water (100 ml) and then 33% sodium hydroxide solution (6 ml) were added. The mixture was stirred at 25° for 1 hr, heated to 50° , cooled to 5° , and filtered to yield a brown solid (11.7 g). Concentration of the filtrate gave additional solid (3.5 g). The combined solid, upon crystallization from benzene-chloroform, yielded 4,4'-azobis[N,N-dimethyl]aniline (36), bright orange needles, mp $265-268^{\circ}$, identical (melting point, mixture melting point, and ir absorption) with an authentic sample. Distillation (0.5 mm) of the remaining product, a dark viscous oil, resulted in recovery of cyclooctatetraene (5.8 g).

Reaction of *N*-Nitrosodiphenylamine and 1. Dropwise addition of 1 (0.028 mol) in ether (150 ml) was effected under nitrogen to *N*-nitrosodiphenylamine (16.6 g, 0.0838 mol) in ether (150 ml) at $0-5^{\circ}$. The brown suspension was stirred 1 hr without the cooling bath, cooled to $5-10^{\circ}$, and ice water (200 ml)-acetic acid was added. The ether phase and ether extracts of the aqueous solution were combined, washed with water and with aqueous solution bicarbonate, dried, concentrated, and distilled (0.5 mm). The distillate was shown by glc to be pure cyclooctaterraene.

The black viscous distillation residue was chromatographed on silica gel. Elution with benzene and recrystallization from hexane

gave diphenylamine (1.90 g), colorless leaflets, mp $52.5-54.0^\circ$, identical (melting point, mixture melting point, and ir absorption) with authentic material. The second compound eluted with benzene was *N*-nitrosodiphenylamine (3.6 g), mp $63.0-66.5^\circ$, identical with initial material. Evaporation of methanol washings of the silica gel column yielded an unidentified dark brown amorphous solid.

Reaction of Cadmium Chloride and 1. Cadmium chloride (18.3 g, 0.1 mol), dried at 100° under vacuum for 24 hr, was added (10 min) under nitrogen to stirred 1 (0.056 mol) in ether (150 ml) at $0-5^{\circ}$. The mixture was refluxed 1.75 hr, stored overnight at room temperature, and then poured into cold water (250 ml). The solid that remained on filtration was metallic cadmium (4.3 g, 0.0384 mol, 69%), identified by solution in hydrochloric acid with evolution of hydrogen, evaporation to dryness, dissolution of the white solid in dilute sulfuric acid, and conversion to yellow cadmium sulfide upon addition of 5% thioacetamide.

Distillation of the ether extract of the initial filtrate yielded cyclooctatetraene (~ 6.0 g, ~ 0.058 mol, $\sim 100\%$), bp 40-42° (10 mm), identified by the superimposability of its infrared spectrum with that from authentic material.

Synthesis and Chemistry of Bicyclo[4.2.1]nona-2,4,7-trien-9-one and of Bicyclo[4.2.1]nona-2,4,7-trien-9-yl Intermediates^{1,2}

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Abstract: Bicyclo[4.2.1]nona-2,4,7-trien-9-one (1), the bicyclo[4.2.1]nona-2,4,7-triene-9-carbene (2), and the bicyclo[4.2.1]nona-2,4,7-triene-9 cation (3) have been studied. Dilithium cyclooctatetraenide (6) and dimethylcarbamoyl chloride, upon acidification, give 1. Decarbonylation of 1 to cyclooctatetraene (12) occurs upon irradiation; tricyclo[4.2.1.0^{2,5}]nona-3,7-dien-9-one (13) and tricyclo[3.3.1.0^{2,8}]nona-2,7-dien-9-one (14) are minor products. Sensitized photolysis results mainly in carbon-skeleton rearrangement to 14. Stereochemically controlled nucleophilic addition of phenyllithium and of sodium borohydride occurs with 1 to give syn-9-hydroxy-9phenylbicyclo[4.2.1]nona-2,4,7-triene (9) and syn-9-hydroxybicyclo[4.2.1]nona-2,4,7-triene (16). Ketone 1 undergoes acid-catalyzed conversion to its ethylenedithioketal (20), oxime (25), tosylhydrazone (26), and 2,4-dinitrophenylhydrazone (27). Ring expansion occurs in the reaction of 1 with diazomethane-lithium chloride to yield bicyclo[4.2.2]deca-2,4,9-trien-7-one (21) and spiro[bicyclo[4.2.1]nona-2,4,7-triene-9,2'-oxirane] (22). Oxime 25 undergoes Beckmann fragmentation by tosyl chloride in pyridine to give cyano-1,3,5,7-cyclooctatetraene (28). Carbene 2, as generated via its diazo precursor 30 from the sodium salt of 26, isomerizes to indene (31). Attempts to generate cation 3 from syn-bicyclo[4.2.1]nona-2,4,7-trien-9-yl tosylate (41) and di-syn-bicyclo[4.2.1]nona-2,4,7trien-9-yl sulfite (42) result in rearrangement and elimination to 31. Reaction of 41 in tetrahydrofuran with lithium aluminum hydride gives bicyclo[4.3.0]nona-2,4,7-triene (43). In boron trifluoride 1 isomerizes to 1-indanone (50). The rearrangements of 2 and 3 and of 1 as catalyzed by boron trifluoride have been rationalized on the basis of migration of C-2 or -5 of the diene bridge to C-9 with subsequent reorganization. The possible roles of bicycloaromaticity and degeneracy in reactions of 1, 2, and 3 have been considered. The synthetic utility of dimethylcarbamoyl chloride (over phosgene) in reactions with organometallics is described.

The bicycloaromatic properties^{3a} of bicyclo[4.2.1]nona-2,4,7-trien-9-one (1) and its related inter-

(1) Abstracted in part from the Ph.D. Dissertation of T. A. Antkowiak, The Ohio State University, Columbus, Ohio, 1968. This research has also been abstracted in part in *Diss. Abstr. Int. B*, 30, 112 (1969) and *Chem. Abstr.*, 72, 110871d (1970).^{1a}

(1a) NOTE ADDED IN PROOF. K. Kurabayashi and T. Mukai, *Tetrahedron Lett.*, 1049 (1972), have recently communicated a study of thermal and photochemical decomposition of bicyclo[4.2.1]nona-2,4,7trien-9-one (1) in which the results are similar to those of the present report. After our manuscript had been submitted (Oct 13, 1971) to J. *Amer. Chem. Soc.*, we learned (Jan 12, 1972) of the similar study by Kurabayashi and Mukai and immediately transmitted to these investigators a copy of our paper along with prior references¹ to our completed study of the thermal and photochemistry of 1.

(2) Acknowledgment is made for support of this research by the Office of Ordnance Research, The National Science Foundation, and the donors of the Petroleum Research Fund, administered by the Ameri-



mediates, the bicyclo[4.2.1]nona-2,4,7-triene-9-carbene (2), 3a,b cation 3, radical 4, 3a and carbanion 5, 3a are sub-

can Chemical Society. We should also like to acknowledge very informative discussions on photochemistry with J. S. Swenton and the contribution of M. J. Broadhurst in detecting and identifying 22 in the reaction of diazomethane with 1.

(3) (a) M. J. Goldstein, J. Amer. Chem. Soc., 89, 6359 (1967); (b) R. E. Leone and P. von R. Schleyer, Angew. Chem., Int. Ed. Engl., 860 (1970).

jects of importance in synthetic and theoretical chemistry.³ We should like to report a simple and efficient synthesis of 1 along with our initial observations of its properties and that of 2 and 3.

