water aspirator. This solution was then analyzed as before by GLC. The only product was the anti alcohol.

Meerwein–Ponndorf Equilibration of II and III. Into a 50-ml round-bottom flask equipped with a magnetic stirrer were placed 100 mg of *syn*-2-*exo*-methyl-7-norbornanol, 1 g of aluminum isopropoxide, 5 ml of isopropyl alcohol, and 5 ml of acetone. Mild heat was applied with stirring for 3 days. The GLC analysis of the hydrolyzed mixture showed the anti alcohol almost exclusively except for a trace of the syn alcohol.

Alkylations of I, II, and III. The same procedure used for the reductions was invoked for the alkylations. All of the products were isolated and identified via ^{1}H NMR, ^{13}C NMR, and GLC.

Acknowledgment. We wish to thank the National Science Foundation for support of this work.

Registry No.—I, 10218-02-7; II, 59532-17-1; III, 59532-18-2; IV, 2207-27-4; VI, 875-04-7; VIII, 10421-72-4; IX, 10265-39-1; X, 60761-81-1; XIa, 60734-22-7; XIb, 60734-23-8; XII, 60734-24-9; XIII, 60734-25-0.

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Thermal and Base-Catalyzed Isomerizations of Birdcage and Half-Cage Compounds

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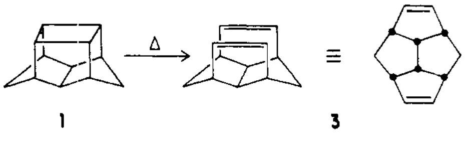
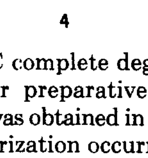
Thermal rearrangements of the birdcage hydrocarbon and alcohol afforded a novel, all-cis fused tetracyclic system containing four five-membered rings. Base-promoted isomerizations of the birdcage alcohol and the half-cage ketone proceeded via a transannular keto–enolization process involving a γ hydrogen to give a new isomeric half-cage ketone.

The birdcage and half-cage compounds[1] have provided attractive frameworks for the study of transannular interactions and for further synthetic investigations.[2] Here, we report new polycyclic systems obtained by thermal and base-promoted[3] isomerizations of these systems.

Thermal Isomerization. Thermal behavior of the birdcage hydrocarbon (1) and its derivatives was initially studied over heated quartz chips using a pyrolytic gas chromatogram unit. Hydrocarbon 1 was stable below 500 °C but between 500 and 650 °C it afforded a mixture of 1 and a new hydrocarbon 3.[4]



1 3



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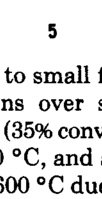

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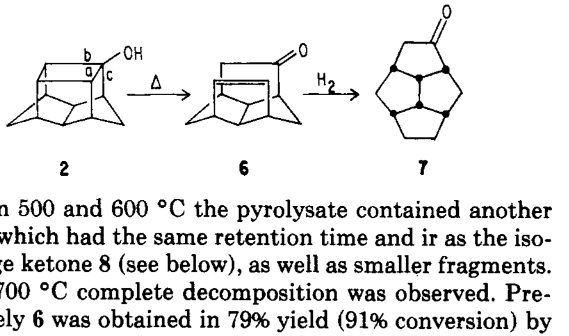
Above 700 °C complete degradation to small fragments resulted. Under preparative conditions over silicon chips, compound 3 was obtained in 27% yield (35% conversion) at 600 °C. No isomerization occurred at 550 °C, and at 650 °C the yield of 3 was about one-half that at 600 °C due to extensive fragmentation. Over platinum, extensive decomposition occurred above 500 °C and naphthalene was the sole identifiable product.

The diene 3 is an air-sensitive, colorless wax, mp 134–136 °C, and the mass spectral fragmentation pattern closely resembled that of 1. The UV spectrum showed only end absorption. The infrared spectrum contained typical cyclopentene bands[2] at 3040, 1615, and 725 cm^{-1} but was significantly different from that of the isomeric diene 4 (3020, 1566, and 725 cm^{-1}). The ^{1}H NMR spectrum showed a sharp singlet at δ 5.40 (4 H) due to olefinic protons and two broad singlets at 1.95 (4 H) and 3.37 (6 H) due to secondary and tertiary protons, respectively. The diene 3 absorbed 2 mol of hydrogen to give an air-stable, tacky hydrocarbon 5.

