stereochemistry, the observed spectra of the bicyclo[4.2.1]nonatrienes are quite reasonable. Nearly planar cyclic dienes such as 1,3-cycloheptadiene and 1,3-cyclohexadiene possess their maxima in the 248–260-mμ region.[29]
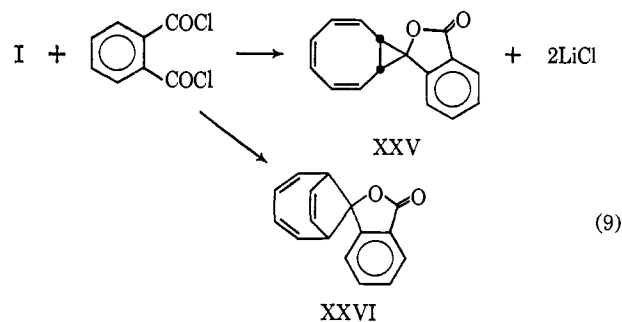
The observation that bicyclo[4.2.1]nonatrienes are strained prompted experiments on the behavior of some of the derivatives at elevated temperatures. Thermolysis of the benzoate XV in refluxing *o*-dichlorobenzene (184°) gave 2-phenylindene (XXIVa, 67%) and benzoic acid (eq 8). The methyl analog V yielded 2-methylindene (XXIVb) and acetic acid (eq 8) under

XXIVa, R = C₆H₅
XXIVb, R = CH₃
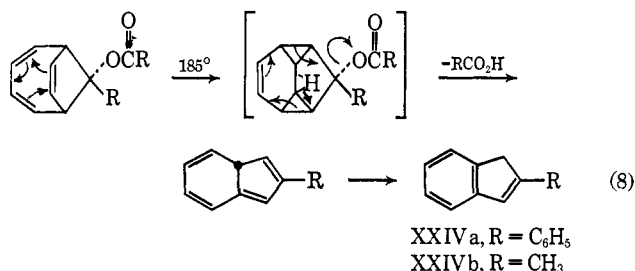
similar conditions. The indenes were identified by comparison with authentic samples obtained by treatment of 2-indanone with the appropriate Grignard reagent and dehydration of the intermediate carbinol.[30]

One possible mechanism (of many) for formation of indenes in the pyrolysis of bicyclo[4.2.1]nonatrienes is shown in eq 8 in which there is valence isomerization, loss of the equivalent of a carboxylic acid, electronic reorganization, and molecular rearrangement. Stepwise mechanisms, both free radical and ionic, can be envisaged which proceed *via* cyclononatetraenyl intermediates. However, both 2- and 3-substituted indenes are likely to be derived from such species and the absence of 3-substituted indenes in the reaction mixtures leads us to favor some directed process as shown. A driving force in any case for decomposition and rearrangement is the gain in resonance energy provided by the formation of the aromatic indene system.

Dilithium cyclooctatetraenide (I) reacts with phthaloyl chloride in ether to give the lactone of 9-(2-carboxyphenyl)-9-hydroxybicyclo[6.1.0]nonatriene (XXV, 28%, eq 9) as the only tractable product. The presence of a lactone ring in the product is indicated by its infrared spectrum (strong absorption at 5.73 μ) and its analysis. The product is thus either the bicyclo[6.1.0]-nonatriene (XXV), or the isomeric bicyclo[4.2.1]nonatriene (XXVI). Assignment of XXV as the correct structure is made on the basis of the following evidence: (1) the lactone readily forms an adduct (mp 325–327°) with N-phenylmaleimide, as does the bicyclo[6.1.0]-nonatriene VI, the structure of which has been proven

(29) E. Pesch and S. L. Friess, *J. Am. Chem. Soc.*, **72**, 5756 (1950).
(30) J. von Braun and G. Manz, *Ber.*, **62**, 1063 (1929).

chemically. The bicyclo[4.2.1]nonatrienes V and XV, on the other hand, are completely inert to N-phenylmaleimide and other Diels–Alder dienophiles; (2) the nmr spectrum has a multiplet attributable only to the bridgehead hydrogens at τ 7.70, or approximately 1.5 ppm further upfield than that of the bridgehead hydrogens in the 9-phenylbicyclo[4.2.1]nonatriene (XV). Since the signal of the bridgehead hydrogen of the bicyclo[6.1.0]nonatriene VI (τ 8.24) appears 1.47 ppm upfield from that of the isomeric 9-methylbicyclo[4.2.1]-nonatriene (V) (τ 6.77), it becomes clear that the high-field position of the bridgehead hydrogens of the lactone is due to their location on a cyclopropane ring and thus the lactone possesses structure XXV.

Experimental Section[31]

Dilithium Cyclooctatetraenide (I). Dry ether (600 ml) in a flask was flushed with helium. A length of lithium wire (4.2 g, 0.60 g-atom) was held in the helium stream emerging from an open neck of the flask and rapidly cut into small pieces which fell directly into the ether. After the ether had been heated to reflux, cyclooctatetraene (31 g, 0.30 mole) was added all at once. The solution was stirred rapidly and after an induction period of a few minutes, vigorous refluxing began, accompanied by color changes from yellow to green to red brown. After the exothermic reaction subsided, the solution was stirred for 10–15 hr under helium. The concentration of I was determined by titration with standard acid, as described[32] for other organolithium compounds. Typical preparations gave a 55–60% yield of I. Solutions were transferred by hypodermic syringe or by siphoning under nitrogen pressure.