Results and Discussion

Bicyclic ketone 1 is prepared readily (76% yield)and in large quantity from dilithium cyclooctatetraenide (6) and dimethylcarbamoyl chloride in ether at 5° and hydrolysis with sulfuric acid (eq 1).^{4,5} The success



of the synthetic method is attributable to the marked ability of the 8-(N,N-dimethylcarboxamido)octatrienyl anion 7 to undergo bicyclization (eq 1) by attack on its amide function to give an adduct 8 that does not decompose to 1 until sulfuric acid is added. The failure of 8 to decompose until treated with aqueous acid is advantageous in that 1 is not subjected to nucleophilic attack by 6.

Ketone 1 is a fairly stable liquid (bp $46-47^{\circ}(0.3 \text{ mm})$) that is stored advantageously at -5° in darkness. Its structure is established by its analytical and spectral properties and by its reaction with phenyllithium (eq 2) to yield after hydrolysis syn-9-hydroxy-9-phenylbicyclo[4.2.1]nona-2,4,7-triene (9).⁶ Infrared absorp-



tion of 1 (neat, sodium chloride plates) at 1780 cm^{-1} with slight shoulders is indicative of its bridged carbonyl group. The nmr spectrum of 1 reveals a mul-

(4) (a) Ketone 1 was not obtained from 6 and methyl chloroformate at -60° nor could it be prepared advantageously from syn-9-hydroxybicyclo[4.2.1]nona-2,4,7-triene as derived from 6 and ethyl formate.^{4b} (b) T. A. Antkowiak and H. Shechter, *J. Amer. Chem. Soc.*, 94, 5361 (1972). (c) After the present method (eq 1) had been perfected (the late) Professor S. Winstein reported to us privately that 1 is produced in extremely poor yield from 6 and phosgene. We made available to Professor Winstein the results of our initial studies so that the degenerate behavior of 3 could be studied in detail.

(5) Utilization of dimethylcarbamoyl chloride to prepare symmetrical ketones has been described by A. Cattaneo, G. Gelmi, and H. Zevin, Farm. (Pavia), Ed. Sci., 16, 741 (1961). Presently phenyllithium and dimethylcarbamoyl chloride have been found to give benzophenone (>67%), and it is apparent that dimethylcarbamoyl chloride is superior for preparing diaryl ketones from aryllithium reagents. Dimethylcarbamoyl chloride is an inexpensive, readily available chemical that is easy to handle; we should like to encourage its use in place of phosgene in reactions with appropriate organometallic reagents.

(6) T. S. Cantrell and H. Shechter, J. Amer. Chem. Soc., 89, 5868 (1967).

tiplet for six olefinic hydrogens (C-2, -3, -4, -5, -7, and -8) centered at τ 4.12 and a multiplet for two bridgehead hydrogens (C-1 and -6) at 6.91. Bicyclo[4.2.1]nona-2,4,7-triene,⁷ its 9-substituted, and its 9,9-disubstituted^{4b,6} derivatives all show absorptions at τ 3.80-4.10 for 4-olefinic hydrogens (C-2, -3, -4, and -5) and at 4.6-4.9 for two olefinic hydrogens (C-7 and -8) along with that at 6.77-7.27 for its two bridgehead protons (C-1 and -6). The deshielding of the C-7 and -8 protons in 1 resulting in their absorption in the τ 4.1 region is thus noted. It is not yet clear whether the downfield shift for the nmr of the C-7 and -8 protons in 1 is the result of ring current effects derived from the carbonyl group or whether there is major interaction of the bishomocyclopropenyl type^{8,9} (10) in 1 involving



its C-7 and -8 double bond and its carbonyl group. The ultraviolet spectrum of **1** in ethanol reveals absorption maxima at 216, 269, 277, and 325 m μ (ϵ 3080, 4010, 3820, and 567, respectively). The spectral properties of compounds having moieties similar to that in **1** are 3-cyclopentenone^{10a} ($\lambda_{max}^{CeH_{14}}$ 190,^{10b} 258–300, and 325 m μ ($\epsilon \sim 4100$, 8–11, and 7, respectively)), 3,5-cycloheptadienone^{10e} ($\lambda_{max}^{EeH_{14}}$ 213 and 278 m μ (ϵ 5495 and 602)), and various bicyclo[4.2.1]nona-2,4,7-trienes^{4b,6} (λ_{max} 258–266 m μ (ϵ 2900–6100)). The ultraviolet properties of **1** may be indicative of delocalization effects as in **10** and/or **11**. Detailed studies of the



possible bicycloaromatic effects^{3a} in 1 are in progress.

 β,γ -Unsaturated ketones have received attention because of their facile photochemical decarbonylation and rearrangement.¹¹ Bicyclononatrienone 1 also responds photochemically. Irradiation of 1 in Pyrex at 20-30° under nitrogen with a high-pressure mercury lamp (450-W Hanovia) gives (eq 3 and 4) cyclooctatetra-

⁽⁷⁾ Prepared by the method of H. Tsuruta, K. Kurabayashi, and T. Mukai, *Tetrahedron Lett.*, 3775 (1967).

^{(8) (}a) S. Winstein, *Chem. Soc.*, *Spec. Publ.*, No. 21, 5 (1964). (b) Independent delocalization of the carbonyl group with the C-2, -3, -4, and -5 diene unit is expected to be unfavored because it is of the bishomocyclopentadienyl type; A. F. Diaz, M. Sakai, and S. Winstein, J. Amer. Chem. Soc., 92, 7477 (1970).

⁽⁹⁾ Molecular models reveal that 1 is a highly strained rigid ketone in which the C-7 and -8 double bond is nearly coplanar with C-1, C-6, and the C=O group; the plane of C-1, C-4, and the C=O group is $\sim 60^{\circ}$ out of the plane of the strained planar C-2, -3, -4, and -5 diene molety in which its C-C bond angles are $\sim 133^{\circ}$.

^{(10) (}a) L. D. Hess and J. N. Pitts, Jr., J. Amer. Chem. Soc., 89, 1973 (1967). (b) The λ_{max} for $\pi - \pi^*$ transition in ethanol is expected to be $\sim 200 \text{ m}\mu$; R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," Wiley, New York, N. Y., 1968, p 160. (c) W. E. Parham, R. W. Soeder, and R. M. Dodson, J. Amer. Chem. Soc., 84, 1755 (1962). (11) (a) D. I. Schuster, B. R. Sokolnick, and F. H. Lee, *ibid.*, 90,

^{(11) (}a) D. I. Schuster, B. R. Sokolnick, and F. H. Lee, *ibid.*, **90**, 1300 (1968); (b) L. A. Paquette, R. P. Eizember, and O. Cox, *ibid.*, **90**, 5153 (1968); and (c) references therein.



ene (12), carbon monoxide, and tricyclo[$4.2.1.0^{2,6}$]nona-3,7-dien-9-one (13) along with tricyclo[$3.3.1.0^{2,8}$]nona-2,7-dien-9-one¹² (barbaralone, 14, eq 5; trace amounts), unidentified volatiles, and polymer. Direct photolysis of 1 in ether at 2537 Å in quartz at $20-30^{\circ}$ yields 12 (70%), carbon monoxide, and 13.