The birdcage alcohol 2 rearranges more readily than 1. Scouting pyrolysis experiments indicated that 2 rearranged cleanly between 255 and 400 °C to unsaturated ketone 6.



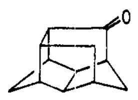
2 6 7

Between 500 and 600 °C the pyrolysate contained another ketone which had the same retention time and ir as the iso-half-cage ketone 8 (see below), as well as smaller fragments. Above 700 °C complete decomposition was observed. Preparatively 6 was obtained in 79% yield (91% conversion) by feeding an alcoholic solution of 2 over silicon chips at 500 °C. The unsaturated ketone 6 was, like 3, air sensitive and satisfactory elemental analyses were difficult to obtain. Compound

6 readily absorbed 1 mol of hydrogen to give 7 and formed air-stable carbonyl derivatives such as the oxime and tosylhydrazone. Thermal decomposition of the tosylhydrazone sodium salt afforded the diene 3.

It has been reported[1e] that the diene 4 can be transformed to 1 photochemically or thermally in the presence of traces of acid. Thus, the present study demonstrates a conversion of the highly strained diene 4 to the practically strain-free diene 3 through the birdcage structure. The double bond stretching frequencies of 3 and 4 clearly reflect strains involved in these ring systems. Furthermore, Dreiding models show that 3 is much more flexible and open than 4. The two double bonds are separated by more than 4 Å in 3, whereas those in 4 are rigidly held within the van der Waals distance. Although the present results suggest high regiospecificity in the thermal reorganization of 3, formation of 4 cannot be totally discounted since it might have rearranged[1e] in our GLC system.

Thermal reorganization of 2, on the other hand, is definitely regiospecific in the direction of the least strained ketone 6. The carbonyl frequencies of 6 (1735 cm^{-1}) and the isomeric ketone 9[2] (1742 cm^{-1}) again reflect angle strains in the ring systems.



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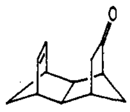

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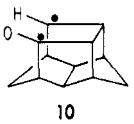
The saturated ketone 7 shows the stretching at 1730 cm^{-1} as does perhydrotriquinacenone.[5] Lack of C–H stretching above 3000 cm^{-1} in the saturated ketone 7 and hydrocarbon 5 further indicates the absence of transannular hydrogen repulsion.[1d] Thermal reorganizations of cyclobutanols[6] have been accounted for by the intermediate formation of 1-hydroxy-1,4-diradicals followed by (1) further bond cleavage to give ketone and olefin, (2) hydrogen migration to ketone, and (3) ring closure to the starting material and its stereoisomers. These three processes are generally competitive and, in the case of unsymmetric cyclobutanols, they proceed with two different 1-hydroxy-1,4-diradicals.[6b] Although the thermal reorganization of 2 is in general accord with the above mechanism, it should be pointed out that we have isolated products only from the diradical 10 generated by cleavage of the bond a in 2. No products from bond cleavage at b or c were detected. Furthermore, 10 fragments preferentially to give 6, and hydrogen migration to form ketone 8 competes only above 500 °C.



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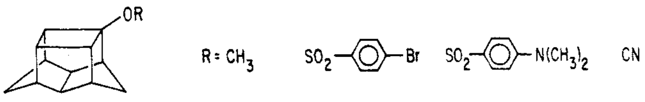
Although 1-hydroxy-1,4-diradicals have never been detected spectrophotometrically,[7] it is well documented[8] that the Norrish type II photoreaction of ketones having γ hydrogens generates 1-hydroxy-1,4-diradicals which behave as do thermally generated diradicals.[6] Irradiation of the half-cage ketone 8 or 11 in cyclohexane, however, resulted in a complete recovery of the starting material either in the presence or in the absence of a sensitizer, benzophenone. The failure of these ketones to undergo the photoreaction may be attributed to unfavorable spacial disposition of the γ hydrogens with respect to the half-filled n orbital of the n–π^* excited carbonyl group.[8b] Thermally, these ketones decompose above 600 °C without prior isomerization.