Reaction of Dilithium Cyclooctatetraenide (I) with Acetyl Chloride. A solution of I in ether (450 ml, containing 0.148 mole of I) was added in 0.5 hr to stirred acetyl chloride (39 g, 0.50 mole) in ether (150 ml) at 0° under nitrogen. The yellow suspension was stirred for 1 hr while warming to room temperature and then filtered. The yellow solid was washed with cold ether; the combined filtrate and washings were poured onto crushed ice and stirred until hydrolysis of the acetyl chloride was complete.

The solid was suspended in water; the suspension was made faintly acidic and extracted several times with methylene chloride under nitrogen. The combined methylene chloride extracts were washed with water, dried, and evaporated. The crude yellow-orange solid was purified by rapid recrystallization from oxygen-free 2:1 hexane–benzene to give *trans,cis,cis,trans*-3,5,7,9-dodeca-tetraene-2,11-dione (III, 2.21 g, 7.9%) as faintly yellow leaflets, mp 110–111.5°; λ_{max}^{KBr} 5.97 (s), 6.27 (vs), 6.54 (m), 7.45 (s), 7.97 (s), 8.50 (s), 10.17 (s), 10.44 (s), 11.59 (m), and 13.20 (s) μ; $\lambda_{max}^{CH_3OH}$ 343, 265, and 211 mμ (ϵ 52,000, 9000, and 10,500). The nmr spectrum con-

(31) (a) Melting points are corrected; boiling points are uncorrected. Infrared spectra were obtained from potassium bromide disks or on pure liquid films. Ultraviolet spectra were determined in methanol unless noted otherwise. Nuclear magnetic resonance spectra were obtained for samples in carbon tetrachloride or deuteriochloroform (Varian Model A-60 instrument) containing tetramethylsilane as an internal standard. Vapor phase chromatographic columns used were 10 ft × ³/₈ in. packed with Firebrick coated with Carbowax 20M polyether (column A) or SE-30 silicone rubber (column B). Cyclooctatetraene was distilled under reduced pressure and stored at −20°. The lithium was ¹/₈-in. wire (Foote Mineral Company). Chromatography was performed on Woelm neutral alumina, classified according to the standard Brockmann scale.[31b] (b) H. Brockmann and H. Schodder, *Ber.*, **74**, 71 (1941).
(32) H. Gilman and R. G. Jones, *Org. Reactions*, **6**, 353 (1951).

sists of signals at τ 2.38 (two doublets, area 2, J = 15.2 cps, J' = 11.8 cps, hydrogens β to carbonyl), τ 3.05 (two doublets, area 2, J = 7.6 cps, J' = 2.2 cps, hydrogens δ to carbonyl), τ 3.60 (multiplet, area 2, hydrogens γ to carbonyl), τ 3.76 (doublet, area 2, J = 15.2 cps, hydrogens α to carbonyl), and τ 7.73 (singlet, area 6, acetyl methyls).

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.80: H, 7.37. Found: C, 75.22; H, 7.15.

Solutions of III are quite air sensitive; the compound is more stable in the solid state, but is best stored under nitrogen.

The ethereal filtrate and washings from the reaction mixture, after having been poured into ice water and stirred for 1 hr, were washed thoroughly with water, dried, and evaporated to give a red oil which was rectified through an 8 × 300 mm wire spiral column to yield the following products.

(1) Fraction I was almost pure *syn*-9-hydroxy-9-methylbicyclo-[4.2.1]nona-2,4,7-triene (IV, 4.20 g, 0.0284 mole, 19%), bp 36-37° (0.6 mm). An analytical sample was obtained by gas chromatography on column B; IV has a retention time of 18.5 min at 185° (30 psi helium). Pure IV shows λ_{max}^{film} 2.80 (m), 7.26, 7.48 (s), 7.71 (s), 8.10 (m), 8.55 (s), 9.31 (m), 9.61 (m), 10.22 (m), 10.63 (m), 11.67 (s), 13.7 (s), and 14.62 (vs) μ, and $\lambda_{max}^{ultraviolet}$ 260 mμ (ϵ 6100). Its nmr spectrum exhibits signals at τ 3.84 (multiplet, area 4, hydrogens on C-2, -3, -4, and -5), τ 4.75 (two doublets, area 2, J = 1.8 cps, J' = 0.4 cps, hydrogens on C-7 and C-8), τ 7.27 (multiplet, area 2, bridgehead hydrogens), τ 8.08 (singlet, area 1, hydroxyl hydrogen), and τ 8.62 (singlet, area 3, methyl hydrogens).

Anal. Calcd for $C_{10}H_{12}O$: C, 81.08; H, 8.11. Found: C, 81.30; H, 8.28.

