3560 (intramolecular hydrogen-bonded OH stretching).

***meso*-3,3′-Biindan-1-one (3).** *meso*-3,3′-Biindan-1-ol (**6f**; 30 mg, 0.1 mmol) was added to a warmed (45 °C) and stirred mixture of 30 mg (0.3 mmol) of CrO_3, 20 mL of glacial HOAc, and 5 mL of H_2O. After 2 h of stirring at 45 °C, the mixture was cooled, diluted with 20 mL of H_2O, and neutralized with solid $NaHCO_3$. The green solution was extracted with EtOAc (5 × 50 mL) and the organic solution was washed with H_2O (3 × 50 mL) and dried over anhydrous $MgSO_4$. The solvent was removed by distillation under reduced pressure and the crystalline residue was 26 mg (88%) of *meso*-**3**, which was recrystallized from hot EtOH: mp 161–162 °C.

Dehydration of *meso*-6: Preparation of a Mixture of *rac*- and *meso*-1,1′-Bi-1*H*-indene (2). A mixutre of 100 mg (0.37 mmol) of *meso*-3,3′-biindan-1-ol (**6f**), 15 mL of dry C_6H_6, and 10 mg of *p*-toluenesulfonic acid monohydrate was heated at the reflux temperature for about 24 h. Water was collected in a Dean and Stark trap during this period. The mixture was washed with 5% aqueous $NaHCO_3$ (2 × 25 mL) and water (2 × 25 mL) and the benzene solution was dried over anhydrous Na_2SO_4. Distillation of the benzene at reduced pressure left 81 mg of an oily residue that resisted crystallization attempts. Gas chromatographic analysis (conditions given under preparation of *rac*-**2**, above) showed this oil to be a mixture of 80% *meso*- and 20% *rac*-**2**. Analysis of the C-1,1′ peaks in the ^{13}C NMR spectrum of this oil showed the isomer percentages to be 76% and 24%, respectively. The total yield of the oil was 95%.

When *rac*-3,3′-biindan-1-ol (**6c**) was dehydrated by the preceding procedure, a 94% yield of product was isolated that was 100% *rac*-**2** by gas chromatography. It readily solidified into yellow needles: mp 99–100 °C.

***rac*-1,1′-Biindan (1).** A solution of 0.5 g (2.1 mmol) of *rac*-1,1′-bi-1*H*-indene (**2**, mp 99–100 °C) and 18 mL of dry C_6H_6 was stirred with 1.0 g of 5% Pd-on-C, while H_2 (generated from 1.13 g of $NaBH_4$ and 20 mL of glacial HOAc) was passed through during a 2-h period. The mixture was filtered and the residue was washed with 100 mL of C_6H_6. The filtrate and washings were distilled under reduced pressure first to remove the solvent and then to purify the product, which weighed 0.5 g (100%): bp 180 °C (2 torr); UV (MeOH) λ_{max} 273.5 (ϵ 3.9), 267 (3.8), 260 (3.7) (identical with reported[1] values).

***rac*-1-(1-Indanyl)indene (8).** Active Mg was prepared by the following procedure.[8] To dried apparatus flushed with Ar were added 0.19 g (4.8 mmol) of freshly cut K, 50 mL of THF (distilled from sodium benzophenone ketyl and passed through a column of 10 g of Woelm neutral Al_2O_3, activity I), 0.25 g (2.6 mmol) of anhydrous $MgCl_2$, and 0.44 g (2.6 mmol) of anhydrous KI. This mixture was stirred and heated to the reflux temperature for 4 h during which time the active Mg separated as a fine black powder. *rac*-3,3′-Dibromo-1,1′-biindan (**5b/c**); 0.94 g, 2.3 mmol) was added to the above slurry of active Mg at room temperature. The resulting mixture was then heated to the reflux temperature under Ar for 24 h. The cooled mixture was diluted with Et_2O and filtered through Celite. The residue was washed with Et_2O. The filtrate and washings were combined and washed with water (3 × 100 mL), 5% aqueous sodium thiosulfate (3 × 100 mL), and 100 mL of brine. After drying, the organic phase was distilled under reduced pressure to afford 530 mg of a yellow oil. This was purified by preparative TLC (on a 2-mm layer of E. Merck silica gel F-254; hexane/EtOAc, 95:5) to yield 252 mg (47%) of **8**: bp 110 °C (2 torr) [lit.[4] value bp 190 °C (12 torr)].

Also isolated from preparative TLC was 261 mg (49%) of *rac*-1,1′-bi-1*H*-indene (**2**): mp 98–101 °C.

If Mg turnings were used in the above procedure in place of the specially prepared active Mg, the yields of **8** and **2** were 44% and 25%, respectively. In this experiment, some starting material was recovered.

Acknowledgement is made to the Analytical Chemistry Research Department of Bristol Laboratories, Syracuse, NY, for their generous assistance in providing all of the microanalyses reported herein. We also acknowledge Dr. Robert M. Metzger of this Department for providing the drawing in Figure 1.

Registry No. *rac*-**1**, 81523-13-9; *rac*-**2**, 81523-14-0; *meso*-**2**, 74339-76-7; *rac*-**3**, 81523-15-1; *meso*-**3**, 81523-16-2; *rac*-**4a**, 81523-17-3; *rac*-**4b**, 81571-00-8; *rac*-**4c**, 81571-01-9; *rac*-**5a**, 81523-18-4; *rac*-**5b**, 81571-02-0; *rac*-**5c**, 81571-03-1; *meso*-**5f**, 81571-04-2; *rac*-**6c**, 81523-19-5; *meso*-**6f**, 81571-05-3; *rac*-**8**, 81523-20-8; indene, 95-13-6.

(8) Klabunde, K. J.; Efner, H. F.; Satek, L.; Donley, W. *J. Organomet. Chem.* **1974**, *71*, 309. Reike, R. D.; Hudnall, P. M. *J. Am. Chem. Soc.* **1972**, *94*, 7178. Reike, R. D.; Bales, S. E.; Hudnall, P. M.; Poindexter, G. S. *Org. Synth.* **1979**, *59*, 85.

A New Entry to the $C_{12}H_{12}$ Energy Surface: Pyrolysis and Photolysis of *trans*-β-[*anti*-9-Bicyclo[6.1.0]nona-2,4,6-trienyl]acrolein Tosylhydrazone Salts

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Thermal decomposition of the lithium salt of *trans*-β-[*anti*-9-bicyclo[6.1.0]nona-2,4,6-trienyl]acrolein tosylhydrazone (**8**) results in the formation of pentacyclo[6.4.0.0^{2,12}.0^{3,7}.0^{4,11}]dodeca-5,9-diene (**12**), *exo*- and *endo*-tricyclo[4.4.2.0^{2,5}]dodeca-3,7,9,11-tetraenes (**9** and **10**), 1,2-benzocycloocta-1,3,7-triene (**11**), and *syn*- and *anti*-9-(5-pyrazolyl)bicyclo[4.2.1]nona-2,4,7-trienes (**14** and **13**). The low-temperature photolysis of the sodium salt of tosylhydrazone **8** gives *anti*-9-(2-cyclopropen-1-yl)bicyclo[6.1.0]nona-2,4,6-triene (**20**), which affords pentacyclo[6.4.0.0^{2,4}.0^{3,10}.0^{5,9}]dodeca-6-11-diene (**22**) on thermolysis. Hydrocarbon **12** was formed in the photolysis of the sodium salt of *trans*-β-[*syn*-9-bicyclo[4.2.1]nona-2,4,7-trienyl]acrolein tosylhydrazone (**15**; available by thermal rearrangement of tosylhydrazone **8**) as the sole $C_{12}H_{12}$ product. Structure determinations and mechanistic investigations are discussed.

The isomeric $(CH)_{12}$ hydrocarbons present an interesting family of compounds because of the theoretical significance of many of the members and the varied electrocyclic and sigmatropic processes expected of the numerous valence tautomers. Despite these attractive features, chemical investigation in this area has been limited because of the relative unavailability of synthetic entries to these compounds. For these reasons, various research groups have

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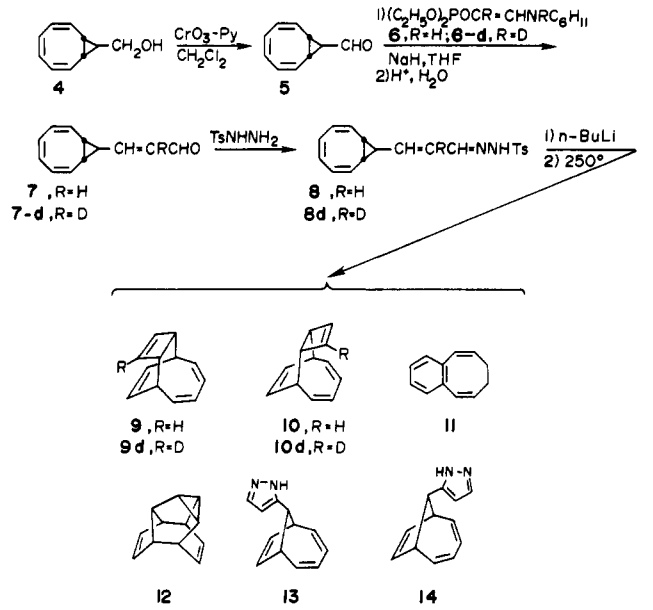
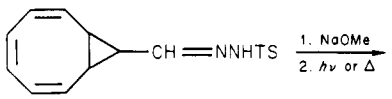


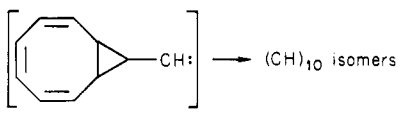
Figure 1. Preparation and pyrolysis of carbene precursor 8.

been interested in the possibility of developing syntheses of $(CH)_{12}$ hydrocarbons.[1] In our continued effort at contributing to the understanding of the $(CH)_{12}$ hydrocarbon energy surface,[2] we report herein a new entry into this system.

Synthesis of a $(CH)_{12}$ Precursor. A number of successful synthetic approaches to the $(CH)_{10}$ hydrocarbons used the carbenoid intermediate 2 generated either thermally[3] or photochemically[4] from the sodium or lithium salt of the corresponding *p*-toluenesulfonylhydrazone 1.