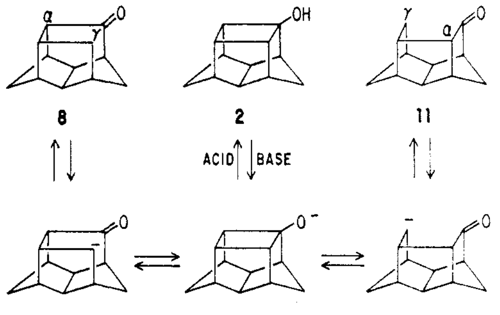
Whereas thermal reorganization of 2 took place more readily than that of 1, the methoxy derivative 12a did not isomerize below 450 °C and decomposed completely above 500 °C. There is no obvious explanation for the greater thermal stability of 12a as compared to 2, since a methoxy group is expected to stabilize the adjacent carbon radical center by 2–3 kcal/mol relative to a hydroxyl group.[9]



12 a b c d

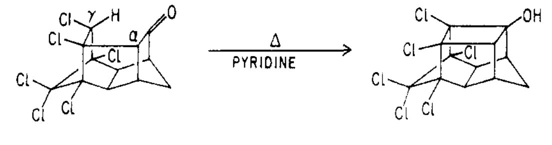
Since cage amines show interesting biological activities[10] and since the birdcage *p*-bromobenzenesulfonate 12b has been reported[11] to solvolyze to unrearranged acetate in acetic acid containing sodium acetate, we have attempted to prepare the birdcage amines by carbonium ion processes. Treatment of 12b with dimethylamine at 200 °C, however, afforded the *p*-dimethylaminobenzenesulfonate 12c. The cyanate 12d was recovered even after distillation at atmospheric pressure in the absence or presence of anhydrous ferric chloride. Rearrangement to the corresponding isocyanate[5,12] could not be accomplished either by acidic alumina or Lewis acids. Treatment of 2 with acetonitrile in the presence of sulfuric acid (Ritter reaction) also failed to give the corresponding acetamide.

Transannular Keto–Enol Isomerization. In contrast to the thermal rearrangement, the birdcage alcohol[11] 2 rearranged[3] in *tert*-butyl alcohol in the presence of potassium *tert*-butoxide at 250 °C to give a mixture of two ketones in approximately 96:4 ratio (GLC analysis). A mixture of virtually identical composition was obtained when the half-cage ketone 11[1d] was subjected to similar treatment. The major product was identified as the isomeric half-cage ketone 8 based on chemical and spectral evidence and the minor component as the starting material 11 by GLC peak matching. Howe and Winstein[3b] found that the isomerization of 11 was first order in its disappearance at 175–200 °C and that homoketonization of 2a proceeded ca. 33 000 times faster than the isomerization of 11 at 100 °C. Under these conditions they observed no homoketonization in the direction of 11. There is no doubt, however, that the isomerization of 11 to 8 involves the transannular enolate 2a common to both ketones 8 and 11. Base-catalyzed transannular ketonization of bridged alcohols can proceed with a high degree of stereoselectivity, and both retention[13] and inversion[14] of configuration have been reported depending upon the ring system. Recently, Crow and Borden[15] found through deuterium labeling studies that the opening of 2 to 8 proceeded with 95 ± 3% retention of configuration in *tert*-butyl alcohol-*d*, the solvent delivering the endo proton at C-γ in 8. Although the stereochemistry of the transformation between 2 and 11 has not been studied, the facile conversion of the hexachloro compound 13 to 14 in re-



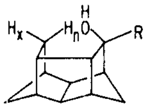
8 2 11

8a 2a 11a



13 14

fluxing pyridine[11] points also to an endo-proton abstraction. Treatment of the half-cage ketone **11** with stronger and more nucleophilic bases like *n*- and *tert*-butyllithium as well as lithium aluminum hydride afforded O-inside alcohols **15** with



15a R = H
15b R = n-C_4H_9
15c R = t-C_4H_9

15

high degrees of stereoselectivity but no transannular enolization process was observed.

Thus, the base-catalyzed homoketonization of **2** proceeded predominantly to give the less strained ketone **8**. Difference in steric hindrance about the carbonyl group of **8** and **11** was demonstrated, dramatically, by their reactivities toward hydroxylamine. Whereas **8** could be converted to oxime **14** under normal conditions, **11** did not react even under 10 000 atm at 75 °C; under these conditions di-*tert*-butyl ketone is reported to give the corresponding oxime in 96% yield.[16] In accord with these results, alcohol **15** showed a sterically compressed, high frequency stretch near 3080 cm^{-1}, whereas the endo alcohol[3b] derived from ketone **8** is reported to show no absorption above 3000 cm^{-1}.