Ketone 13, a viscous unstable liquid isolable by column chromatography, decarbonylates to cyclooctatetraene (12) slowly at room temperature and rapidly upon gas chromatography at 150°. The structure of 13 was assigned on the basis of its ir and its nmr spectra. The ir spectrum of 13 shows carbonyl absorptions at 1800, 1755, and 1725 cm⁻¹ typical of the strained bridged carbonyl groups of norbornenones.¹³ The nmr spectrum of 13 reveals a triplet^{14a} at τ 3.79 (H_a, H_a', area = 2), a singlet in the vinyl region^{14b} at 4.37 (H_b, H_b', area = 2), a doublet^{14c} at 6.92 (H_d, H_d', J =4 Hz), and a complex multiplet at 7.20 (H_c, H_c'; the total area of the τ 6.92 doublet and the 7.20 multiplet is 4). The endo stereochemistry of 13 is based on J =4 Hz for the doublet at τ 6.92.^{14c}

Formation of 12 as the major product of photolysis of 1 (eq 3) adds another example to the growing list of once rare photodecarbonylations of ketones in the condensed phase. Valence tautomerization of dienes to cyclobutenes is a well-known singlet photolytic process;¹⁵ such a transformation of 1 will give 13 (eq 4) and possibly its exo isomer.¹⁶ It is not yet clear whether photolysis of 1 to 12 involves (1) photolytic valence isomerization to 13 and/or its exo isomer followed by disrotatory thermal decarbonylation (4q + 2 electrons) and disrotatory photolytic ring opening (4q electrons), (2) concerted singlet photodecarbonylation^{17a} as a 4q

(12) W. Von E. Doering, B. M. Ferrier, E. T. Fossel, J. H. Hartenstein, M. Jones, Jr., G. Klump, R. M. Rubin, and M. Saunders, *Tetrahedron*, 23, 3943 (1967), and references therein.

(13) S. C. Clarke and B. L. Johnson, Tetrahedron Lett., 617 (1967).

(14) (a) Proton H_a is coupled to neighboring H_c and allylic H_c' ; the latter virtual coupling occurs through neighboring and equivalent H_a' . Virtual coupling effectively averages the actual coupling constants be tween each olefinic proton and both bridgehead hydrogens giving rise to the triplet. (b) The dihedral angle between H_b and H_d is ~90°; thus, the J value is 0 and H_b is a singlet. (c) The endo isomer 13 has a dihedral angle between H_c and H_d of ~40°; in the excisomer of 13 this angle is ~75°. From the Karplus relationship, ¹⁴ J values of 5 and 1 Hz are predicted for the endo and excisomers of 13. (d) J. Karplus, J. Chem. Phys., 30, 11 (1959).

(15) (a) W. G. Dauben, R. L. Cargill, R. M. Coates, and J. Saltiel, J. Amer. Chem. Soc., 88, 2742 (1966); (b) W. G. Dauben and W. T. Wyke, Pure Appl. Chem., 9, 539 (1964), and references therein.

(16) The exo isomer of 13 is expected to be highly unstable because of the unfavorable interaction of the juxtaposed carbonyl and olefin systems.

(17) (a) Photodecarbonylation via the singlet state is predicted to be a general reaction of ketones of type 15 possessing either a C_2 axis or a

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electron system^{17b} undergoing disrotatory collapse to a product **12** which is not inhibited by forbidding intracyclic nonbonded interactions, (3) rupture at C-1 and C-9 with subsequent decarbonylation of the diradical, or (4) some alternate, even more interesting process.

Sensitized photolysis of 1 using benzophenone in ether, acetone (neat), or Michler's ketone in benzene gives 14 (eq 5) as the major product. The yield of 14 varies with the sensitizer and is maximized (68%) with Michler's ketone. Michler's ketone is of preparative advantage in that only small amounts are necessary to absorb 99% of the light, and upon column chromatography of the photolysate, most of the sensitizer remains at the origin. Sensitizer that is eluted with 14 can be separated by sublimation of 14 at 40–50° at reduced pressure.

The formation of 14 from 1, which represents conversion of a β , γ -unsaturated ketone to a conjugated cyclopropyl ketone, is not unprecedented.¹⁸ The reaction must pass through a triplet state of 1.¹⁹ A possible mechanism for photosensitized conversion of 1 to 14 is illustrated in eq 5.



Ketone 1 undergoes normal nucleophilic addition of phenyllithium to give 9 upon hydrolysis (eq 2). Alcohol 9 is identical with that derived by reaction of 6 with benzoyl chloride, methyl benzoate, or benzoic anhydride.^{4b,6} The stereochemistry of 9 is presently assignable on the basis of kinetic steric control in which phenyllithium attacks the carbonyl group of 1 from its C-7 and -8 side rather than across the C-2, -3, -4, and -5 bridge. Reduction of 1 by sodium borohydride in plane of symmetry.^{11a} (b) In concerted photolytic elimination of carbon monoxide, systems possessing 4q electrons require disrototary bond rotation and systems with $4q + 2\pi$ electrons require conrotation; R. B. Woodward and R. Hoffman, Accounts Chem. Res., 1, 17 (1968), and references therein.



(18) (a) J. R. Williams and H. Ziffer, Chem. Commun., 469 (1967);
(b) L. B. Tenney, D. W. Boykin, Jr., and R. E. Lutz, J. Amer. Chem. Soc., 88, 1835 (1966); and (c) T. J. Katz, J. C. Carnahan, Jr., G. M. Clarke, and N. Acton, *ibid*, 92, 734 (1970).

(19) The exact nature of the triplet, whether it be diene-like $\pi - \pi^*$ or ketone-like $n - \pi^*$, cannot be assigned unequivocally. The $\pi - \pi^*$ triplet seems more likely since triplets of dienes are usually less than 60 kcal/mol above the ground state, whereas ketone $n - \pi^*$ triplet have much higher energies (~61-83 kcal/mol). Thus, transfer of energy, especially from Michler's ketone, to give the lower energy triplet of the diene seems reasonable. The diene portion of 1 is planar and should have a triplet energy close to that of a cisoid planar diene (e.g., E_T of 1,3-cyclohexadiene = 54 kcal/mol). methanol occurs similarly to yield syn-9-hydroxybicyclo[4.2.1]nona-2,4,7-triene $(16)^{20}$ exclusively; 16 is converted by acetic anhydride to syn-9-acetoxybicyclo-[4.2.1]nona-2,4,7-triene (17) and by sodium hydride and then methyl iodide to syn-9-methoxybicyclo[4.2.1]nona-2,4,7-triene (18). The stereochemistry of alcohol 16 can be assigned unambiguously upon comparison of its nmr with that of bicyclo[4.2.1]nona-2,4,7-triene (19).



Alcohol 16 exhibits a nmr multiplet for four diene hydrogens (C-2, -3, -4, and -5) at τ 4.11, a multiplet for two olefinic hydrogens (C-7 and -8) at 4.97, a triplet of a doublet for a single hydrogen (on C-9) at 5.74 (J = 12, 6 Hz), a broad triplet for two bridgehead hydrogens at 7.08 (J = 6 Hz), and a doublet for the hydroxyl hydrogen at 8.36 (J = 12 Hz). The nmr of hydrocarbon 19^{7,21} shows a triplet of a doublet for the anti hydrogen (H_a at C-9) at τ 8.08 (J = 11.3, 6.2 Hz), a broad doublet for the syn hydrogen (H_b at C-9) at 8.70 (J = 11.3 Hz), and a broad triplet for two bridgehead hydrogens at 6.87 (J = 6.2 Hz). In 16 there is no resonance for a syn hydrogen at C-9; a triplet of a doublet for anti hydrogen at C-9 is displayed, however, which is merely shifted downfield from that of 19.²²

Ketone 1 undergoes acid-catalyzed addition reactions and conversion to typical carbonyl derivatives. Thus 1 is converted by 1,2-ethanedithiol in the presence of boron trifluoride to bicyclo[4.2.1]nona-2,4,7-trien-9-one ethylenedithioketal (20). Reaction of 1 with diazomethane in methanol-chloroform-ether at 0° using lithium chloride as catalyst²³ yields bicyclo[4.2.2]deca-2,4,9-trien-7-one (21; 63%) and spiro[bicyclo[4.2.1]nona-2,4,7-triene-9,2'-oxirane] (22, 27%). The struc-



ture of **21** is established by its analysis and spectral properties, ^{24a,b} by analyses of its 2,4-dinitrophenyl-

(20) The product is identical with that obtained from ${\bf 6}$ and ethyl formate and then hydrolysis.^{4b}

(21) M. Roberts, H. Hamberger, and S. Winstein, J. Amer. Chem. Soc., 92, 6346 (1970).