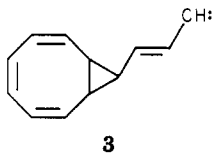


1



2

On the basis of this, we felt that a $(CH)_{12}$ carbene with similar reactive centers such as cyclopropanes and double bonds would serve as an entry to several $(CH)_{12}$ isomers. To this end, we decided to look for precursors to carbene 3.



3

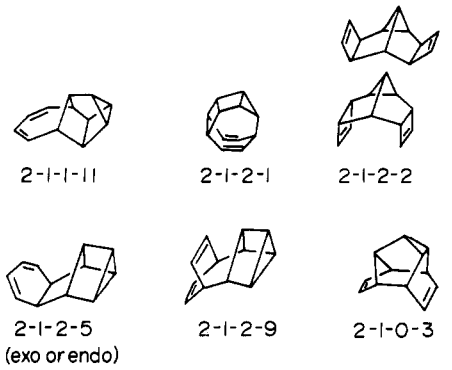


Figure 2. Some possible structures for diene 12 from Balaban's multigraph of order 12.[10a]

Thus, aldehyde 5, prepared from Jones oxidation of alcohol 4,[3,5] on treatment with the anion of the enamine reagent 6[6] gave the unsaturated aldehyde 7 in 68% yield. The unsaturated aldehyde 7 has a trans geometry at the double bond as shown by the coupling constant between the olefinic hydrogens in the ^1H NMR (J = 15.4 Hz). Formation of the corresponding *p*-toluenesulfonylhydrazone 8 in 84% yield was unexceptional (Figure 1).

Pyrolysis and Structure Determinations. The dry lithium salt of tosylhydrazone 8 was "flash" pyrolyzed in a flask at 250 °C. Gas chromatographic separation of the volatiles (collected in a liquid nitrogen trap) yielded four hydrocarbons 9–12, while the less volatile part (deposited on the connecting tube walls) after flash chromatography on silica gel gave two pyrazoles 13 and 14 (Figure 1). Exo and endo tetraenes 9[1c] and 10[1d] and benzocyclooctatriene 11[7] were identified by comparison of their ^1H NMR chemical shifts with the literature values.[8] Identification of 12 was difficult and required careful analysis of the spectroscopic properties. The molecular ion peak at m/e 156 identified the compound as a $(CH)_{12}$ hydrocarbon. No UV absorption characteristic of a conjugated diene was observed. Although the ^1H NMR revealed the presence of two pairs of olefinic hydrogens at δ 5.45 and 6.05, the absence of conjugation was confirmed by the absence of coupling between the olefinic protons. The presence of a plane of symmetry in the molecule reflecting five pairs of carbons and containing the two others was evident from the proton-decoupled ^{13}C NMR, which contained seven signals in the approximate ratio of 2:2:1:2:2:2:1. The presence of one three-membered ring was revealed by the proton-coupled ^{13}C NMR, which gave doublets for all signals as expected with particularly large coupling constants (166.5 and 171.1 Hz, respectively) for the two high-field signals at δ 36.0 and 26.4 (ratio ~2:1).[9] The presence of two pairs of olefinic carbons, as suggested by the ^1H NMR, was confirmed by the appearance of two signals at δ 134.6 (J = 160.9 Hz) and 131.1 (J = 156.4 Hz) in the ^{13}C NMR in a ratio of ca. 2:2. Of the 112 possible

(1) (a) Schröder, G. *Angew. Chem.* **1963**, *75*, 722. (b) Schröder, G. *Chem. Ber.* **1964**, *97*, 3131. (c) Paquette, L. A.; Stowell, J. *Tetrahedron Lett.* **1969**, 4159; *J. Am. Chem. Soc.* **1971**, *93*, 5735. (d) Paquette, L. A.; Kukla, M. J.; Ley, S. V.; Traynor, S. G. *Ibid.* **1977**, *99*, 4756. (e) Schröder, G.; Martin, W. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 130. (f) Oth, J. F. M.; Röttele, H.; Schröder, G. *Tetrahedron Lett.* **1970**, 61. (g) Röttele, H.; Martin, W.; Oth, J. F. M.; Schröder, G. *Chem. Ber.* **1969**, *102*, 3985. (h) Oth, J. F. M.; Gilles, J. M.; Schröder, G. *Tetrahedron Lett.* **1970**, 67. (i) Oth, J. F. M.; Gilles, J. M. *Ibid.* **1968**, 6259. (j) Erhordt, V.; Daub, J. *Chem. Commun.* **1974**, 83. (k) Labows, J. N., Jr.; Meinwald, J.; Röttele, H.; Schröder, G. *J. Am. Chem. Soc.* **1967**, *89*, 612. (l) Vedejs, E.; Shepherd, R. A. *J. Org. Chem.* **1976**, *41*, 742.

(2) Farnum, D. G.; Hagedorn, A. A., III *Tetrahedron Lett.* **1975**, 3987.

(3) Jones, M., Jr.; Reich, S. D.; Scott, L. T. *J. Am. Chem. Soc.* **1970**, *92*, 3118.

(4) Masamune, S.; Seidner, R. T.; Zenda, M.; Weisel, M.; Nakatsuka, N.; Bigam, G. *J. Am. Chem. Soc.* **1968**, *90*, 5286.

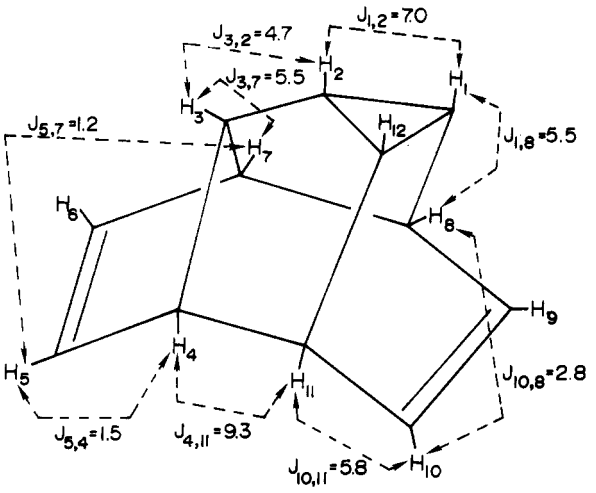
(5) (a) The melting point of alcohol 4 was found to be 60–61 °C as opposed to 52–53 °C reported by Cheer, C. J.; Rosen, W.; Uebel, J. J. *Tetrahedron Lett.* **1974**, 4045. (b) Burkoth, T. L. *J. Org. Chem.* **1966**, *31*, 4259.

(6) Nagata, W.; Wakabayashi, T.; Hayase, Y. *Org. Synth.* **1973**, *53*, 44. Our modified procedure for the preparation of enamine reagent 6 yields a white solid in 70% yield, mp 60–62 °C (see Experimental Section).

(7) Although we did not find the ^1H NMR spectrum of hydrocarbon 11 in the literature, it was similar to that of the 5,6-dideuterated derivative reported by Buchana, G. W.; McCarville, A. R. *Can. J. Chem.* **1973**, *51*, 177.

(8) We thank Professor Paquette for spectra of compounds 9 and 10 and for private communications of results prior to publication.

(9) Stothers, J. B. "Carbon-13 NMR; Organic Chemistry, A Series of Monographs"; Academic Press: New York, 1972; Vol. 24, p 336.



δ	$H_{1,12}$	H_2	H_3	$H_{4,7}$	$H_{5,6}$	$H_{8,11}$	$H_{9,10}$
	1.91	1.75	3.35	3.15	5.45	2.9	6.05

Figure 3. Proton NMR parameters for diene 12.

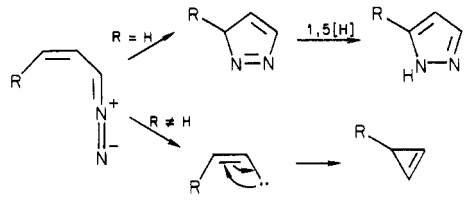
$(CH)_{12}$ dienes (excluding stereoisomers) reported in Balaban's[10a] trivalent multigraph of order 12, only six isomers (Balaban's designations 2-1-2-1, 2-1-2-5, 2-1-2-2, 2-1-2-9, 2-1-1-11 and 2-1-0-3)[10b] have the symmetry, the two double bonds, and the one cyclopropane ring required by the above data (Figure 2). However, structures 2-1-2-1, 2-1-1-11, 2-1-2-5, and 2-1-2-2 would require coupling between the olefinic protons, which was not observed. Structure 2-1-2-9 was eliminated because the two olefinic pairs should be coupled with the same bridgehead protons. As a matter of fact, the spin-decoupling studies showed that the olefinic pairs in diene **12** were coupled with different bridgehead protons. These considerations, and also the direct generation of diene **12** from decomposition of lithium and sodium salts of tosylhydrazone **15** both thermally and photochemically (see next part), convinced us that the structure of diene **12** was 2-1-0-3.

Proton chemical shift and coupling constant assignments in diene **12** were made on the basis of spin decoupling experiments and are illustrated in Figure 3. The multiplet signal at δ 2.9 (2 H) was coupled to signals at δ 6.05 (2 H), 3.15 (2 H), and 1.91 (2 H). Thus, this was assigned to the bridgehead protons $H_{8,11}$ which are adjacent to the olefinic protons $H_{9,10}$, the bridgehead protons $H_{4,7}$, and the *two bridge protons* $H_{1,12}$. This assignment was confirmed since the signal at δ 3.15 (2 H) was coupled to the signals at δ 5.45 (2 H), 3.35 (1 H), and 2.9 (2 H). As a result, the signal at δ 3.15 was assigned to the bridgehead protons $H_{4,7}$ which are vicinally related to the olefinic protons $H_{5,6}$, the *single bridge proton* H_3, and the bridgehead protons H_8 and H_{11}.

The mass spectrum of both pyrazoles **13** and **14** showed the expected molecular ion peak at *m/e* 184. The absence of the bicyclononatriene unit of **8** was evidenced by major changes in the olefinic region of the ^1H NMR (in particular, the appearance of a two hydrogen singlet at δ 5.08–5.12 characteristic of the bridging ethylene group in bicyclo[4.2.1]nonatrienes)[11] and by the absence of signals for the cyclopropane carbons (ca. 30) in the ^{13}C NMR. The pyrazole ring[12] gave rise to proton signals near δ 7.0 for both **13** and **14**, and weak carbon signals[13] at δ 145.7, 134.5, and 104.2 for **14**. The pyrazole carbon signals for **13** were too weak to distinguish from the noisy base line. The plane of symmetry present in **13** and **14** was evidenced by the appearance of three olefinic and two aliphatic signals in the ^{13}C NMR in approximate ratio 2:2:2:2:1.