(2) Fraction 2, bp 56-58° (0.6 mm), solidified and on recrystallization from ethanol-water at 0° gave *syn*-9-acetoxy-9-methylbicyclo[4.2.1]nona-2,4,7-triene (V, 3.68 g, 0.0195 mole, 13%) as large colorless blades, mp 47-47.5°; λ_{max}^{KBr} 3.33 (m), 3.42 (m), 5.76 (s), 7.32 (s), 8.01 (vs), 8.83 (s), 9.00 (s), 13.25 (s), 13.40 (s), 14.12 (s), and 14.59 (s) μ. V has ultraviolet absorption maxima at 265, 256, and 219 mμ (ϵ 3600, 3750, and 3200). Its nmr spectrum shows signals at τ 3.98 (multiplet, area 4, hydrogens on C-2 through C-5), τ 4.74 (two doublets, area 2, J = 1.6 cps, $J' \cong$ 0.5 cps, hydrogens on C-7 and C-8), τ 6.77 (multiplet, area 2, bridgehead hydrogens), τ 8.21 (singlet, area 3, acetate methyl), and τ 8.45 (singlet, area 3, C-methyl).

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.80; H, 7.37. Found: C, 75.68; H, 7.26.

(3) Fraction 3, bp 70-72° (0.6 mm), solidified; recrystallization from ethanol-water at 0° yielded *syn*-9-acetoxy-9-methylbicyclo-[6.1.0]nona-2,4,6-triene (VI, 5.89 g, 0.0308 mole, 22%) as large white prisms, mp 52-53°; λ_{max}^{KBr} 5.75 (s), 7.09 (m), 7.34 (s), 8.05 (vs), 8.68 (s), 8.99 (m), 9.86 (m), 10.85 (m), 11.54 (m), 11.91 (m), 12.82 (s), 13.59 (s), and 14.41 (s) μ; $\lambda_{max}^{ultraviolet}$ 247 mμ (ϵ 4100). The nmr spectrum of VI consists of signals at τ 3.94 (narrow multiplet, area 4, vinyl hydrogens), τ 4.07 (narrow multiplet, area 2, vinyl hydrogens), τ 8.02 (singlet, area 3, acetate methyl), τ 8.24 (narrow multiplet, area 2, bridgehead hydrogens), and τ 8.64 (singlet, area 3, C-methyl).[33]

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.80; H, 7.37. Found: C, 74.53; H, 7.33.

Isomerization of *trans,cis,cis,trans*-3,5,7,9-Dodecatetraene-2,11-dione (III) to *trans,trans,trans,trans*-3,5,7,9-Dodecatetraene-2,11-dione (VII). A solution of III (0.046 g, 0.24 mmole) in chloroform (1 ml) was treated with hydrogen chloride in the following manner. A bottle of concentrated hydrochloric acid was shaken, the cap was removed, and a small amount of the emitted vapor was blown into the reaction mixture by a nitrogen stream. The solution was stored at room temperature for 3 days and the chloroform was then removed by distillation. Recrystallization of the residue from benzene-hexane gave VII (0.038 g, 83%), as pale yellow needles, mp 137-138°; λ_{max}^{KBr} 5.98 (s), 6.26 (s), 6.43 (m), 7.44 (s), 7.63 (m), 7.89 (m), 8.24 (s), 8.51 (m), 8.89 (w), and 9.98 (vs) μ; $\lambda_{max}^{ultraviolet}$ 347 and 363 mμ (ϵ 65,000 and 63,000). The nmr spectrum shows signals at τ 2.85 (two doublets, area 2, J = 16.4 cps, J' = 11.2 cps, hydrogens β to carbonyl), τ 3.52 (sharp doublet, J = 16.4 cps, area 2, hydrogens α to carbonyl), τ 3.3-3.7 (multiplets, area 4, hydrogens λ and δ to carbonyl), and τ 7.71 (singlet, area 6, acetyl methyls).

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.80; H, 7.37. Found: C, 76.06; H, 7.26.

Hydrogenation of *trans,cis,cis,trans*-3,5,7,9-Dodecatetraene-2,11-dione (III). A solution of III (30 mg) in ethyl acetate (30 ml) was

hydrogenated (1 atm) over platinum oxide (15 mg). After 30 min, the solution was filtered and the solvent evaporated. The white semisolid residue was chromatographed on a 16 × 200 mm column of activity II alumina. The column was eluted with benzene and 4:1 benzene-chloroform. Evaporation of the eluates yielded an oil which crystallized. Recrystallization from hexane at –20° gave 2,11-dodecanedione (22 mg, 74%) as white leaflets, mp 66-67°, identical (mixture melting point, superimposable infrared spectra) with that obtained by the route described below.

Reaction of Dimethylcadmium with Sebacoyl Chloride. A stirred solution of dimethylcadmium (*ca.* 0.12 mole) in benzene, prepared as described by Cason,[12] was refluxed while sebacoyl chloride (12 g, 0.050 mole) in benzene (30 ml) was added. The mixture was refluxed for 1 hr, cooled, and poured onto crushed ice-hydrochloric acid. The aqueous layer was extracted with ether. The combined organic layers were washed with water, 5% sodium carbonate, and water, and then dried. Evaporation of the solvents gave a white semisolid residue. Recrystallizations from hexane at –20° yielded 2,11-dodecanedione (5.7 g, 59%), mp 66-67°, identical with that obtained by hydrogenation of III.

Conversion of *syn*-9-Acetoxy-9-methylbicyclo[4.2.1]nonatriene (V) to *syn*-9-Hydroxy-9-methylbicyclo[4.2.1]nonane (IX). A solution of V (0.65 g, 0.0034 mole) in ethanol (30 ml) was shaken with 5% palladium on charcoal (30 mg) under 2 atm of hydrogen until absorption ceased (25 min). Evaporation of the filtered solution gave crude *syn*-9-acetoxy-9-methylbicyclo[4.2.1]nonane as a colorless oil (0.65 g, 98%) which was used in the next step.