(22) In 19 H_c is orthogonal to H_a and parallel to H_b . Hence, the nmr of H_a , split only by H_b , appears as a doublet, whereas that of H_b , split by H_a and H_c , occurs as a triplet of doublets. Replacement of H_b by hydroxyl will result in disappearance of the H_b doublet.

(23) A modification of the method of M. Stoll and W. Scherrer, Helv. Chim. Acta, 23, 941 (1940).

(24) (a) The carbonyl group in 21 absorbs at 1700 cm⁻¹. (b) The nmr of 21 consists of a multiplet of six olefinic hydrogens (C-2, -3, -4, -5, -9, and -10) at τ 3.6-4.5, multiplets for each bridgehead hydrogen (C-6 and C-1) at 6.3-6.7 and 6.8-7.3, respectively, and a multiplet for the two methylenic protons (C-8) at 7.4-7.6.^{24d} (c) The nmr of 22 appears as a multiplet for four olefinic protons (C-2, -3, -4, and -5) at 3.7-4.4, a doublet for two olefinic protons (C-7 and C-8) at 4.5-4.7, a singlet for two methylene protons (C-3') at 7.1-7.3, and a multiplet for two bridgehead protons (C-1 and -6) at 7.3-7.6.^{24d} (d) The chemistry and synthetic utility of 21 and 22 are subjects of investigation of this laboratory.

hydrazone, toluenesulfonylhydrazone, and benzenesulfonylhydrazone derivatives, and by its hydrogenation to bicyclo[4.2.2]decan-7-one (23, 95%). Ketone 23 was prepared independently by reaction of diazomethane with bicyclo[4.2.1]nonan-9-one^{25b} (24) as de-



rived by hydrogenation (85%) of 1. The structure of **22** is assigned from its analysis, its spectra,^{24c} and its chemical origin.

Treatment of 1 with hydroxylamine, tosylhydrazine, and 2,4-dinitrophenylhydrazine, respectively, gives the corresponding oxime 25, tosylhydrazone (26), and 2,4dinitrophenylhydrazone (27). Reaction of ketoxime 25 with tosyl chloride in pyridine results in Beckmann fragmentation²⁶ (eq 6) to give cyano-1,3,5,7-cyclooctatetraene (28, 57%); conversion of 25 to 7-azabicyclo[4.2.2]deca-2,4,9-trien-8-one (29, eq 7) or its struc-



tural isomers was not observed.²⁷ Analysis, mass spectroscopy (m/e 129), absorption at 2240 cm⁻¹ for a nitrile group, and nmr which reveals only the presence of olefinic hydrogen (a broad singlet at τ 4.05) affirm the structure of **28**.

Bicyclo[4.2.1]nona-2,4,7-trien-9-ylidene (2), the carbene presumably generated by decomposition of 9diazobicyclo[4.2.1]nona-2,4,7-triene (30) as derived by pyrolysis of the dry sodium salt²⁸ of 26 at 190°, isomerizes to give indene (31) as the major (95%) hydrocarbon product. Conversion of 2 to 31 must involve carbon-skeleton rearrangement and hydrogen migration. A relatively simple path (eq 8) for isomerization of 2, which might be considerably delocalized (32) or isomerize to bishomotropylidene (33) or other intermediates, involves the equivalent of a 1,2 shift of C-2 or -5 of its diene bridge to carbenic center $C-9^{29}$ to give bicyclo[4.3.0]nona-2,4,6,8-tetraene (35) which undergoes 1,5-sigmatropic rearrangement to 31. Indeed, other C_9H_8 species such as tricyclo[3.3.1.0^{2,8}]nona-3,6-dien-9ylidene (36, barbaralylidene), bicyclo[4.2.0]nona-2,4,8trien-8-ylidene (37), cyclononatetraenylidene (38), and

^{(25) (}a) M. Jones, Jr., S. D. Reich, and L. T. Scott, J. Amer. Chem. Soc., 92, 3118 (1970); (b) C. D. Gutsche and T. D. Smith, *ibid.*, 82, 4067 (1960).

⁽²⁶⁾ See the discussion by A. F. Ferris, J. Org. Chem., 25, 12 (1960).
(27) L. A. Paquette, J. R. Malpass, and T. J. Barton, J. Amer. Chem.
Soc., 91, 4714 (1969).

⁽²⁸⁾ Prepared by reaction of sodium hydride and 26 in methylene chloride.

^{(29) 34} might also be highly delocalized through its olefinic and cyclopropyl moieties.



bicyclo[4.3.0]nona-2,4,6,8-tetraene (39), among others,



may play roles in transformation(s) of 2 to $31.^{30}$ The many important questions of the interrelationships, the multiplicities, and the possible degeneracy of various C_9H_8 species await resolution.

Attempts to generate the bicyclo[4.2.1]nona-2,4,7triene-9 cation 3 and derivatives 40 of the 9-hydroxybicyclo[4.2.1]nona-2,4,7-triene-9 cation (see later text) result in deep-seated rearrangement and elimination. Thus, syn-bicyclo[4.2.1]nona-2,4,7-trien-9-yl tosylate (41) and di-syn-bicyclo[4.2.1]nona-2,4,7-trien-9-yl sulfite (42) each give indene (31) on heating.³¹ Similarly,



reaction of **41** in acetone in the presence of sodium iodide yields **31**. Use of lithium aluminum hydride as a possible trapping agent in reaction of **41** in tetrahydrofuran results in formation of bicyclo[4.3.0]nona-2,4,7triene (**43**, *cis*-8,9-dihydroindene).³² The structure of **43** is indicated by its elemental and mass spectral analyses, its nmr spectra (a multiplet for six olefinic hydrogens at τ 4.0 and a broad multiplet for a total of four methylene and methyne hydrogens at τ 6.1), its conversion by air to 31, and its Diels-Alder addition of tetracyanoethylene.³³ Formation of 31 from 41 and/or 42 might arise (eq 9) from 3,^{3a} its delocalized analog 44,



and/or bishomotropylium ion 45^{34} by migration of C-2 or -5 to cationic site C-9 to yield, via 46, the cis-8,9dihydro-1-indenyl cation 47^{35} and then 35 which undergoes sigmatropic isomerization. Reduction of 47 by lithium aluminum hydride will result in 43. Other C₉H₉+ ions^{3b} and more complex isomerizations^{3b} might be involved in formation of 31 from 41 and 42 and thus appropriate labeling and diagnostic experiments are necessary to provide information concerning such possibilities.^{4c, 36}

Reaction of 1 with boron trifluoride-etherate at 25– 30° and hydrolysis of the mixture results in acid-catalyzed isomerization of the ketone to 1-indanone (50). The conversion of 1 to 50 may be rationalized simply (eq 10), among many possibilities, ^{3b} by migration of C-2 or -5 to the cationic center of 40 to give 48 which reorganizes to 50 and boron trifluoride. The details of the structure of 40 and its conversion to 50 are unknown. However, the isomerization path pictured is analogous to the cationic rearrangement process indicated in eq 9 and the carbenic process of eq 8.

The chemistry of 1-5 will be the subject of additional reports from this laboratory.

(33) T. J. Katz and P. J. Garratt, J. Amer. Chem. Soc., 86, 5194 (1964).

(34) Participation from the underside (the 2,4,7-cycloheptatriene moiety) might provide assistance for ionization of 41 and 42.

(35) This mechanism is consistent with the observation that 2,3,4,5tetradeuterio-syn-9-hydroxy-9-phenylbicyclo[4.2.1]nona-2,4,7-triene reacts with thionyl chloride (2 equiv) and pyridine (1 equiv) to give 1chloro-5,6,7,8-tetradeuterio-9-phenyl-cis-8,9-dihydroindene; (b) footnote 57 (personal communication by A. S. Kende) in ref 3b.