Assignment of pyrazoles **13** and **14** to anti and syn isomers, respectively, was based on the observed coupling pattern of bridge and bridgehead protons.[11] In a molecular model of the bicyclo[4.2.1] system, the dihedral angle of H_{syn} and the bridgehead protons is 90°, while the dihedral angle of H_{anti} with the bridgehead protons is close to 0°.[11a] As a consequence, the H_{syn} in *anti*-pyrazole **13** appeared as a singlet at δ 2.95. On the other hand, the H_{anti} in *syn*-pyrazole **14** was a triplet which overlapped with the bridgehead signal and all together appeared as a multiplet at δ 3.1–3.4.

Mechanistic Investigation. Carbenes are certainly known to arise from thermal decomposition of tosylhydrazone salts.[14] In the case of tosylhydrazone salts of α,β-unsaturated carbonyl compounds, when the β position is not substituted (R = H), pyrazole formation (through cyclization of the diazo intermediate) is predominant.[15] It



is clear that the hydrocarbons **9**–**12** could have arisen through the carbene intermediate while the pyrazoles **13** and **14** were formed through cyclization of either the salt or diazo intermediate with subsequent [1,5] hydride shift.

Paquette[1c] has reported that pyrolysis of *cis,syn,cis*-tricyclo[8.2.0.0^{2,4}]dodeca-3,5,7,11-tetraene (**16**) at 120 °C afforded the exo tetraene **9** stereospecifically. It seems possible that the anti isomer **17** would isomerize to endo tetraene **10** in an analogous fashion. As a result, both compounds **16** and **17** could have arisen from the decomposition of the lithium salt of tosylhydrazone **8** to corresponding carbene **3** followed by ring expansion with concomitant or subsequent cyclization.[3,16] These two hydrocarbons could then rearrange to the exo and endo tetraenes **9** and **10**.

The high stereoselectivity observed by Paquette[1c] in the thermolysis of compound **16** to exo tetraene **9** suggested the operation of either a suprafacial [1,5] shift or, in the case of syn tetraene **16**, a Cope rearrangement. If inter-

(10) (a) Balaban, A. T. *Rev. Roum. Chim.* **1972**, *17*, 865. (b) Balaban's nomenclature (β, t, g, s, where β is the number of double bonds, t is the number of three-membered rings, g is the number of four-membered rings, and s is a serial number).

(11) (a) Antkowiak, T. A.; Sanders, D. C.; Trimistis, G. B.; Press, J. B.; Shechter, H. *J. Am. Chem. Soc.* **1972**, *94*, 5366. (b) Boche; Martens, D. *Chem. Ber.* **1979**, *112*, 157.

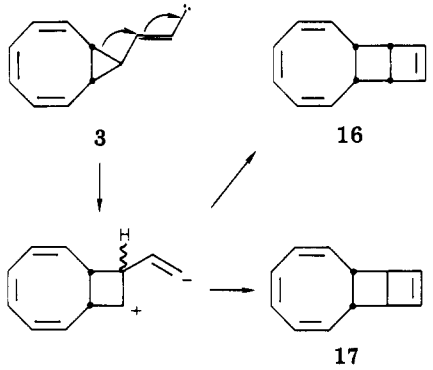
(12) Jackman, L. M.; Sternhell, S. "Applications of Nuclear Magnetic Resonance in Organic Chemistry", 2nd ed.; Oxford: New York, 1969.

(13) (a) Green, M. J.; Rees, R. G. *J. Chem. Soc. B* **1968**, 387. (b) Reference 9, pp 246–252.

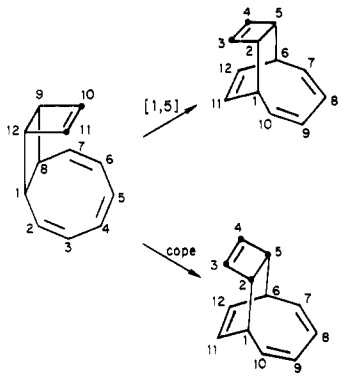
(14) Baron, W. J.; DeCamp, M. R.; Hendrick, M. E.; Jones, M., Jr.; Levin, R. H.; Sohn, M. B. "Carbenes"; Jones, M., Jr.; Moss, R. A. Ed.; Wiley: New York, 1973; Vol. 1, pp 1–151.

(15) (a) Closs, G. L.; Closs, L. E.; Böll, W. A. *J. Am. Chem. Soc.* **1963**, *85*, 3796. (b) Brewbaker, J. L.; Hart, H. *Ibid.* **1969**, *91*, 711. (c) We suspect that formation of carbene rather than pyrazole is favored by bringing the precursor to a high temperature as quickly as possible. If so, our procedure could stand some improvement because of the slow heat transfer from glass beads to solid in a vacuum. If we continue this work, we will try adding a solution or fine suspension of the solid in a nonvolatile liquid to the hot liquid in a vacuum.

(16) (a) Friedman, L.; Shechter, H. *J. Am. Chem. Soc.* **1960**, *82*, 1002. (b) Kirmse, W. *Chem. Ber.* **1965**, *98*, 4002. (c) Reference 14, pp 32–40. Formation of either *syn*-**16** or *anti*-**17** by the proposed mechanism depends upon the anti or syn relationship, respectively, of the vinylcarbene and cyclopropane in precursor **3**. Either ionic or free-radical intermediates could intervene.



mediates **16** and **17** are the precursors to tetraenes **9** and **10** in our work, then deuterium labeling would distinguish between the [1,5] shift and Cope rearrangement. Thus, deuteration at the olefinic **10** or **11** positions of **16** would give tetraene **9** labeled exclusively at the olefinic 3 or 4 position for a [1,5] sigmatropic shift, while a Cope rearrangement would lead to scrambling of the deuterium between the aliphatic and olefinic carbons.



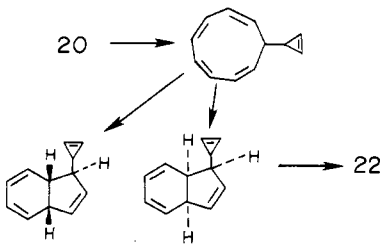
The required deuterated aldehyde **7-*d*** was prepared (see Figure 1) by using deuterated enamine reagent **6-*d***, prepared in 58% yield as a white, crystalline solid (60–62 °C) by stirring **6** with sodium deuteroxide. Mass spectroscopy of **6-*d*** showed ca. 67% d_2, 28% d_1 and 5% d_0. The ^1H NMR showed a one-proton doublet in the vinyl region (δ 6.82, $J_{P-C=CH}$ = 16 Hz). This led us to believe **6-*d*** was at least 90% deuterated at the carbon next to phosphorus. In any event, treating aldehyde **5** with the anion of the deuterated enamine reagent followed by mild acid hydrolysis gave the deuterated extended aldehyde **7-*d***. The ^1H NMR showed ca. 80% deuteration with the olefinic region (δ 6.23, m) integrating to 1.2 protons and the aldehyde proton (δ 9.22) changing from a sharp doublet to a broad singlet. The mass spectrum showed ca. 75% deuterium incorporation and the ^{13}C NMR showed loss of the line at δ 130.6.[17]

The deuterated tosylhydrazone **8-*d***, prepared like the undeuterated compound, had the same deuterium content (ca. 80%, by loss of 0.8 proton in the olefinic region in the ^1H NMR). The mass spectrum showed a molecular ion at *m/e* 341 (consistent with $C_{19}H_{19}DN_2O_2S$). Likewise, except for the absence of the peak at δ 124.4, the proton-decoupled ^{13}C NMR was almost unchanged from that of the undeuterated compound.

Pyrolysis of the lithium salt of the deuterated tosylhydrazone **8-*d*** gave the stereoisomeric deuterated tetraenes **9-*d*** and **10-*d*** (see Figure 1). Each showed a molecular ion peak at *m/e* 157 consistent with the molecular formula

(17) Spiesecke, H.; Schneider, W. G. *J. Chem. Phys.* **1961**, *35*, 731. (b) Reich, H. J.; Jautelat, M.; Messe, M. T.; Weigeit, J. J.; Roberts, J. D. *J. Am. Chem. Soc.* **1969**, *91*, 7445.

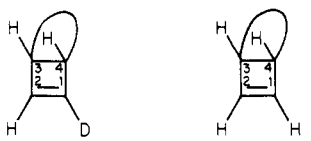
Scheme I



$C_{12}H_{11}D$. In each case, integration of the ^1H NMR spectrum showed reduction of the sharp singlet for the vinyl cyclobutene position from 2.0 to 1.2 protons. There was no evidence for deuterium incorporation elsewhere in either spectrum.

The ^{13}C NMR spectra of these deuterated hydrocarbons (summarized in Table I) confirmed the location of the deuterium. However, the results require discussion, since deuterium substitution affects both the chemical shifts and intensities of neighboring carbon signals.[18] Carbons α to a deuterium (i.e., attached to a deuterium) are reported to shift 0.2–0.5 relative to the hydrogen analogue, while carbons β to a deuterium have been shown to move upfield ca. 0.12 ± 0.04.[18] Often, especially when no other hydrogens are at the α position, deuterium substitution causes the α carbon signal to disappear in the ^{13}C NMR spectrum.[17] This is due primarily to the increased relaxation time of the deuterated carbon, plus a decreased nuclear Overhauser effect, and spin–spin splitting of the carbon into a triplet.[17a]

Thus, we might predict the following for a symmetrically substituted cyclobutene which is 80% deuterated and 20% undeuterated (analogous to **9-*d*** and **10-*d***). The signal for



carbon 1 of the D_1 molecule would disappear. The β shift for the D_1 molecule would cause carbons 2 and 4 to move ca. 0.1 relative to carbons 1,2 and 3,4, respectively, of the D_0 molecules. Since γ shifts are reported to be only 0.02–0.04, we would expect the resonance for carbon 3 of the D_1 molecules to coincide with the resonance for carbons 3,4 for the D_0 molecules. The result would be two closely spaced lines in the ratio 2:1 for the olefinic carbons and two closely spaced lines in the ratio 3:2 for the aliphatic ones. If the deuterium is randomly distributed in the deuterated cyclobutene, then the lines should be of equal intensity. In Table I it can be seen that the intensity ratios are more consistent with *d* substitution only on the vinyl carbons (positions 3 and 4) than with detectable leakage of deuterium elsewhere. The deviation from the calculated intensity for the low-field signal of the aliphatic pair (C_2, C_5) we attribute to signal broadening by allylic 3-bond C–D coupling.[18g] Thus, if tetraene **9** does result from isomerization of **16**, we can rule out the Cope rearrangement path in favor of the [1,5] sigmatropic shift.[19]

(18) (a) Bell, R. A.; Chan, C. L.; Sayer, B. G. *Chem. Commun.* **1972**, 67. (b) Breitmaier, E. *Chimia* **1974**, *28*, 120. (c) Eggert, H.; Djerassi, C. *Tetrahedron Lett.* **1975**, 3635. (d) Stothers, J. B.; Tan, C. T. *J. Am. Chem. Soc.* **1972**, *94*, 8581. (e) Tulloch, A. P.; Mazurek, M. *Chem. Commun.* **1973**, 962. (f) Vogel, P.; Delseth, R.; Quarrox, D. *Helv. Chem. Acta* **1975**, *58*, 508. (g) Breitmaier, E.; Voelter, W. "^{13}C NMR Spectroscopy"; Verlag Chemie: New York, **1978**; pp 100, 101.