A solution of the crude acetoxybicyclononane (0.65 g) in ether (5 ml) was added dropwise to stirred lithium aluminum hydride (0.4 g, 0.010 mole) in ethyl ether (25 ml) at 0°. After the mixture had been refluxed for 15 min, the excess hydride was destroyed with ethyl acetate (2 ml). The products were then poured into ice-ammonium chloride solution. The aqueous layer was extracted with ether. The combined ether solutions were washed with water and dried. Evaporation of the ether yielded a residue which upon fractional sublimation gave *syn*-9-hydroxy-9-methylbicyclo[4.2.1]-nonane (IX, 0.29 g, 56% from V) as a white waxy solid, mp 54-55° [sublimes at 60° (5 mm)], with a menthol-like odor; λ_{max}^{KBr} 3.02 (s), 3.49 (s), 6.97 (m), 7.36 (m), 8.88 (s), and 10.57 (m) μ.

Anal. Calcd for $C_{10}H_{18}O$: C, 77.92; H, 11.69. Found: C, 77.80; H, 11.51.

Conversion of *syn*-9-Hydroxy-9-methylbicyclo[4.2.1]nonatriene (IV) to IX. A solution of IV (0.60 g, 0.0041 mole) in 95% ethanol (30 ml) was hydrogenated (2 atm) over 5% palladium on charcoal (40 mg) until hydrogen uptake ceased (30 min). Filtration of the catalyst and evaporation of the solvent yielded a white solid which on sublimation at 55° (5 mm) gave IX (0.52 g, 85%) identical with that prepared from V.

Preparation of IX from Bicyclo[4.2.1]nonan-9-one (X). A solution of X (0.171 g, 0.00125 mole) in ether (4 ml) was added at 0° to stirred methylmagnesium iodide (*ca.* 0.004 mole) in ethyl ether (5 ml). The mixture was refluxed for 20 min and then poured onto a slurry of ice and saturated aqueous ammonium chloride. The aqueous layer was washed with ether. The combined ether solutions were washed with water, dried, evaporated, and sublimed (5 mm). The first fraction, a colorless oil (*ca.* 20 mg), distilled onto the cold finger at 40-45°. Its infrared spectrum has a hydroxyl band at 2.84 μ; it may be the *anti*-9-hydroxy epimer of IX.

The second fraction, subliming at 55-60° (5 mm), is *syn*-9-hydroxy-9-methylbicyclo[4.2.1]nonane (IX, 0.144 g, 0.00092 mole, 76%), mp 54-55°. This sample is identical (mixture melting point, identical infrared spectra) with those obtained by degradation of IV and V.

Hydrogenation of 9-Acetoxy-9-methylbicyclo[6.1.0]nonatriene (VI) to *syn*-9-Acetoxy-9-methylbicyclo[6.1.0]nonane (XII). A solution of VI (0.80 g, 0.0042 mole) in 95% ethanol (25 ml) was shaken with 5% palladium on charcoal (50 mg) under 2 atm of hydrogen. After hydrogen uptake had ceased (*ca.* 25 min), the solution was filtered and the solvent evaporated. Distillation of the residue gave XII (0.71 g, 87%) as a colorless oil, bp 60-70° (bath temperature) (0.5 mm), λ_{max}^{film} 5.75 (s), 6.87 (s), 6.96 (s), 7.38 (s), 8.11 (s), 8.37 (s), 8.90 (s), 9.80 (s), 10.53 (m), and 10.91 (m) μ.

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.58; H, 10.21. Found: C, 73.74; H, 9.96.

1-Acetylcyclooctene. A mixture of acetyl chloride (40 g, 0.51 mole) and cyclooctene (55 g, 0.50 mole) was added in 1.5 hr to stirred stannic chloride (130 g, 0.50 mole) in carbon disulfide (1400 ml) at –10 ± 3°. The clear tan solution was stirred 15 min at –10°, let warm to 0°, and then poured onto a slurry of ice and hydrochloric acid. The organic layer was separated, washed with

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(33) It has been observed that the three types of vinyl hydrogens in bicyclo[6.1.0]nonatrienes exhibit nearly identical chemical shifts.[21b]

water, dried, and evaporated. The brown oil obtained was distilled (1 mm) rapidly from sodium carbonate to give a sweet-smelling oil (47 g, bp 62–100°). This material was fractionated as: (1) a colorless oil (28 g, 0.19 mole, 38%), bp 58–64° (1 mm), whose infrared spectrum indicated that it consisted of approximately 70% 1-acetylcyclooctene and 30% unidentified saturated ketone (infrared bands at 5.97 and 5.83 μ, intensity ca. 70:30) and (2) a colorless oil (17 g), bp 89–93° (1 mm), exhibiting an infrared band at 5.84 μ. This higher boiling fraction was not investigated further.