(36) (a) It is to be noted that syn-9-acetoxy-9-methylbicyclo[4.2.1]nonatriene and syn-9-benzoyloxy-9-phenylbicyclo[4.2.1]nonatriene decompose by mechanisms different from that in eq 9 in that at 184° 2methylindene and 2-phenylindene are formed, respectively. In the present study it has been found that acetate 17 does not decompose at temperatures up to 300°. (b) These systems are of additional complication in that J. A. Berson, R. R. Boettcher, and J. J. Vollmer, J. Amer. Chem. Soc., 93, 1540 (1970), have revealed that "hydrogen rebound" occurs in pyrolysis of bicyclo[4.2.1]nona-2,4,7-triene to 42.

⁽³⁰⁾ Intermediates 36-39 may be involved via isomerization of 2, 32, or 33. (b) For related discussion of the structures, degeneracy, and intramolecular chemistry of various C_9H_9 cations, see ref 3b and subsequent sections of the present manuscript. (c) The intermediates 2, 32-34, and 36-38 might be triplets rather than singlets.

⁽³¹⁾ Tosylate 41 was prepared from 16 and tosyl chloride in pyridine at 0° ; sulfite 42 was obtained from 16 and thionyl chloride in pyridine at 0° .

⁽³²⁾ W. Grimme, Chem. Ber., 100, 113 (1967); E. Vogel, W. Wiedemann, H. Kiefer, and W. F. Harrison, Tetrahedron Lett., 11, 673 (1963); and J. Schwartz, Chem. Commun., 833 (1969).



Experimental Section

Synthesis of Bicyclo[4.2.1]nona-2,4,7-trien-9-one (1). Dry ether (200 ml) was placed in a 1-l., three-necked flask equipped with a stirrer, thermometer, condenser, and a nitrogen line. Small pieces of lithium (1.6 g) were cut and then hammered into sheets on glassine powder paper moist with paraffin. The thin sheets were held over the flask and, with a steady stream of nitrogen flowing, shavings were cut directly into the flask with scissors.

The lithium-ether mixture was cooled to -70° and cyclooctatetraene (10.4 g) was added all at once. The mixture was stirred at -70° for 4 hr with constant nitrogen purge. The Dry Ice-acetone bath was then removed and the mixture stirred overnight (10-12 hr) under nitrogen. Sufficient dry ether was added to dissolve all of the precipitated dilithium cyclooctatetraenide (6).

Dimethylcarbamoyl chloride (11.9 g, 0.11 mol) in dry ether (70 ml) was added dropwise (40 min) to the stirred solution of 6 under nitrogen. The mixture was stirred for 2 hr and warmed to 15°. Dilute sulfuric acid (3 N, 100 ml) was added to the stirred reaction mixture at 10°. The mixture was separated and the aqueous layer extracted with ether. The ether extract was washed with water, saturated sodium bicarbonate solution, and water, dried over magnesium sulfate, filtered, and concentrated (50 ml) under reduced pressure. On storage a yellow solid (0.25 g, unidentified) precipitated. Distillation of the liquid residue yielded 1 (7.1 g, bp 46-47° (0.3 mm)) as a colorless liquid. The conversion of cyclooctatetraene (12) to 1 is 54%; the yield of 1 from dimethylcarbamoyl chloride and 6 is considerably higher in that the latter reagent is usually formed in 60-70% efficiency from cyclooctatetraene. Ketone 1 solidifies and is conveniently stored in a freezer compartment at $\sim -5^{\circ}$. After a few weeks solid 1 turns vellow; however, simple vacuum distillation results in effective repurification of 1.

Anal. Calcd for C_9H_8O : C, 81.04; H, 6.11. Found: C, 81.00; H, 6.00.

Reaction of 1 and Phenyllithium. An ether solution (10 ml) of 1 (1.32 g, 0.01 mol) was added dropwise to a stirred solution of phenyllithium (from 3.14 g, 0.02 mol, of bromobenzene and 0.32 g, 0.463 mol, of lithium) in ether (15 ml) at 5° under nitrogen. The mixture was stirred for 0.5 hr at 5°, then allowed to warm to room temperature, and poured in cold dilute acetic acid. The ether layer was combined with the ether extract of the aqueous layer and washed with saturated sodium bicarbonate solution and then water, dried over magnesium sulfate, filtered, and concentrated. On storage of the solution at 0-5°, large colorless crystals of syn-9-hydroxy-9phenylbicyclo[4.2.1]nona-2,4,7-triene (9, 0.8 g, 37.1%), mp 105-107°, formed which were identical (mixture melting point and superimposable ir spectrum) with that obtained from 6 and methyl benzoate. 4b

Photolysis of 1 in Ether. An ether solution (300 ml) of 1 (2.0 g, 0.151 mol) was purged with nitrogen for 0.75 hr and then irradiated at room temperature for 6 hr with a 450-W Hanovia high-pressure mercury lamp through a Pyrex sleeve. A positive nitrogen pressure was maintained over the photolysis solution during the entire experiment.

The above procedure was repeated six times and the reaction mixtures were combined. A white powder, possibly polymeric material, was filtered. Examination of the remaining photolysate by micro tlc using benzene as solvent revealed the presence of four products along with 1. The ether solution of photolysis products was concentrated and the residue then distilled at a pot temperature of 25°, at 8-9 mm and then at 0.6 mm. The distillate condensed at -80° was identified as cyclooctatetraene (12, 7.5 g, 0.0721 mol, 80%) from its ir and nmr (a singlet at τ 4.25) spectra.

as eluent, the first compound to be removed was tricyclo[4.2.1.0^{2,5}]nona-3,7-dien-9-one (13, 0.40 g, 3.4%). On standing at room temperature, 13 decomposes with loss of carbon monoxide. An attempt to gas chromatograph 13 at 150° resulted in its decarbonylation to cyclooctatetraene (12).

The slowest moving compound from chromatography was identified as tricyclo[3.3.1.0^{2,8}]nona-2,7-dien-9-one (14, 0.1 g) by its unique nmr spectrum¹² and upon comparison with 14 as prepared by photosensitized isomerization of 1. The remaining two compounds observed by tlc were isolable only in small amounts and their instability precluded preparation of pure samples and identification. The tarry materials adhering to the chromatographic column were not identified.

Sensitized Photolysis of 1. (a) Benzophenone as Sensitizer. A solution of 1 (0.5 g, 0.0038 mol) and benzophenone (1.5 g, 0.082 mol) in anhydrous ether (250 ml) was purged with nitrogen and irradiated for 45 hr with a 450-W Hanovia high-pressure mercury lamp using a filter solution for isolation of the 3650-3663 Å region.³⁷ The reaction mixture including the photosensitizer contained eight components of which one was major. The principal component was separated via chromatography on silica gel (1.7 \times 73.0 cm) using benzene-ether (20:1) as eluent. Following fractions consisting of benzpinacol, benzophenone, and 1 came the major product along with another component. Sublimation of this mixture yielded 14 (0.20 g, 40%), a white solid, mp 50-51°, which was identified by its ir and nmr spectra¹² and upon conversion to its semicarbazone, mp 207-209° (lit, 12 mp 205-207°).

Isolation of the other components of the reaction product was precluded because of small amounts and the complexity of the mixture.

(b) Michler's Ketone as Sensitizer. A mixture of 1 (0.6 g, 0.00045 mol) and Michler's ketone³⁸ (1.25 g) in benzene (300 ml) which had been purged with nitrogen was irradiated at 10° with a 450-W Hanovia high-pressure lamp and Pyrex optics. After 2 hr, all of 1 had disappeared (determined by tlc using benzene as eluent). The solution was concentrated and then chromatographed on silica gel (5.5 \times 76.2 cm). Rapid elution with ether yielded a solid mixture of product and sensitizer which was then washed with ether and filtered (the product is extremely soluble whereas Michler's ketone is sparsely soluble in ether). The filtrate, still containing some sensitizer, was sublimed at 40-50° (8 mm) to give 1412 (0.41 g, 68.4%), white crystals, mp 50-51°, identical with previous samples.