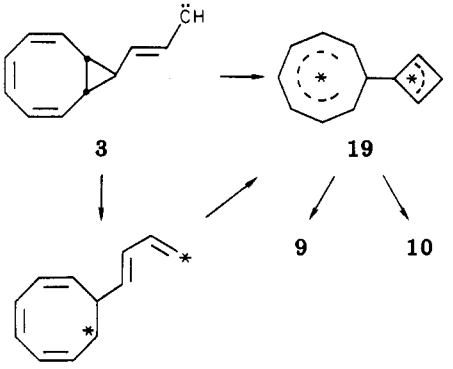
Table I. Comparison of ^{13}C NMR Data (ppm) for Deuterated and Undeuterated Tetraenes 9 and 10

position[a]	10	10-*d*	rel intensity obsd	rel intensity calcd[b]	9	9-*d*	rel intensity obsd	rel intensity calcd[b]
3, 4	140.02	140.03	1.0	1.0	139.19	139.23	1.0	1.0
		139.84	2.1	2.0		139.02	2.1	2.0
	134.59	134.52	4.5	5.0	136.89	136.93	4.3	5.0
	126.85	126.83	4.5	5.0	125.18	125.20	4.2	5.0
	123.31	123.30	4.4	5.0	120.78	120.78	3.5	5.0
2, 5	48.64	48.62	1.7	3.0	50.54	50.54	1.2	3.0
		48.52	2.2	2.0		50.40	2.0	2.0
1, 6	34.68	34.67	4.7	5.0	36.33	36.34	4.5	5.0

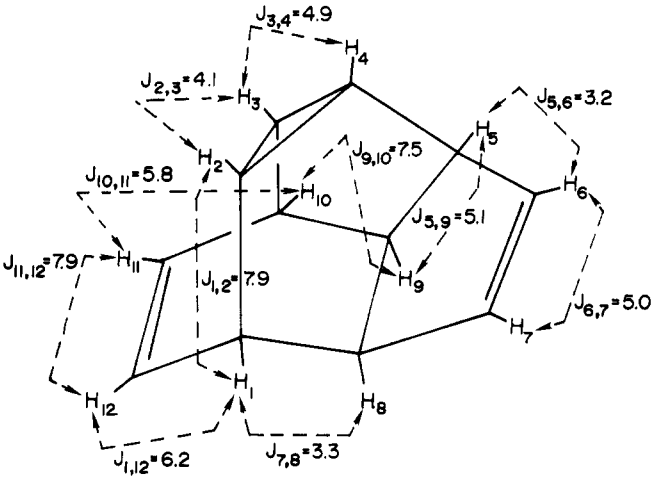
[a] Numbering is as follows: 

[b] Calculated assuming 80% deuterium incorporation at position 3 only, and no long-range C-D coupling.

On the other hand, the carbene intermediate **3** could have generated the biradical or ionic intermediate **19** which upon subsequent cyclization could lead to the formation of tetraenes **9** and **10**. (The high stereoselectivity observed by Paquette[1c] ruled out **19** in his case.) Deuterium-labeling studies are currently in progress to distinguish between these two remaining mechanisms. (The above deuterium study rules out **19** as an intermediate if it is formed from **16** and **17**, but not if it is formed directly from **3**.)

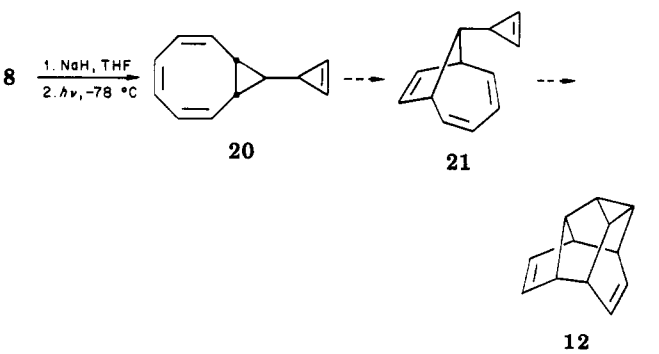


A straightforward mechanistic pathway leading to diene **12** might be through the intramolecular Diels–Alder addition of compound **21**, which could have been formed from a suprafacial [1,5] sigmatropic shift of cyclopropene **20**. To test this, we prepared cyclopropene **20** by the photolysis of the sodium salt of tosylhydrazone **8** at −78 °C in dry tetrahydrofuran and examined its pyrolysis.



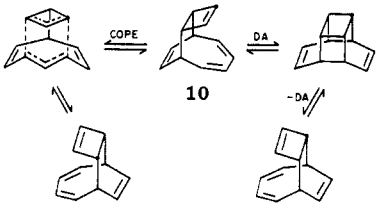
δ	H_1	H_2	$H_{3,4}$	H_5	H_6	H_7	H_8	H_9	H_{10}	H_{11}	H_{12}
	2.48	1.75	0.7-0.9	2.82	6.12	5.55	1.85	2.35	3.06	6.33	6.55

Figure 4. Proton NMR parameters for Mock-like diene **22**.

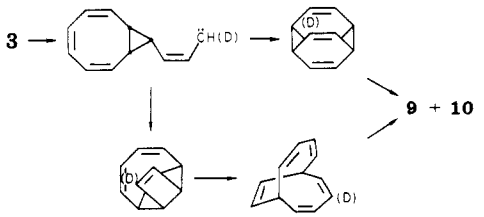


Its structure (Balaban's number 4-2-0-4) was confirmed by its spectroscopic properties. The mass spectrum showed the $(CH)_{12}$ parent molecular ion peak at *m/e* 156. The presence of a cyclopropene was revealed by ^1H NMR, which gave a doublet of doublets (J = 2.0 and 0.4 Hz) at δ 7.2 integrating to two protons identified as the olefinic protons of the cyclopropene ring,[20] and a doublet of triplets at δ 1.8 (1 H, J = 5.0 and 2.0 Hz) for the remaining cyclopropene proton. The presence of a cyclopropane ring

(19) Deuterated **10** also gave us an opportunity to test for the operation of two plausible rearrangements: the Diels–Alder, reverse Diels–Alder, or the Cope (see below), which would have scrambled deuterium.



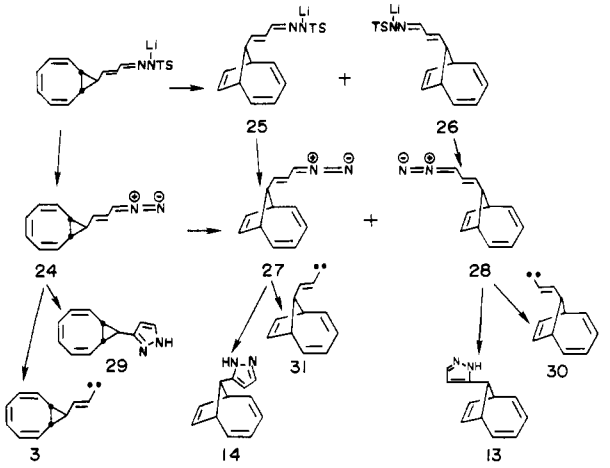
The deuterium label in **9** and **10** was unscrambled on heating overnight at 200 °C in Me_2SO. Thus, the activation energies for these two processes are probably greater than 35 kcal, perhaps because of the skewed diene system. These results also rule out the operation of mechanisms suggested by a referee which proceed through the symmetrical intermediates derived by anti → syn isomerization in **3** followed by carbene addition:



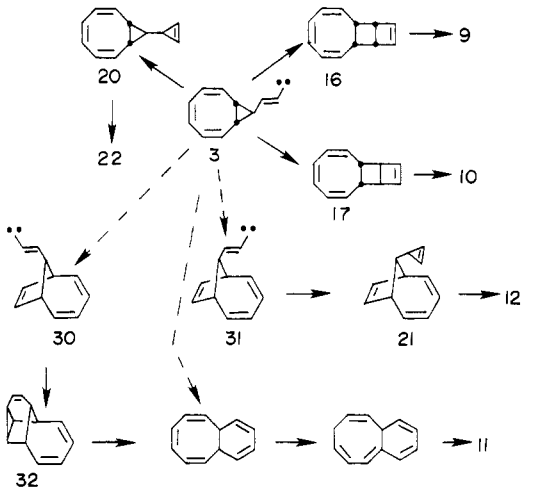
A related mechanism was rejected for C_{10} isomerizations by Jones.[3]

(20) DeWolf, W. H.; Stol, W.; Landheer, J. J.; Bickelhaupt, F. *Recl. Trav. Chim. Pays-Bas* **1971**, *90*, 405.

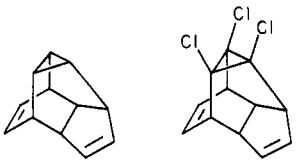
Scheme II



Scheme III



was evident from the observed doublet at δ 1.2 for two protons with J = 5.5 Hz belonging to the bridgehead cyclopropyl hydrogens and a one-proton multiplet at δ 0.5–0.8. Finally, the cyclooctatrienyl unit had the characteristic multiplet[21] at δ 5.9–6.0.