Fraction 1 (40 g, 0.26 mole) and semicarbazide hydrochloride (34 g, 0.28 mole) in 70% ethanol (400 ml) were warmed at 90° for 10 min, and water was added until the solution became slightly turbid. Filtration after crystallization gave 1-acetylcyclooctene semicarbazone (18 g) as white needles, mp 191–192°; further cooling gave a second crop, 10 g, mp 190–192°. Concentration of the solution and further cooling gave additional material melting at 175–179, 201–203, and 202–203°, respectively. Recrystallization of the first two crops of material (28 g) from ethyl acetate gave pure 1-acetylcyclooctene semicarbazone (24 g), mp 192–193°.

A mixture of 1-acetylcyclooctene semicarbazone (50 g, 0.24 mole) and phthalic anhydride (100 g, 0.68 mole) was steam distilled. The distillate was extracted with ethyl ether; the extracts were washed with water, dried, and evaporated. Distillation of the residue yielded 1-acetylcyclooctene (17 g, 0.11 mole, 42% recovery), a colorless liquid, bp 64–66° (0.8 mm), n^{22}D 1.4918; λ_{max}^{film} 5.97 (s), 6.10 (w), 6.83 (m), 6.92 (m), 7.25 (m), 7.40 (m), 7.79 (s), and 8.33 (s) μ.

3-Methyl-4,5-hexamethylene-2-pyrazoline (XI). A mixture of 1-acetylcyclooctene (16 g, 0.105 mole) and 95% hydrazine (30 ml) in 95% ethanol (150 ml) was refluxed for 2 hr. The yellow solution was concentrated to ~50 ml under reduced pressure, poured into ice–water, and extracted with ether. After the combined extracts had been washed with water and dried, evaporation gave a residue which on distillation yielded XI (13 g, 0.079 mole, 75%), a colorless oil, bp 88–90° (0.4 mm), which solidified on standing; mp 41–43°.

Preparation of 3-Acetoxy-3-methyl-4,5-hexamethylene-1-pyrazoline and Its Pyrolysis to 9-Acetoxy-9-methylbicyclo[6.1.0]nonane (XIII). A solution of XI (8.2 g, 0.050 mole) in methylene chloride (20 ml) was added in 20 min to stirred lead tetraacetate (23 g, 0.053 mole) in methylene chloride (200 ml) at 10 ± 2°. The brown suspension was warmed to room temperature, stirred for 1 hr, and filtered through Celite; the Celite and lead dioxide were washed with cold methylene chloride. The combined filtrate and washings were washed with water and dried. Evaporation of the solvent gave a brown oil which evolved nitrogen at room temperature and was taken to be the crude 1-pyrazoline. The product (4.0 g) was slowly heated to 100° in a semimicro distillation apparatus; gas evolution was noticeable during the early stages of heating. Two fractions were collected: (1) a colorless oil, bp 100–115° (1 mm) (1.2 g), and (2) a yellow oil, bp 140–150° (1 mm) (2.0 g). Gas chromatography of fraction 1 on column B at 210° showed two main peaks of retention time 14 min (60% of total area) and 25 min (27% of total area). The sample was rechromatographed on column B; the infrared spectrum of the material of 14-min retention time is identical with that of XII prepared from VI. A mixture of the two samples showed a single peak at 210° on columns A and B, with respective retention times of 12 and 14 min.

Reaction of 9-Acetoxy-9-methylbicyclo[6.1.0]nonatriene (VI) and N-Phenylmaleimide. A solution of VI (0.19 g, 1.00 mmole) and N-phenylmaleimide (0.17 g, 1.00 mmole) in tetrahydrofuran (5 ml) was refluxed 20 hr. Evaporation of the solvent gave a viscous residue which crystallized on trituration with ethanol. Two recrystallizations from ethanol yielded the pure adduct XIII (0.27 g, 0.75 mmole, 75%) as shiny white prisms, mp 213–214°; λ_{max}^{KBr} 5.73 (s), 5.85 (vs), 6.70 (m), 7.24 (s), 8.05 (s), 8.17 (s), 8.42 (s), 8.78 (m), 13.19 (s), 13.58 (s), and 14.47 (s) μ.

Anal. Calcd for $C_{22}H_{21}NO_4$: C, 72.75; H, 5.78; N, 3.86. Found: C, 72.58; H, 5.90; N, 3.91.

Pyrolysis of 9-Acetoxy-9-methylbicyclo[6.1.0]nonatriene (VI). Thermolysis of VI (0.70 g, 3.7 mmoles) was effected at 150° under nitrogen for 1 hr. Evaporative distillation of the resulting material at 60–65° (4 mm) yielded crude 3-methylindene (0.41 g, 3.2 mmoles, 85%). Final purification was effected by gas chromatography using column B at 200°. The major peak (93% of total area) has a retention time of 16 min and is identified as 3-methylindene by comparison of its infrared spectrum and retention time with those of an authentic sample.