Reduction of 1 with Sodium Borohydride. To 1 (2.6 g, 0.02 mol) in methanol (18 ml) at 5° was added sodium borohydride (0.236 g, 0.00624 mol) in 2 N sodium hydroxide (0.25 ml) diluted with water (1.8 ml). After the mixture had been stirred for 0.25 hr at 5°, the methanol was evaporated and the residue was diluted with water. The suspension produced was extracted with ether, and the ether portion was washed with water, dried (MgSO₄), filtered, and evaporated. The semisolid was recrystallized from hexane to yield syn-9-hydroxybicyclo[4.2.1]nona-2,4,7-triene (16, 2.0 g, 74%) as white plates, mp 51.0-52.5°, uv maxima at 220 and 262 mµ (ϵ 3300 and 4360).

Anal. Calcd for C₉H₁₀O: C, 80.60; H, 7.46. Found: C, 80.38; H, 7.48.

Reaction of 16 and Acetic Anhydride. Acetic anhydride (3.2 g, 0.037 mol) was added to 1 (1.2 g, 0.00895 mol) in anhydrous pyridine (4 ml). The solution was refluxed 0.75 hr, stirred overnight at room temperature, poured into ice water, and extracted with ether. The ether extract was washed with 2% aqueous hydrochloric acid, water, sodium bicarbonate solution, and water, then dried over magnesium sulfate, filtered, evaporated, and distilled to yield syn-9-acetoxybicyclo[4.2.1]nona-2,4,7-triene (17, 1.1 g, 70%) as a colorless liquid, bp 61.5-62.5° (0.5 mm). Anal. Calcd for C₁₁H₁₂O₂: C, 74.97; H, 6.86. Found: C,

74.99; H, 6.86.

Conversion of 16 to syn-9-Methoxybicyclo[4.2.1]nona-2,4,7-triene (18). To a stirred mixture of alcohol 16 (8.89 g, 0.06 mol) and methyl iodide (9.93 g, 0.07 mol) in anhydrous 1,2-dimethoxyethane (120 ml) was added sodium hydride (1.68 g, 0.07 mol) in 15 min. Hydrogen was evolved vigorously and the mixture was stirred 1.5 hr at room temperature. After filtering the excess sodium hydride,

⁽³⁷⁾ For a description of the details see J. G. Calvert and J. N. Pitts, "Photochemistry," Wiley, New York, N. Y., 1966, p 734.

⁽³⁸⁾ From the extinction of the photosensitizer at 3130 Å, 0.8 g in 300 ml of solvent will absorb 90% of the light. For the 450-W lamp 80.3 % of the optical distribution in the presence of Pyrex filters occurs at 3130 and 3600 Å. At 3600 Å, the extinction of 1 is almost zero.

the mixture was flash evaporated and the residue was distilled to give 8 (8.30 g, 80%) as a colorless liquid: bp 39-41° (0.2 mm); nmr τ 4.0 (m, 4 H, H at C-2, -3, -4, and -5), 4.85 (m, 2 H, H at C-7 and -8), 6.15 (broad t, 1 H, H at C-9), and 6.90 (m, 5 H, H at C-1 and -6 and CH₃).

Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.17. Found: C, 81.29; H, 8.11.

Reaction of 1 and 1,2-Ethanedithiol. Boron trifluoride etherate (1 ml, 45%) was added in 10 min to a stirred mixture of **1** (2.0 g, 0.015 mol) and 1,2-ethanedithiol (1.41 g, 0.015 mol) at 0°. A yellow viscous material formed to which methanol (15 ml) was added. The mixture partly solidified in a freezer and the liquid was removed. Upon column chromatography of the semisolid on silica gel with hexane-benzene as eluent, bicyclo[4.2.1]nona-2,4,7-trien-9-one ethylenedithioketal (**20**, 2.45 g, 0.012 mol, 79%) was isolated as white crystals, mp 83-85°, upon recrystallization from methylene chloride-hexane: nmr τ 4.05 (m, 4 H, H at C-2, -3, -4, and -5), 4.65 (m, 2 H, H at C-7 and -8), 6.65 (m, 2 H, bridgehead H), and 6.80 (s, 4 H, methylene H).

Anal. Calcd for $C_{11}H_{12}S_2$: C, 63.41; H, 5.86. Found: C, 63.15; H, 5.64.

Reaction of 1 with Diazomethane. Ethereal diazomethane (300 ml of 0.33 *M* solution, 0.1 mol) at 0° was added all at once to a solution of **1** (5.00 g, 0.038 mol) in methanol (20 ml)-chloroform (40 ml) containing lithium chloride (0.35 g, 0.008 mol) at 0°. The mixture was stored at 0° until **1** disappeared (\sim 3 hr) as indicated by micro tlc analysis on silica gel G using ether-hexane (2:3) as solvent. Formic acid (3 ml, 0.075 mol) was added dropwise (5 min) and the mixture was extracted with water, saturated sodium bicarbonate solution, and saturated brine solution, and filtered through Drierite. Subsequent concentration *in vacuo* followed by vacuum distillation of the oily residue yielded a water white mixture (4.87 g, 90%) of **21** and **22**, bp 43-47° (0.15 mm), mass spectrum *m/e* 146.

Anal. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.89. Found: C, 81.70; H, 6.72.

Separation, analysis, and isolation of the products by glc (15% SE 30 on Chromosorb W 45-60) gave spiro[bicyclo[4.2.1]nona-2,4,7-triene-9,2'-oxirane] (22, relative retention time = 1.0, 30%) and bicyclo[4.2.2]deca-2,4,9-trien-7-one (21, relative retention time = 1.2, 70%).

As a preparative method for isolating ketone 21, the oily residue was refluxed with Girard's reagent T (8.6 g, 0.05 mol) for 1 hr in acetic acid (5 ml), ethanol (30 ml), and water (2 ml). The reaction mixture was diluted with water, brine, and ether. After the ether layer had been separated, the aqueous portion was heated with concentrated hydrochloric acid on a steam bath for 15 min. The aqueous mixture was cooled and extracted with ether, and the aqueous layer was reheated with steam. These operations were repeated several times and the various ether extracts were combined, washed with aqueous sodium bicarbonate and brine, filtered through Drierite, and concentrated *in vacuo*. Distillation of the residue yielded 21 as an oily water-white solid (2.32 g, 42%), bp 66–70° (0.06 mm).

Bicyclo[4.2.2]deca-2,4,9-trien-7-one 2,4-Dinitrophenylhydrazone. Reaction of 21 (0.21 g, 0.0014 mol) with 2,4-dinitrophenylhydrazine³⁹ gave bicyclo[4.2.2]deca-2,4,9-trien-7-one 2,4-dinitrophenylhydrazone (0.3 g, 64%) as bright orange needles, mp 221–222.5° (from chloroform-methanol, 1:1), mass spectrum m/e 326.

Anal. Calcd for $C_{16}H_{14}N_4O_4$: C, 58.89; H, 4.32; N, 17.17. Found: C, 58.64; H, 4.20; N, 17.20.