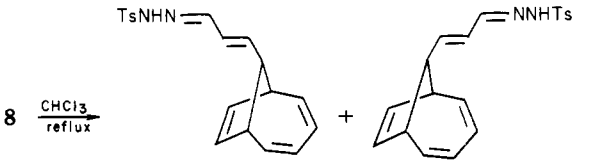
22 23

We found that the best method for pyrolysis of **20** was to add its solution in tetrahydrofuran to a hot flask connected to a hot column containing glass beads, both at 300 °C, under an argon stream. The volatiles were pumped and collected in a trap kept in liquid nitrogen. Gas chromatography separated a major product as a colorless liquid (yield 2.6%) from a minor component (~0.5%), which was not investigated further. The major product was identified as pentacyclo[6.4.0.0^{2,4}.0^{3,10}.0^{5,9}]dodeca-6,11-diene (**22**), a new $(CH)_{12}$ member (Balaban's number, 2-1-0-2),[10] because of its closely parallel ^{1}H NMR spectrum with that of the known compound **23** reported by Mock,[21] whose structure was established by X-ray crystallography. The proton chemical shift assignments were straightforward (Figure 4) because of the similarity to compound **23**. The three cyclopropane protons in **22** appeared at δ 1.75 and 0.75–0.9 as a doublet of doublet of doublets and a multiplet, respectively, in a ratio of 1:2. A molecular model showed that H_2 can have a dihedral angle close to 0° with the bridgehead proton H_1. As a result, the signal at δ 1.75 was assigned to H_2 because of the observed large vicinal coupling of 7.9 Hz in the pattern. Hydrocarbon **22** could arise as proposed by Mock[21] for the similar compound **23** (Scheme I).

Summary Mechanistic Proposal. It seems likely that any explanation for the formation of the sundry products observed on pyrolysis of the lithium salt of tosylhydrazone **8** must involve the diazo compounds **24**, **27**, and **28**, which partition between their respective pyrazoles and carbenes (Scheme II). We have no evidence about the timing of the decomposition and rearrangement steps in this scheme.

Formation of the several observed $C_{12}H_{12}$ hydrocarbons from the carbenes could follow standard mechanistic paths[14] as shown in Scheme III. (Dotted arrows indicate paths which seem to us less likely, though possible, alternatives.) Although a number of questions remain unanswered in this scheme (e.g., we have no evidence to distinguish between formation of **11** via carbene **30** or direct formation from carbene **3**), some possible transformations can be ruled out. Paquette[1c,d] has shown that **11** is not a product of the pyrolysis of tetraenes **10** or **16**. If cyclopropene **20** is involved in the pyrolysis, it is not the source of diene **12**, since it gave only the Mock-like hydrocarbon **22**, which may in fact be the unidentified minor product of the same GC retention time obtained in the pyrolysis of the salt of tosylhydrazone **8**.

The possibility that **9** or **10** arises from carbene **31** was ruled out by the pyrolysis of the lithium salt of rearranged tosylhydrazone **15** prepared by heating tosylhydrazone **8** in chloroform.



33 15

Structure assignment of **15** followed from its spectroscopic data. The mass spectrum showed a parent ion peak at m/e 340, corresponding to $C_{19}H_{20}N_2SO_2$. The appearance of a two-proton singlet at δ 5.1 and the absence of cyclopropane protons in its ^{1}H NMR revealed the presence of the bridged olefinic unit of the bicyclo[6.2.1] system.[11] The presence of two high-field signals at δ 47.3 and 39.8 in a ratio of approximately 2:1 and the absence of signals for the cyclopropane carbons (ca. 30) in the ^{13}C NMR also confirmed the assigned structure for **15**.

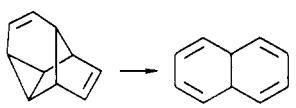
Pyrolysis of the lithium salt of tosylhydrazone **15** gave diene **12** as the sole $C_{12}H_{12}$ product (2%), also obtainable in 32% yield by photolysis at 0 °C (pyrazole **14** was also obtained in the pyrolysis or room temperature photolysis). Thus, the proposed route to diene **12** finds support.

Anti tosylhydrazone **33**, a minor product in the thermal rearrangement of tosylhydrazone **8**, was not obtained pure[22] and we did not examine its photolysis or pyrolysis. However, it seems unlikely that it would give hydrocarbons **9** or **10**. The formation of **11** from it by the suggested route finds a parallel in the formation of dihydronaphthalene **35** from **34**.[3]

(21) Mock, W. L.; Sprecher, C. M.; Stewart, R. F.; Northolt, M. G. *J. Am. Chem. Soc.* **1972**, *94*, 2015.

(22) Continued fractional crystallization failed to purify this compound from its epimer **15**. Separation of these two epimers also failed by column chromatography because of polymerization of compounds.

(23) Kofron, W. G.; Baclauski, L. M. *J. Org. Chem.* **1976**, *41*, 1879.



34 35

General Conclusions. This work has revealed several points worth emphasizing. It is apparently possible to obtain significant proportions of carbene-derived products from pyrolysis of tosylhydrazone salts from lightly substituted α,β-unsaturated aldehydes,[15] although we do not believe we have yet found the best way to do this.[15c] Some new $(CH)_{12}$ hydrocarbons have been identified and characterized as products of these pyrolyses, which show the usual mix of orbital symmetry controlled (e.g., perhaps **9** and **10**) and random (e.g., **15** and **33**) products. A novel cyclopropylvinylcarbene ring expansion (**3** → **16** and **17**) is strongly suggested. The rather unusual cyclopropenylbicyclononatriene, **20**, has been prepared by a reasonable synthesis, and its pyrolysis to the "Mock-like" hydrocarbon, **22**, established. A further contribution has been made to the confusion over whether bicyclo[6.1.0]nonatrienes will rearrange to bicyclo[4.2.1]nonatrienes or dihydroindenes.

Experimental Section

General Data. Melting points were taken in open capillaries with a Thomas-Hoover apparatus. The IR spectra were recorded on a Perkin-Elmer Model 137B Infracord spectrophotometer. The NMR spectra were recorded on a Varian T-60 (60 MHz), Bruker WH 180 MHz, Varian CFT-20, and Bruker WM 250 spectrometer operating at 250 MHz for ^1H and 62.86 for ^{13}C. Chemical shifts are reported in parts per million downfield from internal standard tetramethylsilane. The coupling constants are given in hertz. Signal intensities are reported as nearest integral number of hydrogens (e.g., 2 H) or carbons and are only very approximate for carbon. GC/MS data were obtained on a Finnigan 4021 with INCOS system equipped with a $^1/_8$ in. × 6 ft glass column packed with 4% OV-225 on Chromosorb G acid washed and silanized, operated at 85 °C. The compositions reported were calculated by comparing the area of 1,2,3,4-tetramethylbenzene as internal standard with the peak areas (determined by weight). GC separations were achieved at 120 °C, using an F&M Model 700 chromatograph equipped with a thermal conductivity detector. Helium was used as the carrier gas at flow rates 35–40 mL/min; an injector temperature of 240 °C and a detector temperature of 250 °C were used in all cases. The column employed was 0.25 in. × 6 ft aluminum column packed with 4% OV-225 on Chromosorb G acid washed and silanized. The concentration of *n*-butyllithium, used for preparation of the salts of tosylhydrazones, was determined according to the procedure described by Kofron.[23]

Preparation of 9-(Hydroxymethyl)bicyclo[6.1.0]nona-2,4,6-triene (4).[3,5] Lithium aluminum hydride (8 g) and anhydrous ether (300 mL) were taken in a 500-mL three-necked round-bottomed flask fitted with a reflux condenser and an addition funnel. 9-Carbethoxybicyclo[6.1.0]nona-2,4,6-triene[3] (30 g, 0.158 mol) dissolved in ether (50 mL) was added dropwise, with magnetic stirring. The addition was controlled to maintain gentle reflux. After the addition was complete, the mixture was stirred overnight, and then sodium hydrogen tartrate (30 g) was added followed by water (10 mL) dropwise. The white precipitate formed was filtered and washed with methylene chloride. The filtrate was dried over anhydrous sodium sulfate, and the solvent was removed on a rotary evaporator to give a pale-yellow liquid. Recrystallization from hexane gave the alcohol (**4**) as white needles (17.7 g, 77%), 60–61 °C.[5] The ^1H NMR spectrum was identical with that in the literature.[5b]

Preparation of Bicyclo[6.1.0]nona-2,4,6-triene-9-carboxaldehyde (5).[3] To a solution of pyridine (200 mL) in dry methylene chloride (1600 mL) in a 3-L Erlenmeyer flask was added chromic anhydride (64 g) in small amounts with vigorous stirring. After all the chromium trioxide had been added, the mixture was further stirred for 15 min. A solution of alcohol (**4**; 14.8 g, 0.1 mol) in methylene chloride (100 mL) was added to the solution, which was stirred vigorously for 15 min. Black polymeric chromium oxide deposited on the sides of the flask. The solution was then filtered and the residue was washed with 300 mL of methylene chloride. The filtrate was transferred to a 4-L separatory funnel and washed twice with ice cold dilute hydrochloric acid (3 N, 500 mL). The organic layer was then washed with sodium bicarbonate solution and water and then dried over anhydrous magnesium sulfate. The solvent was removed on a rotary evaporator and the residue was distilled to give the aldehyde **5** as a pale-yellow liquid (11 g, 75.3%, bp[3] 58–62 °C (0.25 mm)): IR (neat) 2970, 2810, 2710, 1700, 1640, 1610 cm^{-1}; 60-MHz ^1H NMR ($CDCl_3$) δ 9.26 (d, J = 6 Hz, 1 H), 6.0 (s, 4 H), 5.9 (s, 2 H), 2.24 (d, J = 5 Hz, 2 H), 1.7 (dt, J = 6.0, 5.0 Hz).