Reaction of Dilithium Cyclooctatetraenide (I) with Benzyl Chloride. A solution of I in ether (100 ml, containing approximately 0.023 mole of I) was added in 30 min to stirred benzoyl chloride

(10 g, 0.07 mole) in ether (50 ml) at 0° under nitrogen. The yellow suspension was stirred while warming to room temperature and then filtered. The yellow solid was washed with cold ether, briefly air dried, and extracted with boiling benzene. Cooling the benzene extracts and filtration gave trans,cis,cis,trans-1,10-diphenyl-2,4,6,8-decatetraene-1,10-dione (XIV, 0.49 g, 7%) as silky yellow needles, mp 172–173°. Infrared absorption of XIV occurs at λ_{max}^{KBr} 6.05, 6.31 (s), 6.54 (m), 7.28 (m), 7.50 (m), 7.83 (s), 8.24 (m), 9.64 (m), 9.78 (s), 9.99 (m), 10.33 (s), 12.74 (s), and 14.44 (s) μ. The ultraviolet spectrum of XIV in methanol has maxima at 378, 271, and 248 mμ (ϵ 47,000, 9000, and 10,500); in ethyl acetate, maxima occur at 366, 265, and 245 mμ (ϵ 46,000, 9000, and 10,000).

Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.20; H, 5.74. Found: C, 84.33; H, 5.82.

The ethereal mother liquor and washings from filtration of the reaction mixture were washed with water and dried. The solution, after dilution with methanol (50 ml), was evaporated; the viscous dark red residue was chromatographed on a 30 × 350 mm column of alumina, activity I. Elution with 3:1 hexane–benzene (500 ml) yielded a viscous oil which crystallized. Recrystallization from ethanol gave syn-9-benzoyloxy-9-phenylbicyclo[4.2.1]nonatriene (XV, 4.38 g, 0.0140 mole, 61%), mp 122–123°. A second recrystallization from ethanol gave the analytical sample at thick white prisms, mp 123–124°. Key infrared bands occur at 5.83 (s), 6.24 (m), 6.33 (m), 7.78 (vs), 8.10 (m), 8.97 (s), 9.71 (m), 11.12 (m), 11.82 (s), 13.10 (s), 13.38 (s), 14.04 (s), 14.17 (s), 14.40 (s), 14.65 (s), and 14.78 (s) μ. The ultraviolet spectrum displays maxima at 266, 258, and 224 mμ (ϵ 2900, 3050, and 11,800). The nmr spectrum reveals signals at τ 1.8–2.9 (multiplets, area 10, phenyl hydrogens), τ 3.91 (multiplet, area 4, hydrogens on C-2, -3, -4, and -5), τ 4.69 (narrow multiplet, area 2, hydrogens on C-7 and 3-8), and τ 6.16 (broad multiplet, area 2, bridgehead hydrogens).

Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.20; H, 5.74. Found: C, 84.45; H, 5.82.

Elution of the column with benzene gave a small amount of an unidentified orange oil exhibiting an infrared band at 5.87 μ; benzene–methylene chloride eluents yielded only viscous dark gums.

Preparation of 1,10-Diphenyl-1,10-decanedione from 1,10-Diphenyl-2,4,6,8-decatetraene-1,10-dione (XIV). A solution of XIV (0.15 g, 0.47 mmole) in ethyl acetate (45 ml) was shaken with platinum oxide (40 mg) and hydrogen (2 atm) for 2 hr. Filtration of the catalyst and evaporation of the solvent gave a white solid which was chromatographed on a 16 × 200 mm column of alumina, activity II. Elution with chloroform containing 1% methanol gave 1,10-diphenyl-1,10-decanedione (0.12 g, 0.38 mmole, 80%) as white plates, mp 91–92° (lit.[23] 90–92°) on recrystallization from ethanol. This sample was identical (melting point and mixture melting point, superimposable infrared spectra) with an authentic sample.[23]

Isomerization of trans,cis,cis,trans-1,10-Diphenyl-2,4,6,8-decatetraene-1,10-dione (XIV) to trans,trans,trans,trans-1,10-Diphenyl-2,4,6,8-decatetraene-1,10-dione (XVI). The tetraene XIV (0.10 g, 0.32 mmole) was heated under nitrogen at 180 ± 5° for 1 min and then cooled. The yellow-orange solid was recrystallized from ethyl acetate to give XVI (0.76 g, 0.245 mmole, 76%) as tiny, lemon-yellow needles, mp 200–201°; λ_{0max}^{KBr} 6.05 (s), 6.26 (s), 6.45 (s), 7.41 (s), 7.62 (s), 7.83 (s), 8.07 (m), 8.41 (m), 9.67 (m), 9.86 (vs), 11.93 (m), 13.00 (m), and 14.45 (s) μ. The ultraviolet spectrum of XVI in ethyl acetate exhibits maxima at 385, 371, and 248 mμ (ϵ 66,000, 69,000, and 10,200); in methanol the long-wavelength maxima occur at 383 and 392 mμ.

Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.20; H, 5.74. Found: C, 84.51; H, 5.68.

The isomerization could also be effected by allowing a solution of XIV in chloroform containing a trace of hydrochloric acid to stand at room temperature for several days.

Hydrogenation of syn-9-Benzoyloxy-9-phenylbicyclo[4.2.1]nonatriene (XV) to syn-9-Benzoyloxy-9-phenylbicyclo[4.2.1]nonane (XVII). A solution of XV (2.40 g, 7.65 mmoles) in 1:1 ethanol–ethyl acetate (100 ml) was shaken with 5% palladium on charcoal under 2 atm of hydrogen until uptake ceased (50 min). The catalyst was then filtered and the solvent evaporated. Recrystallization of the residue from ethanol gave XVII (2.33 g, 7.27 mmoles, 95%) as long white needles, mp 119–120°; λ_{max}^{KBr} 5.81, 6.91, and 7.80 μ.