Bicyclo[4.2.2]deca-2,4,9-trien-7-one Tosylhydrazone. A solution of tosylhydrazine (2.54 g, 0.0136 mol) and concentrated hydrochloric acid (1 drop) in absolute ethanol (50 ml) was combined with **21** (1.40 g, 0.0105 mol) in absolute ethanol (50 ml). The mixture was stirred at room temperature for 12 hr, concentrated at reduced pressure, and then cooled to $0-5^{\circ}$. White crystals of bicyclo[4.2.2]deca-2,4,9-trien-7-one tosylhydrazone separated (2.32 g, 70%), which upon repeated recrystallization from ethanol melted at 156–158°: mass spectrum m/e 314; ir absorption (KBr pellet) 3450 (w), 3250 (m), 3050 (m), 2950 (m), 1640 (w), 1610 (m), 1510 (m), 1470 (m), 1400 (s), 1340 (s), 1190 (s), 1100 (m), 030 (broad), 990 (w), 960 (w), 930 (w), 905 (m), 820 (s), 800 (m), 780 (w), and 730 cm⁻¹ (m); nmr (CCl₄) τ 2.4 (AB splitting, 4 H, aromatic C-H), 2.48 (s, 1 H, N-H), 3.6–4.6 (m, 6 H, olefinic C-H), 6.25–6.65 (quintet, 1 H, bridgehead C-H), 6.8–7.3 (m, 1 H; bridge-

head C–H), and 7.3–7.7 (s imposed on split d, methylene C–H and methyl C–H).

Anal. Calcd for $C_{17}H_{18}N_2O_2S$: C, 64.94; H, 5.77; N, 8.91. Found: C, 64.84; H, 5.74; N, 8.73.

Bicyclo[4.2.2]deca-2,4,9-trien-7-one Benzenesulfonylhy drazone. A mixture of 21 (1.40 g, 0.0105 mol), benzenesulfonylhydrazine (2.34 g, 0.0136 mol), ethanol (100 ml), and hydrochloric acid (1 drop), after 12 hr at 25-30°, was concentrated *in vacuo*. The residue, upon solution in methylene chloride (20 ml) and hexane (20 ml) and storage at -5° , yielded white crystals of bicyclo[4.2.2]-nona-2,4,9-trien-7-one benzenesulfonylhydrazone (2.70 g, 85%): mp 62-65°; nmr (CCl₄) τ 1.8-2.7 (m, 6 H, aromatic C-H, N-H), 3.6-4.3 (m, 6 H, olefinic C-H), 6.3-6.6 (br q, 1 H, bridgehead C-H), 6.8-7.2 (m, 1 H, bridgehead C-H), and 7.3-7.5 (d, 2 H, methylene C-H).

Anal. Calcd for C₁₆H₁₆N₂O₂S: N, 9.32. Found: N, 9.05.

Hydrogenation of 21 to Bicyclo[4.2.2]decan-7-one (23). A mixture of 21 (2.00 g, 0.0136 mol) and palladium on carbon (0.2 g, 5%) in ethanol (150 ml) was placed in a Paar hydrogenator; hydrogenation was complete in 30 min. After the reaction mixture had been filtered and concentrated *in vacuo*, the residue was dissolved in ether, washed with saturated brine, and filtered through Drierite. Upon removal of the ether, 23 (1.97 g, 95%) was isolated as a white oily solid. After sublimation and crystallization from pentane, white crystals of 23^{25a} were obtained: mp 155–157°; ir absorption (KBr pellet) at 1720 cm⁻¹.

Ketone 23 (0.70 g, 0.0046 mol) in ethanol (10 ml), upon reaction with semicarbazide hydrochloride (1 g) and sodium acetate (1.5 g) at 80-85°, gave bicyclo[4.2.2]decan-7-one semicarbazone (0.57 g, 60%) as a white solid, mp 208-210°, lit. mp 205-207°.^{25a} The derivative, after recrystallization from 50% ethanol-water, melts at 220-222°, exact mass, calcd 209.1528, found 209.1531.

Ketone 23 was converted by 2,4-dinitrophenylhydrazine in sulfuric acid-ethanol to bicyclo[4.2.2]decan-7-one 2,4-dinitrophenylhydrazone: orange crystals; mp (from ethanol) 179.5-181°; mass spectrum m/e 332.

Anal. Calcd for $C_{16}H_{20}N_4O_4$; C, 57.82; H, 6.06; N, 16.86. Found: C, 57.79; H, 5.96; N, 16.57.

Hydrogenation of 1 to Bicyclo[4.2.1]nonan-9-one (24). Conversion of 24 by Diazomethane to 23. A mixture of 1 (1.16 g, 0.00879 mol) and palladium on carbon (0.05 g, 5%) in ethanol (100 ml) was hydrogenated and worked up as was 21 in the previous experiment. Concentration of the product gave 24 (1.03 g, 85%) as a white oily solid. After sublimation and crystallization from pentane, crude 24 was obtained as white crystals: mp 98-101° (lit.^{25b} mp 109-111°); ir absorption (KBr pellet) at 1740 cm⁻¹ (lit.^{25b} 1737 cm⁻¹); exact mass calcd for C₉H₁₄O, 138.1045; found, 138.1046.

Ethereal diazomethane (50 ml, 0.3 M; 0.015 mol) was added at 0° to crude 24 (0.5 g, 0.0036 mol) in ether (6 ml)-methanol (1 ml).⁴⁰ After 5 days formic acid was added to destroy excess diazomethane. The solution was washed with saturated sodium bicarbonate solution, filtered through Drierite, and concentrated. Analysis of the concentrate by glc (10 ft of 15% SE-30 at 150°) revealed the presence of initial 24 (relative retention time = 1.0; area = 10) and 23 (relative retention time = 1.75; area = 1); the retention time of 23 is identical with 23 as obtained from 21.

Bicyclo[4.2.1]nona-2,4,7-trien-9-one Oxime (25). A mixture of 1 (2.0 g, 0.015 mol), hydroxylamine hydrochloride (3.0 g, 0.043 mol), and anhydrous sodium carbonate (3.0 g, 0.028 mol) in water (20 ml) was stirred for 1 hr at 0°. Water was added and the mixture was extracted with ether. The organic portion was dried (MgSO₄), concentrated, and upon crystallization from methylene chloride and hexane, yielded **25** (1.61 g, 79%) as white crystals: mp 112-113°; ir spectrum (KBr pellet) 3180 (s), 2910 (s), 1680 (w), 1460 (m), 1260 (w), 1220 (w), 965 (m), 945 (m), 915 (m), 890 (w), 880 (m), 860 (m), 745 (s), and 690 cm⁻¹ (s); nmr τ 0.65 (s, 1 H, OH), 4.05 (m, 4 H, H at C-2, -3, -4, and -5), 4.55 (m, 2 H, H at C-7 and -8), 5.75 (m, 1 H, bridgehead C–H), and 6.45 (m, 1 H, bridgehead C–H).

Bicyclo[4.2.1]nona-2,4,7-trien-9-one Tosylhydrazone (26). Ketone 1 (5.0 g, 0.038 mol) was added to a refluxing solution of tosylhydrazine (7.4 g, 0.040 mol) in methanol (40 ml) and heating was discontinued. After 0.5 hr the mixture was concentrated and the product was crystallized at 0°. Recrystallization from methanol gave 26 (9.60 g, 85%) as a near-white solid: mp 177-179°; nmr τ 2.4 (m, 4 H, aromatic H), 4.15 (m, 4 H, H at C-2,

⁽³⁹⁾ According to the procedure of R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd ed, Wiley, New York, N. Y., 1948, p 171.

⁽⁴⁰⁾ A modification of the procedure of ref 25a.

-3, -4, and -5), 4.81 (m, 2 H, H at C-7 and -8), 6.15 (m, 1 H, bridgehead C-H), 6.50 (m, 1 H, bridgehead C-H), and 7.55 (s, 3 H, CH_s). Anal. Calcd for $C_{18}H_{16}N_2O_2S$: C, 62.72; H, 5.27; N, 9.14.