Preparation of Diethyl 2-(Cyclohexylamino)vinylphosphonate (6). Into a 1-L three-necked round-bottomed flask fitted with a magnetic stirrer, dropping funnel, and nitrogen inlet was placed diethyl formylmethyl)phosphonate[6] (149.4 g, 0.83 mol) in dry acetonitrile (625 mL). The solution was cooled at 0–5 °C with ice cooling and the system was flushed with nitrogen. Freshly distilled cyclohexylamine (95 mL, 0.83 mol) was added over a period of 30 min with the temperature maintained at 0–5 °C. The solution turned yellow upon addition of cyclohexylamine. The mixture was stirred at room temperature for an additional 15 min. The solvent and the unreacted cyclohexylamine were removed on a rotary evaporator at 100 °C, and the residue was taken up in ether (300 mL) and dried over anhydrous sodium sulfate. The ether was partly evaporated so that the volume of the solute to the solvent became 1:1. This solution was then put in the freezer (−40 °C) for several days. Crystallization yielded white crystalline enamine reagent **6** (151 g, 70%), 60–62 °C,[6] with all spectroscopic properties consistent with literature values.[6]

Preparation of Deuterated Enamine Reagent 6-*d*. Into a 500-mL round-bottomed flask equipped with a magnetic stirrer and nitrogen inlet was placed enamine reagent **6** (50 g, 0.193 mol) dissolved in 200 mL of carbon tetrachloride. To this was added 40 mL of NaOD (~0.5 g of metallic sodium in 40 mL of D_2O). After 2 days the aqueous layer was removed and 20 mL of fresh NaOD was added. After a total of 3 days the aqueous layer was removed, and the organic layer was washed with 10 mL of D_2O and dried with anhydrous potassium carbonate. The solvent was removed on a rotary evaporator and the residue was recrystallized from D_2O saturated ether to give the deuterated enamine **6-*d*** (29.2 g, 58%): 60–62 °C; mass spectrum, m/e 264; 60-MHz ^1H NMR (CCl_4) δ 6.82 (d, J = 16 Hz, 1 H), 3.81 (quint, J = 7 Hz, 4 H), 3.0 (br s, 1 H), 1.0–2.0 (m, 16 H including triplet centered at 1.25).

***trans*-β-[*anti*-9-Bicyclo[6.1.0]nona-2,4,6-trienyl]acrolein (7).** Into a 500-mL three-necked round-bottomed flask fitted with a mechanical stirrer, dropping funnel, and nitrogen inlet were placed sodium hydride (57% oil dispersion, 4.34 g, 0.1 mol) and anhydrous tetrahydrofuran (150 mL). The flask was flushed with nitrogen and brought to 0 °C with an ice bath. A solution of enamine reagent **6** (26.8 g, 0.1 mol) in dry tetrahydrofuran (50 mL) was added dropwise to the stirred mixture while the temperature was maintained at 0–5 °C. The mixture was further stirred for 15 min at 0–5 °C to ensure complete reaction. A solution of aldehyde **5** (10.0 g, 68.2 mmol) in dry tetrahydrofuran (100 mL) was added dropwise to the mixture at a rate such that the temperature did not exceed 5 °C. The mixture was warmed to room temperature and stirred overnight. During this time, the solution became quite dark, almost black, and a gummy precipitate of sodium diethyl phosphate was observed. The solvent was removed on a rotary evaporator and the residue was poured into cold water and extracted with three 100-mL portions of ether. The combined ether layers were washed with saturated aqueous salt solution and dried over anhydrous sodium sulfate, and the solvent was rotary evaporated. The residue was dissolved in benzene (300 mL) and transferred to a 2-L round-bottomed flask equipped with a magnetic stirrer and nitrogen inlet. To this was added 900 mL of 1% oxalic acid (1.36 g of oxalic acid dihydrate/100 mL of H_2O). This mixture was stirred overnight under nitrogen. The benzene layer was separated and the aqueous layer was extracted twice with 300-mL portions of ether. The combined organic layers were washed with 200 mL of water and 200 mL of saturated salt solution and dried over anhydrous sodium sulfate. The solvent was removed on a rotary evaporator and the residue was chromatographed on Florisil (80 g). The column was

prepared with hexane as the solvent. The residue was dissolved in methylene chloride and absorbed on about 3 g of Florisil, the methylene chloride was evaporated, and the residue was added to the top of the column. The product was eluted first with hexane (ca. 1500 mL) and later with methylene chloride (ca. 1000 mL). The solvent was evaporated and the residue was recrystallized from hexane to give the unsaturated aldehyde **7** as shiny white plates (8.03 g, 68%): 88–90 °C; mass spectrum, m/e 172; IR (Nujol) 2980, 2890, 2800, 1690, 1625 cm^{-1}; UV (hexane) 254 nm (ϵ 28500); 250-MHz ^1H NMR ($CDCl_3$) δ 9.5 (d, J = 7.6 Hz, 1 H), 6.45 (dd, J = 15.4, 9.6 Hz, 1 H), 6.25 (dd, J = 15.4, 7.6 Hz, 1 H), 6.0 (s, 4 H), 5.9 (s, 2 H), 1.9 (d, J = 5.2 Hz, 2 H), 1.4 (quint, 1 H); CFT-20 ^{13}C NMR ($CDCl_3$) δ 192.7 (1 C), 160.8 (1 C), 130.3 (1 C), 128.7 (2 C), 126.5 (2 C), 125.0 (2 C), 32.0 (1 C), 29.7 (2 C). Anal. ($C_{12}H_{12}O$) C, H.

Preparation of Deuterated Aldehyde 7-*d*. Except for the use of deuterated enamine reagent **6-*d***, the preparation of the deuterated aldehyde was analogous to that of the undeuterated aldehyde **7**: mass spectrum, m/e 174; 60-MHZ ^1H NMR (CCl_4) δ 9.22 (br s, 1 H), 6.23 (m, ~1.2 H), 5.85 (s, 4 H), 5.77 (br s, 2 H), 1.8 (d, J = 6 Hz, 2 H), 1.33 (dt, J = 9.0, 4.5 Hz, 1 H); CFT-20 ^{13}C NMR ($CDCl_3$) δ 192.4 (1 C), 160.5 (1 C), 128.4 (2 C), 126.4 (2 C), 124.8 (2 C), 31.8 (1 C), 29.5 (2 C).

Preparation of *p*-Toluenesulfonylhydrazone 8. The unsaturated aldehyde **7** (1.0 g) was dissolved in ethanol (10 mL). *p*-Toluenesulfonylhydrazine (1.1 g) was dissolved in diglyme (6.0 mL). The two solutions were mixed, and glacial acetic acid (2.0 mL) was added. The mixture was shaken for 2 min and allowed to stand for 15 min. The white precipitate of *p*-toluenesulfonylhydrazone was filtered and washed with a little ethanol. Addition of 2 mL of water to the filtrate gave a second crop of product. The combined solids were recrystallized from 95% ethanol to give the tosylhydrazone **8** as a white solid (1.7 g, 84%): 148–150 °C; mass spectrum, m/e 340; IR (Nujol) 3200, 1750, 1670, 1585, 1460, 1440 cm^{-1}; 60-MHz ^1H NMR ($CDCl_3$) δ 8.1–7.3 (m, 6 H becomes 5 H in D_2O), 6.0 (s, 4 H), 5.9 (s, 2 H), 6.5–5.5 (AB pattern, 2 H), 2.4, (s, 3 H), 1.65 (d, J = 5 Hz, 2 H), 1.2 (m, 1 H), CFT-20 ^{13}C NMR ($CDCl_3$) δ 150.3 (1 C), 146.2 (1 C), 143.9 (1 C), 135.3 (1 C), 129.5 (2 C), 128.0 (2 C), 127.7 (2 C), 124.9 (2 C), 124.4 (1 C), 32.2 (1 C), 28.1 (2 C), 21.4 (1 C).

Anal. Calcd for $C_{19}H_{20}N_2O_2S$: C, 67.06; N, 8.24; H, S. Found: C, 66.64; N, 8.75.

Preparation of Deuterated Tosylhydrazone 8-*d*. The deuterated tosylhydrazone was prepared in an analogous fashion to the undeuterated compound **8**: mass spectrum, m/e 341; 60-MHz ^1H NMR ($CDCl_3$) δ 7.9–7.1 (6 H, becomes 5 H in D_2O), 5.9 (s, 4 H), 5.8 (s, 2 H), 6.1–5.1 (m, 1.2 H), 2.37 (s, 3 H), 1.58 (d, J = 5 Hz, 2 H), 1.4–0.9 (m, 1 H). Except for the absence of the peak at 124.4 ppm, the ^{13}C NMR spectrum was unchanged from that of the undeuterated compound **8**.

Preparation of the Lithium Salt of Tosylhydrazone 8. In a 100-mL three necked round-bottomed flask equipped with a magnetic stirrer, 50-mL dropping funnel, and nitrogen inlet were placed tosylhydrazone **8** (0.5 g, 1.46 mmol) and anhydrous tetrahydrofuran (10 mL). The flask was flushed with nitrogen and the solution was cooled to −78 °C in a dry ice/acetone bath. *n*-Butyllithium in hexane (1.47 N, 1.0 mL) was slowly added through the dropping funnel. A tannish yellow color developed and a precipitate fell out immediately. After the addition was finished, the solution was kept at −78 °C for 15 min and then slowly warmed to room temperature and allowed to stir another 15 min. Pentane (60 mL) was added and the mixture was filtered. The lithium salt was obtained as a yellow solid in a nearly quantitative yield. This salt is stable in air and can be stored for a long time.

Pyrolysis of the Lithium Salt of Tosylhydrazone 8. A 250-mL three-necked round-bottomed flask containing some glass beads was equipped with two bent Pyrex tubes with male ground glass joints and another extension Pyrex tube connected to a cold finger kept in liquid nitrogen (Figure 5). The lithium salt (0.5 g, 1.44 mmol) was placed in the bent Pyrex tube and the second bent tube was filled with glass beads. The system was then opened to vacuum (ca. 0.03 mmHg) and the flask was warmed to 250 °C. The lithium salt was added in small portions to the flask. Periodically, approximately 5–10 glass beads were added to the flask to provide fresh surface. Newly added beads were allowed to warm

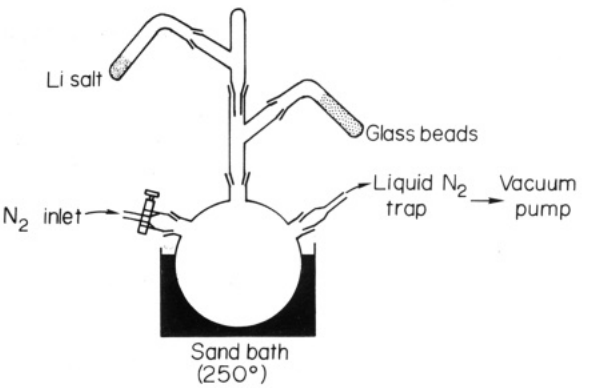


Figure 5. Pyrolysis apparatus for decomposition of the lithium salt of tosylhydrazone **8**.

up for about 20 min before addition of more lithium salt. After addition of all the lithium salt (approximately 2 h), the flask was cooled to room temperature, the vacuum was disconnected, and nitrogen was slowly bled into the apparatus. It was observed that some less volatile compounds were deposited on the extension tube. This portion was separately washed into a flask with methylene chloride. The contents of the cold finger were washed with methylene chloride into another flask. This solution was concentrated on a rotary evaporator and subjected to GC/MS analysis. Five GC peaks were evident at 9.20, 12.80, 16.68, 18.30, and 33.40 min in a ratio of 1.2:6.8:7.5:13.5:3.3, respectively. All mass spectra exhibited parent peaks at 156 for $(CH)_{12}$'s. All these compounds were separated on the preparative column. The first compound was not investigated further because of the small amount of material.