Anal. Calcd for $C_{22}H_{24}O_2$: C, 82.52; H, 7.50. Found: C, 82.20; H, 7.77.

Synthesis of syn-9-Hydroxy-9-phenylbicyclo[4.2.1]nonane (XVIII) from syn-9-Benzoyloxy-9-phenylbicyclo[4.2.1]nonane (XVIII). A solution of XVII (1.50 g, 4.70 mmoles) in ether (30 ml) was added to stirred lithium hydride (0.7 g, 18 mmoles) in ether (30 ml). The solution was refluxed for 0.5 hr and then treated with ethyl acetate

(2 ml). The suspension was poured onto ice–ammonium chloride solution and extracted with ether. The combined ether layers were washed with water, dried, and distilled to give a colorless oil (0.89 g), bp 75–80° (bath temperature) (0.4 mm), which partially crystallized. Recrystallization yielded XVIII (0.52 g, 2.40 mmoles, 51%) as flat white prisms, mp 59–59.5°. Infrared absorption occurs at λ_{max}^{KBr} 2.97 (s), 6.72 (m), 6.84 (s), 6.97 (s), 9.20 (m), 9.36 (s), 9.61 (m), 9.74 (m), 10.61 (m), 11.05 (m), 12.49 (m), 13.24 (s), and 14.34 (s) μ.

Anal. Calcd for $C_{15}H_{20}O$: C, 83.33; H, 9.26. Found: C, 83.37; H, 9.43.

Synthesis of *syn*-9-Hydroxy-9-phenylbicyclo[4.2.1]nonane (XVIII) from Bicyclo[4.2.1]nonan-9-one (X). A solution of X (0.140 g, 1.02 mmoles) in ether (5 ml) was added to phenylmagnesium bromide in ether (5 ml, containing *ca.* 5 mmoles of the Grignard reagent). The mixture was refluxed for 0.5 hr and poured into ice–ammonium chloride solution. Upon work-up, a semisolid residue was obtained which was chromatographed on a 20 × 200 mm column of activity II alumina. Elution with benzene gave 0.06 g of uncrystallizable oil; elution with chloroform containing 1% methanol yielded a crystallizable product. Recrystallization from ethanol at 5° gave XVIII (0.13 g, 0.59 mmole, 58%), white prisms, mp 58.5–59°, identical (mmp 58.5–59°; superimposable infrared spectra) with material prepared previously.

Reaction of Dipotassium Cyclooctatetraenide with Benzoyl Chloride. Potassium (4.7 g, 0.12 g-atom) was added to cyclooctatetraene (6.2 g, 0.06 mole) in dry tetrahydrofuran (150 ml) under nitrogen. The mixture was stirred at ~30° until all of the potassium had reacted (*ca.* 2.5 hr).

A portion of the above solution (105 ml) was added to stirred benzoyl chloride (14 g, 0.10 mole) in tetrahydrofuran (40 ml) at 0°. The mixture was warmed to room temperature, stirred for 2 hr, poured into ice water, and then extracted with ether. The extracts were washed with water, dried, and evaporated. The brown residue was chromatographed on a 30 × 300 mm column of activity I alumina. Elution with 2:1 hexane–benzene (800 ml) gave *syn*-9-benzoyloxy-9-phenylbicyclo[4.2.1]nonatriene (XV, 3.8 g, 0.015 mole, 38%) as white prisms, mp 122–123° after recrystallization from ethanol, identical with material obtained from dilithium cyclooctatetraenide (I) and benzoyl chloride.

Elution with benzene (300 ml) and 4:1 benzene–methylene chloride (200 ml) gave an unidentified viscous yellow oil (4.1 g) whose infrared spectrum showed a benzoate ester band at 5.81 mμ. The latter benzene–methylene chloride fractions contained a mixture of yellow oil and yellow-orange needles. The solid was recrystallized from chloroform to give *trans*-1,10-dibenzoyl-1,10-diphenyl-1,3,5,7,9-decapentaene (XX, 0.056 g, 0.3%) as short yellow-orange needles, mp 211–213°. Its infrared spectrum displays strong bands at 5.83 and 8.04 μ (benzoate ester). The ultraviolet spectrum of XX shows maxima at 421, 397, and 378 mμ (ϵ 50,000, 63,000, and 47,000).

Reaction of Dilithium Cyclooctatetraenide with *p*-Bromobenzoyl Chloride. A solution of I in ether (100 ml, containing *ca.* 0.03 mole of I) was added to stirred *p*-bromobenzoyl chloride (18 g, 0.08 mole) in ethyl ether (60 ml) at 0°. The reaction mixture was worked up as described for reaction of I with benzoyl chloride. Purification of the benzene extracts of the initial precipitate gave 1,10-bis(*p*-bromophenyl)-2,4,6,8-decatetraene-1,10-dione (XXI, 0.56 g, 0.0015 mole, 5%) as golden yellow leaflets, mp 214–215°. Key infrared bands occur at 6.06 (s), 6.30 (vs), 7.85 (s), and 12.06 (s) μ. The ultraviolet spectrum has maxima at 388, 280, and 236 mμ (ϵ 60,000, 13,000, and 14,000).

Anal. Calcd for $C_{22}H_{16}O_2Br_2$: C, 55.94; H, 3.39. Found: C, 56.48; H, 3.62.