Found: C, 62.96; H, 5.11; N, 9.36. Beckmann Fragmentation of 25. Tosyl chloride (5.14 g, 0.027 mol) was added in 0.5 hr to oxime 25 (2.0 g, 0.014 mol) in pyridine (20 ml) at 0°. The mixture turned black on storage. After 2 days at -20° , the mixture was poured on ice, and extracted with ether. The organic layer was washed with cold 6 N hydrochloric acid, saturated sodium bicarbonate, and saturated sodium chloride, dried, and vacuum evaporated. Column chromatography on alumina (Woelm, neutral grade 1) with benzene-hexane (1:1) afforded cyano-1,3,5,7-cyclooctatetraene (28, 1.02 g, 57%) as a yellow liquid after distillation: bp 66° (1.5 mm); mass spectrum m/e 129; ir absorption at 3060 (m), 2940 (w), 2160 (w), 2230 (s), 1635 (w), 895 (w), 815 (s), 785 (m), 755 (s), and 695 cm⁻¹(s).

Anal. Calcd for C₉H₇N: C, 83.69; H, 5.46; N, 10.89. Found: C, 83.46; H, 5.27; N, 10.58.

Carbenic Decomposition of 26. Sodium hydride (0.272 g of 59% mineral oil dispersion, 0.0068 mol) was added slowly to 26 (2.0 g, 0.0067 mol) in methylene chloride (30 ml) at 0°. After evolution of hydrogen ceased, the solvent was stripped at reduced pressure leaving the salt of 26 as a white powder coated on the flask walls. The flask was attached *via* an adapter (partially packed with glass wool to prevent spatter entrainment) to a series of traps and a vacuum system. Upon decomposing the salt of 26 at 190° (0.3 mm), a liquid was trapped which was shown to be 95% indene (31, 0.32 g, 42%) by glc analysis (comparative retention times) and by the nmr of a preparative sample. The single minor volatile product has not been identified.

Preparation of syn-Bicyclo[4.2.1]nona-2,4,7-trien-9-yl Tosylate (41). A mixture of syn-9-hydroxybicyclo[4.2.1]nona-2,4,7-triene (16, 2.0 g, 0.015 mol), tosyl chloride (5.64 g, 0.030 mol), and pyridine (20 ml) was stored at -20° for 3 days, poured on ice, and extracted with ether. The ethereal layer was washed with cold 6 N hydrochloric acid, saturated sodium bicarbonate solution, saturated sodium chloride, and water, dried (MgSO₄), and evaporated at reduced pressure. The resulting white solid (41, 3.81 g, 86%), mp 83-85°, was crystallized at -78° from hexane containing sufficient chloroform to clear the solution at room temperature: nmr τ 2.4 (m, 4 H, aromatic H), 4.0 (m, 4 H, H at C-2, -3, -4, and -5), 4.85 (d, 2 H, H at C-7 and -8), 5.1 (br t, 1 H, H C-9), 6.95 (br t, 2 H, bridgehead CH), and 7.55 (s, 3 H, CH₃).

Anal. Calcd. for $C_{16}H_{16}SO_3$: C, 66.64; H, 5.59. Found: C, 66.77; H, 5.63.

Preparation of Di-syn-bicyclo[4.2.1]nona-2,4,7-trien-9-yl Sulfite (42). To 16 (2.0 g, 0.015 mol) in pyridine (10 ml) and hexane (20 ml) was added thionyl chloride (1.8 g, 0.015 mol) at 0°. A white precipitate formed immediately which remained while the mixture was refluxed 1 hr. The mixture was worked up as was 41. Crystallization from hexane yielded 42 (2.17 g, 93%) as a white solid: mp 117-118°; nmr τ 3.95 (m, 8 H, H at each C-2, -3, -4, and -5), 4.75 (m, 4 H, H at each C-7 and -8), 5.08 (br t, 2 H, H at each C-9), and 6.85 (br t, 4 H, H at each bridgehead).

Anal. Calcd for C₁₈H₁₈SO₃: C, 68.76; H, 5.77. Found: C, 68.70; H, 5.77.

Rearrangement and Elimination in Decomposition of 41 and 42. Esters 41 and 42 were dissolved individually in methylene chloride and injected into a gas chromatograph with its inlet at 200° and its column at 160° . Indene (31) was the hydrocarbon produced from decomposition of 41 and of 42.

Reaction of 41 with Sodium Iodide in Acetone. A mixture of 41 (1.0 g, 0.0035 mol) and sodium iodide (3.0 g, 0.020 mol) in acetone (25 ml) was refluxed 12 hr and poured into water. Sodium thiosulfate was added a crystal at a time until the iodine disappeared and the aqueous layer was extracted with ether. Analysis by glc revealed the presence of indene (31, 59%; identified by its retention time and its nmr); the two volatile minor products have not been identified.

Reaction of 41 with Lithium Aluminum Hydride. A solution of tosylate **41** (8.1 g, 0.028 mol) and lithium aluminum hydride (27 ml of 4.4 *M* solution in ether) was refluxed 96 hr, cooled to 0°, hydrolyzed with 3 N sodium hydroxide, and worked up as was the previous experiment. Chromatography (10 ft of 30% 20 M on Chromosorb P) revealed a major component (90%) and various minor contaminants. The product upon distillation gave a near-colorless liquid identified as bicyclo[4.3.0]nona-2,4,7-triene (**43**, *cis*-8,9-dihydroindene): 2.30 g, 85%, bp 65° (50 mm); mass spectrum *m/e* 118; nmr spectrum τ 4.0 (m, 6 olefinic H) and 6.7 (br m, 4 methylene and methyne H). Triene **43** was oxidized by air in several days to indene (**31**). A solution of **43** (0.2 g, 0.0017 mol) and tetracyano-ethylene (0.22 g, 0.0017 mol) in tetrahydrofuran (1 ml) at 85° for 1 hr and recrystallization of the product from benzene gave the white 1:1 adduct: mp 231–233° (lit.²³ mp 231.0–231.5°).

Isomerization of 1 by Boron Trifluoride. A mixture of 1 (2.0 g, 0.015 mol) and boron trifluoride etherate (15 ml, 45%) was stirred at room temperature for 48 hr. Water was added and the product was separated and concentrated by the method used for 41. Column chromatography of the residue on silica gel using hexane-benzene gave, after recovery of 1 (0.71 g, 0.0052 mol), 1-indanone (50, 0.76 g, 39%), mp 39-41°, as identified by its mixture melting point, ir spectrum, and R_f value on tlc on silica gel.

Attempted Pyrolysis of syn-9-Acetoxybicyclo[4.2.1]nona-2,4,7triene (17). A solution of 17 (0.8 g) in dimethyl sebacate (6 ml) was flushed with nitrogen, heated at 210° for 35 hr, and then distilled. The distillate was identified as 17 with no trace of rearrangement products as evidenced by gas chromatography (identical retention times, one peak) and its infrared spectrum (superimposable with that of starting material).

A sample of 17 was syringed into a gas chromatograph having an injection temperature of 300° . One major peak was produced; the material collected was identical with 17 (superimposable ir spectra). Minor peaks amounted to less than 1%.

Reaction of Dimethylcarbamoyl Chloride and Phenyllithium. Dimethylcarbamoyl chloride (7.3 g, 0.08 mol) in ether was added in 0.5 hr to phenyllithium (15.7 g, 0.1 mol of bromobenzene and 1.5 g (0.22 mol) of lithium) in ether (75 ml) at $15-20^{\circ}$ under nitrogen. The blue suspension was stirred at room temperature for 1.25 hr. Sulfuric acid (3 N, 50 ml) was then added and the mixture was stirred 0.25 hr. After the aqueous layer had been extracted with ether, the combined ether extracts were worked up conventionally and concentrated. On standing, the viscous liquid solidified. Recrystallization from ethanol yielded benzophenone (6.10 g, 67%), white plates, mp 46.0-48.0°, identical (mixture melting point and superimposable ir spectra) with authentic material.