The second compound was isolated as a white solid (3.0% yield) identified as diene **12**: mass spectrum, m/e 156 (20), 155 (49), 154 (16), 153 (31), 152 (28), 141 (39), 129 (20), 128 (41), 127 (18), 115 (31), 91 (100), 78 (13), 77 (7.0); 250-MHz ^1H NMR ($CDCl_3$) δ 1.75 (dt, J = 7.0, 4.7 Hz, 1 H), 1.91 (ddd, J = 8.0, 5.5, 1.5 Hz, 2 H), 2.90 (m, 2 H), 3.15 (ddd, J = 9.3, 5.5, 1.5 Hz, 2 H), 3.35 (dt, J = 5.5, 4.7 Hz, 1 H), 5.45 (t, J = 1.2 Hz, 2 H), 6.05 (dd, J = 5.8, 2.8 Hz, 2 H); WM-250 proton-decoupled ^{13}C NMR ($CDCl_3$) δ 134.8 (2 C), 131.3 (2 C), 66.3 (1 C), 62.8 (2 C), 41.8 (2 C), 36.1 (2 C), 26.6 (1 C); proton-coupled ^{13}C NMR ($CDCl_3$) δ 134.6 (d, J = 160.9 Hz, 2 C), 131.1 (d, J = 156.4 Hz, 2 C), 66.2 (d, J = 137.8 Hz, 1 C), 62.3 (d, J = 137.8 Hz, 2 C), 41.6 (d, J = 135.9 Hz, 2 C), 36.06 (d, J = 166.5 Hz, 2 C), 26.4 (d, J = 171.1 Hz, 1 C).

The third compound was isolated as a clear liquid (3.3% yield) and identified from its ^1H NMR as the known[1c] exo tetraene **9** from its spectroscopic properties.

The fourth compound was isolated as a white solid (6.0% yield) and was identified as the known[1d] endo tetraene **10** from its spectra.

The last compound was isolated as a yellow liquid (1.5% yield) and was identified as benzocyclooctatriene (**11**) according to its NMR spectrum: 250-MHz ^1H NMR ($CDCl_3$) δ 2.29 (m, 4 H), 5.92 (m, 2 H), 6.25 (d, J = 12.3 Hz, 2 H), 7.13 (m, 2 H), 7.22 (m, 2 H).

Spin-Decoupling Studies of Diene 12. Decoupling experiments were carried out at seven positions, using 250-MHz ^1H NMR. Irradiation at δ 1.75 caused the doublet of doublet of doublets at 1.91 ppm and doublet of triplets at 3.35 ppm to collapse to a doublet of doublets (J = 5.5 and 1.5 Hz) and a triplet (J = 5.5 Hz), respectively. Irradiation at δ 1.91 caused the doublet of triplets at 1.75 ppm to collapse to a distorted doublet (J = 4.7 Hz) and also caused some change in the multiplet at 2.90 ppm. Irradiation of δ 2.90 caused the doublet of doublet of doublets at 1.91 ppm, doublet of doublet of doublets at 3.15 ppm, and doublet of doublets at 6.05 ppm to collapse to a doublet of doublets (J = 7.0 and 1.5 Hz), a broad doublet (J = 5.5 Hz), and a sharp singlet, respectively. Irradiation at δ 3.15 collapsed the doublet of triplets at 3.35 ppm and the triplet at 5.45 ppm to a doublet (J = 4.7 Hz) and a sharp singlet, respectively. Irradiation at δ 3.35 collapsed the doublet of triplets at 1.75 ppm and doublet of doublet of doublets at 3.15 ppm to a triplet (J = 7.0 Hz) and a doublet of doublets (J = 9.3 and 1.5 Hz). Finally, irradiation at δ 5.45 caused the doublet of doublet of doublets at 3.15 ppm

to collapse to a doublet of doublets (J = 9.3 and 5.5 Hz), while irradiation at δ 6.05 caused only some distortion in the multiplet at 2.9 ppm as the only change in the spectrum.

Analysis of the Less Volatile Part. The less volatile part was flash chromatographed on silica gel with ether. The first eluting material, whose ^{1}H NMR showed it to be an aromatic compound, was not investigated further.

The second eluting compound was obtained as a yellow greasy material (6.7 mg, 2.2% yield). This compound was identified as *anti*-pyrazole **13** from its spectroscopic data: mass spectrum, m/e 184; 60-MHz ^{1}H NMR ($CDCl_3$) δ 2.95 (s, 1 H), 3.12 (d, J = 6.0 Hz, 2 H), 5.08 (s, 2 H), 5.6–6.1 (m, 5 H), 6.98–7.1 (m, 2 H); CFT-20 proton-decoupled ^{13}C NMR ($CDCl_3$) δ 135.75 (2 C), 124.26 (2 C), 121.21 (2 C), 50.08 (2 C), 40.22 (1 C). Because of a noisy base line, the peaks belonging to the pyrazole ring were not observed.

The third eluting material was separated as a yellow greasy compound (17.5 mg, 6.1% yield). This compound was identified as the *syn*-pyrazole **14** from its spectroscopic properties: mass spectrum, m/e 184; 60-MHz ^{1}H NMR ($CDCl_3$) δ 3.1–3.4 (m, 3 H), 5.12 (s, 2 H), 5.8 (br s, 5 H), 7.1 (br s, 1 H), 11.0 (br s, 1 H); CFT-20 proton-decoupled ^{13}C NMR ($CDCl_3$) δ 145.69 (w), 135.44 (2 C), 134.48 (w), 126.09 (2 C), 122.87 (2 C), 104.20 (w), 46.37 (2 C), 36.07 (1 C).

Pyrolysis of the Lithium Salt of Deuterated Tosylhydrazone 8-*d*. Preparation of the lithium salt and the pyrolysis and separation of products were carried out as mentioned for the analogous undeuterated compound. The mass spectrum of each of the two tetraenes **9** and **10** showed a M^+ peak at 157. The ^{1}H NMR spectrum (δ, CCl_4) for compound (**9-*d***) consisted of peaks at 2.57 (pseudo t, 2 H), 3.25 (s, 2 H), and 5.96–5.0 (m, 7.2 H) and for compound **10-*d*** 2.82 (br s, 4 H), 5.63–5.4 (unsymmetrical m, 6 H), and 6.04 (sh s, 1 2 H).

Preparation of *anti*-9-(2-Cyclopropen-1-yl)bicyclo-[6.1.0]nona-2,4,6-triene (20). The tosylhydrazone **8** (510 mg, 17 mmol) was taken in dry tetrahydrofuran (60 mL) and placed in a Pyrex tube equipped with a magnetic stirrer and nitrogen inlet. Sodium methoxide (81 mg, 15 mmol) was added and the mixture was stirred for 10 min. The tube was then placed in a dry ice/acetone bath next to a Pyrex immersion well and the solution was photolyzed with a 200-W Hg vapor lamp for 4 h. The solution was transferred to a 100-mL round-bottomed flask and concentrated to 20 mL at −30 to −40 °C, using a high vacuum. The solution was then poured into 300 mL of ice water and 200 mL of pentane. The pentane layer was separated, and the aqueous layer was extracted with another 100 mL of pentane. The pentane extracts were combined, washed with ice cold water, and dried over anhydrous sodium sulfate. The solution was then rapidly filtered through silica gel (20 g) to remove unreacted tosylhydrazone. Evaporation of solvent at −30 °C gave the cyclopropene **20** as a light-yellow liquid (87 mg, 37% yield): mass spectrum, m/e 156; 60-MHz ^{1}H NMR (CS_2) δ 7.2 (dd, J = 2.0, 0.4 Hz, 2 H), 6.0–5.9 (d, 6 H), 1.8 (dt, J = 5.0, 2.0 Hz, 1 H), 1.2 (d, J = 5.5 Hz, 2 H), 0.8–0.5 (m, 1 H).

Thermolysis of Cyclopropene Hydrocarbon 20. A 60-cm Pyrex tube, packed with 25 cm of glass beads, was connected to a 250-mL three-necked round-bottomed flask containing glass beads, a serum cap, and an argon inlet. The top of the column was connected to the cold finger kept in liquid nitrogen (Figure 6). Argon was slowly bled into the apparatus and the system was opened to vacuum (ca. 0.3 mmHg). Both flask and Pyrex tube were heated to 300 °C with a sand bath and oven, respectively. Hydrocarbon **20** (52 mg, 0.3 mmol) was dissolved in dry tetrahydrofuran (2 mL) and injected in small portions through the serum cap into the hot flask. After all the solution was injected (2 h), the system was cooled to room temperature and the vacuum disconnected. The contents of the cold finger were rinsed with pentane into a flask and concentrated at −20 °C, using a high vacuum. GC/MS analysis showed two GC peaks at 9.20 and 11.40 min in a ratio of 14.0:3.2. Mass spectra taken of these peaks showed a parent peak at 156 corresponding to $(CH)_{12}$'s. The first compound was separated on the preparative column and was obtained as a clear liquid (1.5 mg, 2.6% yield). It was identified as polycyclic **22** from its spectroscopic data: mass spectrum, m/e 156 (10), 155 (11), 141 (11), 128 (14), 115 (15), 91 (100), 78 (16); 250-MHz ^{1}H NMR ($CDCl_3$) δ 0.7–0.9 (m, 2 H), 1.75 (ddd, J = 7.9, 4.9, 4.1 Hz, 1 H), 1.85 (dd, J = 6.2, 3.3 Hz, 1 H), 2.35 (ddd, J = 7.5, 6.2, 5.1 Hz, 1 H), 2.48 (dd, J = 7.9, 6.2 Hz, 1 H), 2.82 (dd, J = 5.1, 3.2 Hz, 1 H), 3.06 (dd, J = 7.5, 5.8 Hz, 1 H), 5.55 (dd, J = 5.0, 3.3 Hz, 1 H), 6.12 (dd, J = 5.0, 3.2 Hz, 1 H), 6.33 (dd, J = 7.9, 5.8 Hz, 1 H), 6.55 (dd, J = 7.9, 6.2 Hz, 1 H).