The mother liquor from isolation of XXI was washed with water, dried, and evaporated to give a thick brown oil which was chromatographed on alumina, activity I. Elution with 1:1 benzene–

hexane gave *syn*-9-bromobenzoyloxy-9-*p*-bromophenylbicyclo-[4.2.1]nonatriene (XXII, 6.0 g, 0.013 mole, 44%) as thick white prisms, mp 166–167° after recrystallization from ethanol; λ_{max}^{KBr} 5.83 (s) and 7.79 (s) μ. XX showed $\lambda_{max}^{ultraviolet}$ 242 mμ (ϵ 3600).

Anal. Calcd for $C_{22}H_{16}O_2Br_2$: C, 55.94; H, 3.39. Found: C, 56.32; H, 3.54.

Pyrolysis of *syn*-9-Benzoyloxy-9-phenylbicyclo[4.2.1]nonatriene (XV). A solution of XV (1.40 g, 4.46 mmoles) in *o*-dichlorobenzene (25 ml) was flushed with nitrogen for 1 hr and then refluxed under nitrogen for 44 hr. The solvent was then evaporated (1 mm). The tan semisolid residue obtained was taken up in warm benzene and chromatographed on a 20 × 250 mm column of activity I alumina. Elution with 10% benzene–hexane (200 ml) and with 20% benzene–hexane (300 ml) gave several fractions containing a white solid. Recrystallization of this material from benzene–ethanol gave 2-phenylindene (XXIVa, 0.58 g, 3.05 mmoles, 68%) as shiny white leaflets, mp 165–166°; λ_{max}^{KBr} 10.86 (s), 11.45 (s), 11.67 (s), 13.20 (vs), 13.94 (s), and 14.53 (s) μ.

Anal. Calcd for $C_{15}H_{12}$: C, 93.75; H, 6.32. Found: C, 93.54; H, 6.54.

This product is identical (melting point and mixture melting point; superimposable infrared spectra) with authentic 2-phenylindene.

Pyrolysis of *syn*-9-Acetoxy-9-methylbicyclo[4.2.1]nonatriene (V). A solution of V (1.2 g, 6.3 mmoles) in dimethyl sebacate (6 ml) was flushed with nitrogen and heated at 200° for 30 hr. The solution was then fractionally distilled to yield crude 2-methylindene (XXIVb), bp 47–53° (2 mm) (0.51 g, 3.9 mmoles, 62%). Pure XXIVb was obtained by gas chromatography on column B at 200°; the retention time is identical with that of an authentic sample. A mixture of the two samples gave one peak on gas chromatography; the infrared spectra of the two samples are identical.

Reaction of Dilithium Cyclooctatetraenide (I) with Phthaloyl Chloride. A solution of I in ether (200 ml, containing *ca.* 0.059 mole of I) was added to stirred phthaloyl chloride (18 g, 0.088 mole) in ether (100 ml) at 0° under nitrogen. The mixture was stirred for 1 hr while warming to room temperature and then filtered. The solid was washed with cold ether and stirred with water; the resulting suspension was extracted with warm chloroform. Concentration of the chloroform extracts, trituration with 1:1 benzene–hexane, and filtration gave a crude orange solid. The ethereal mother liquor from filtration was diluted with methanol and concentrated, and the resulting thick suspension filtered. The crude product was washed free of tar, combined with the crop obtained above, and recrystallized from chloroform–benzene to give the lactone of 9-hydroxy-9-(2-carboxyphenyl)bicyclo[6.1.0]nonatriene (XXV, 3.9 g, 0.0165 mole, 28%), mp 164–166°. Recrystallization from chloroform–benzene gave the analytical sample as chunky white prisms, mp 165–166°; λ_{max}^{KBr} 5.69 (s), 6.24 (m), 6.88 (m), 7.54 (m), 7.94 (m), 8.05 (m), 8.17 (m), 8.49 (m), 9.02 (s), 9.39 (s), 9.90 (s), 10.28 (m), 10.57 (s), 11.04 (m), 11.51 (m), 12.85 (s), 13.36 (s), and 14.54 (s) μ. The nmr spectrum consists of signals at τ 2.2–2.9 (multiplets, area 4, aromatic hydrogens), τ 3.93 (multiplet, area 4, vinyl hydrogens), τ 4.08 (multiplet, area 2, vinyl hydrogens), and τ 6.70 (narrow multiplet, area 2, bridgehead hydrogens).

Anal. Calcd for $C_{16}H_{12}O_2$: C, 81.36; H, 5.09. Found: C, 81.77; H, 5.43.

N-Phenylmaleimide Adduct of Lactone XXV. A solution of XXV (0.24 g, 1.00 mmole) and N-phenylmaleimide (0.17 g, 1.00 mmole) in dry tetrahydrofuran (10 ml) was refluxed under nitrogen for 4 hr. Cooling and filtration gave a nearly pure product (3.8 g, 92%); recrystallization from acetone gave the adduct as white prisms, mp 325–327°; λ_{max}^{KBr} 5.84 (s), 6.27 (m), 7.22 (s), 8.42 (s), and 9.26 (m).

Anal. Calcd for $C_{26}H_{19}NO_4$: C, 76.27; H, 4.65. Found: C, 76.41; H, 4.80.