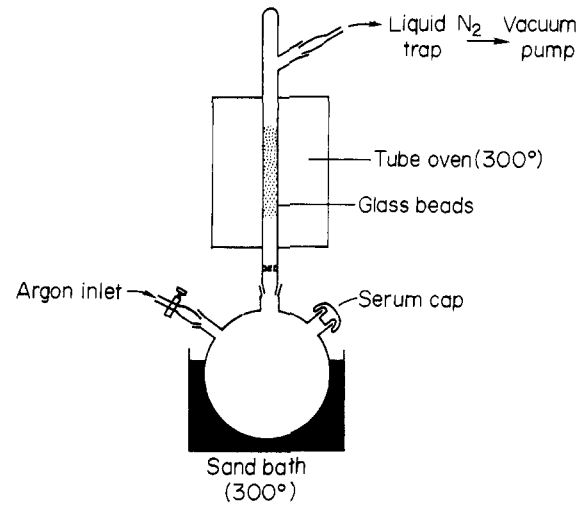


Figure 6. Thermolysis apparatus for isomerization of hydrocarbon **20**.

Preparation of *trans*-β-[*syn*-9-Bicyclo[4.2.1]nona-2,4,7-trienyl]acrolein Tosylhydrazone (15). Tosylhydrazone **8** (1.0 g, 2.9 mmol) was refluxed in 50 mL of chloroform overnight. Solvent was removed by a rotary evaporator and the residue was recrystallized from a mixture of methylene chloride–carbon tetrachloride to give 290 mg of a light-yellow solid. The mother liquor was concentrated and recrystallized from a mixture of methylene chloride–hexane to give another 200 mg of the solid compound (49% total yield). This compound was identified as the titled compound **15** from its spectra: mp 151–153 °C; mass spectrum, m/e 340; IR (Nujol) 3100, 1670, 1550, 1390, 1350, 1310, 1180 cm^{-1}; 60-MHz ^{1}H NMR ($CDCl_3$) δ 2.4 (s, 3 H), 3.0 (t, J = 6.0 Hz, 1 H), 3.18 (m, 2 H), 5.1 (sh s, 2 H), 5.7–6.0 (m, 6 H), 7.1–8.0 (m, 6 H); CFT-20 ^{13}C NMR ($CDCl_3$) δ 150.1 (1 C), 144.0 (1 C), 142.8 (1 C), 135.3 (1 C), 134.2 (2 C), 129.5 (2 C), 127.8 (2 C), 127.0 (1 C), 126.0 (2 C), 123.0 (2 C), 47.3 (2 C), 39.8 (1 C), 21.5 (1 C).

The filtrate was concentrated and was shown by NMR to be a mixture of **15** and its epimer **33**. Continued fractional crystallization failed to separate this mixture (separation of these two epimers by column chromatography also failed due to the polymerization of products).

Pyrolysis of the Lithium Salt of Tosylhydrazone 15. The lithium salt of tosylhydrazone **15** (0.5 g, 1.44 mmol) was prepared and pyrolyzed in the same way as described for the lithium salt of tosylhydrazone **8**. GC/MS analysis of the volatiles showed a single peak at 12.8 min with a parent peak of 156. The ^{1}H NMR spectrum showed this to be the diene **12** (1.9–2.3% yield). The ^{1}H NMR and MS data of the less volatile material were indistinguishable from those of pyrazole **14** (13.2% yield).

Photolysis of the Sodium Salt of the Tosylhydrazone 15 Using a Sunlamp. In a 50-mL three-necked round-bottomed flask equipped with a magnetic stirrer, condenser, and nitrogen inlet was placed a solution of tosylhydrazone **15** (100 mg, 0.29 mmol) in dry tetrahydrofuran (10 mL). To this solution was added 99% soldium hydride (7.0 mg, 0.29 mmol) and the mixture was stirred for 15 min. The flask was then placed close to a sunlamp and was irradiated for 1 h. During this time, the solution warmed up and began to boil. The solution was cooled to room temperature and filtered to remove the unreacted salt, and the filtrate was concentrated at −20 °C, using a high vacuum. MS and ^{1}H NMR were identical with those of pyrazole **14** (20 mg, 37% yield).

Photolysis of the Sodium Salt of the Tosylhydrazone 15 through a Quartz Filter Using a 200-W Mercury Lamp. A solution of tosylhydrazone **15** (100 mg, 0.29 mmol) in dry tetrahydrofuran (60 mL) was placed in a Pyrex tube containing a magnetic stirrer and nitrogen inlet. The tube was flushed with nitrogen, and 99% sodium hydride (7.0 mg, 0.29 mmol) was added to the solution and the mixture was stirred for 15 min. This solution was then placed close to a quartz immersion well and

photolyzed for 1 h, using a 200-W medium-pressure Hg vapor lamp. The solution was poured into a mixture of 200 mL of 1:1 cold water and pentane. The pentane layer was separated, and the aqueous layer was extracted with another 100 mL of pentane. The pentane extracts were combined, washed with 50 mL of cold water, and dried over anhydrons sodium sulfate. Most of the solvent was removed on a rotary evaporator and the rest of the solvent was removed at −30 °C using a high vacuum. MS and ^{1}H NMR were identical with those of pyrazole 14 (15 mg, 28% yield).

Low-Temperature Photolysis of the Sodium Salt of the Tosylhydrazone 15 through a Pyrex Filter with a 200-W Mercury Lamp. The above experiment was repeated, but the solution was photolyzed in an ice bath through a Pyrex filter with the 200-W medium-pressure Hg vapor lamp. GC/MS analysis of the product showed a single peak at 12.8 min with a molecular ion peak of 156 (31–33% yield). The ^{1}H NMR spectrum of this product was identical with that of diene **12**.

Registry No. **4**, 13380-66-0; **5**, 28860-69-7; **6**, 20061-84-1; **6**-*d*, 81121-06-4; **7**, 81121-07-5; **7**-*d*, 81121-08-6; **8**, 81121-09-7; **8** Li, 81176-65-0; **8**-*d*, 81132-92-5; **8**-*d* Li, 81177-13-1; **9**, 26333-43-7; **9**-*d*, 81121-10-0; **10**, 63162-54-9; **10**-*d*, 81176-66-1; **11**, 40644-06-2; **12**, 63064-34-6; **13**, 81121-11-1; **14**, 81121-12-2; **15**, 81121-13-3; **15** Li, 81176-67-2; **15** Na, 81176-68-3; **20**, 81121-14-4; **22**, 81121-15-5; **33**, 81176-69-4.

Synthesis of 2,5-Disubstituted 3,6-Diamino-1,4-benzoquinones

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A general synthetic approach to a wide variety of 2,5-disubstituted 3,6-diamino-1,4-benzoquinones was developed. Bromanil was diaminated with ammonia, and adjacent NH_2 and OH groups were protected as benzoxazoles by treatment with a carboxylic acid chloride followed by a polyphosphate ester cyclization–dehydration. The resulting 2,5-dibromobenzobis(oxazoles) were monolithiated by halogen–metal exchange with *n*-butyllithium and then reacted with a variety of electrophiles. The remaining bromide was replaced in a similar fashion. Alternatively the second bromide was replaced by reaction with π allylnickel halide complexes. The benzoxazole protecting group could be hydrolyzed with zinc(II) chloride/HCl–aqueous ethanol under an inert atmostphere. Air oxidation of the resulting hydroquinone under neutral conditions gave the desired 2,5-disubstituted 3,6-diamino-1,4-benzoquinone in good to excellent overall yield. This method was used to synthesize precursors to the basic ring system of the mitomycin antineoplastic antibiotics. Acid hydrolysis of the benzoxazole protecting group under oxidizing conditions resulted in the production of 2,5-disubstituted 3,6-dihydroxy-1,4-benzoquinone. Methylation followed by reaction with ammonia gave the desired diaminoquinone.

Introduction

A number of palladium-assisted heterocyclization reactions have been developed in these laboratories[1-7] with the long-range intent of application in the synthesis of pyrroloindoloquinone ring systems found in the mitomycin antineoplastic antibiotics.[8] For these processes, specifically alkylated 3,6-diaminoquinones were required as substrates. Although the parent compound 2,5-diamino-1,4-benzoquinone has long been known,[9,10] there is, as yet, no general synthetic approach to 2,5-disubstituted 3,6-diamino-1,4-benzoquinones, in spite of many recent studies concerning the synthesis of substituted quinones.[10-14] An attractive starting point for the synthesis of these compounds is 2,5-dibromo-3,6-diamino-1,4-hydroquinone (1), readily available from the reaction of bromanil with ammonia.[15a] This compound has the amino groups in the desired positions, and the halogens are, in principle, reactive in a number of alkylation processes. In this paper a general approach to the desired tetrasubstituted benzoquinones from this precursor is presented.

Results and Discussion

Two major problems faced in synthesis using diaminoquinones as intermediates are the high reactivity of this system toward a variety of reagents and the insolubility of these substrates in common organic solvents. A general approach to the practical management of both of these problems is to block both the amino and the quinone groups and then carry out substitution chemistry at the 2,5-dibromo positions. Thus, 2,5-dibromo-3,6-diamino-1,4-benzoquinone was reduced with sodium dithionite, and a number of attempts to introduce difunctional protecting groups were made. Surprisingly, protecting groups normally used for *o*-dihydroxy aromatics such as methylenedioxy, acetonide, dialkylsilyl, and carbonate groups failed to produce the corresponding aminal or carbamate compounds from 1 (eq 1). In contrast, conversion of 1 to the

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