Although the syntheses of **1** and **2** have been described previously,[1] the improved and large-scale preparations are included in the Experimental Section.

Experimental Section

General. Infrared spectra were recorded on a Perkin-Elmer Model 21 spectrophotometer as potassium bromide pellets, unless otherwise noted. Ultraviolet spectra were recorded on a Cary Model 14 spectrophotometer on solutions in 95% ethanol, unless otherwise noted. Nuclear magnetic resonance spectra were recorded on a Varian Associates A-60 spectrophotometer (60 MHz), unless indicated otherwise, on solutions (10–40%) in deuteriochloroform, with chemical shifts reported in parts per million downfield from an external standard of tetramethylsilane, and with coupling constants in hertz. Melting points and boiling points were uncorrected.

Pyrolysis. A. In pyrolysis studies using a pyrolytic gas chromatogram unit, approximately 15 mg of a solid sample or 10 μl of ca. 50% solution was injected into a preheated part of a pyrolysis tubing filled with 20 mesh quartz chips maintained at various temperatures. The pyrolysate was directly introduced into a gas chromatogram unit and each peak was separately collected for spectral analysis.

B. In preparative scale pyrolysis, a quartz pyrolysis tube, 28 cm × 1.6 cm i.d., was packed with 30 mesh silicon chips and was heated by nichrome ribbon which was wound around the tube and insulated with asbestos. A thermocouple was placed at the hottest point in the tube—about one-half the way down. Temperature was recorded and maintained with a Brown Pyr-O-Vane. The pyrolysis tube was surmounted either by a jacketed vapor feeder or by a specially designed dropping funnel. The vapor feeder permitted the substrate to be carried by a stream of nitrogen directly into the pyrolysis tube in the vapor state, the temperature for vaporization being maintained by reflux of the appropriate solvent in the jacket of the feeder. The dropping funnel was designed to permit simultaneous flow of the liquid charge and the carrier gas (nitrogen) directly into the tube. The exit from the pyrolysis tube led directly into a dry ice trap where the pyrolysate was condensed.

Pyrolysis of Birdcage Hydrocarbon. A. A solid sample or pentane solution of **1** was pyrolyzed in the pyrolytic gas chromatogram unit and the pyrolysate was analyzed on a 6 ft × 0.25 in. o.d. copper column packed with 20% silicon grease on 35–48 mesh Chromosorb P at 168 °C and 100 ml/min helium flow. Below 500 °C the pyrolysate showed a single peak at 8.6 min due to **1** (confirmed by the ir and mass spectra). Between 500 and 650 °C, a new peak appeared at 9.4 min. The IR, NMR, and mass spectra of this material were practically identical with those of an analytical sample of **3** (see below). Above 700 °C complete fragmentation was observed. The optimum temperature for **3** was 600 °C and the products consisted of approximately equal amounts of **1** and **3**.

B. The birdcage hydrocarbon (7.0 g) was placed in the jacketed vapor feeder and pyrolyzed at 600 °C, a vaporization temperature of 140 °C, and in a nitrogen flow of 50 ml/min. Seven hours was required for the pyrolysis. The pyrolysate, an olive-green liquid, was taken up in pentane (10 ml) and chromatographed on silicic acid (300 g) with pentane as the eluting solvent. After collection of the column volume of solvent, 17-ml fractions were collected and assayed by GLC. Fractions 3–15 gave 1.60 g (23% recovery) of **1**. Fractions 20–39 gave 1.90 g (27%) of **3**. An analytical sample was obtained as a waxy, white solid, mp 134.0–138.6 °C (sealed capillary), by sublimation at room temperature and 0.05 mm: ν_{max} (film) 3040, 2920, 2880, 1660, 1615, and 725 cm^{-1}: UV (CH_3OH) no maximum above 200 nm, ϵ 1200 at 210 nm.

Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found (after 2 h): C, 91.23; H, 8.92; mol wt, 158 (mass spectrum), 161 (cryoscopic, benzene). Found (after 5 days): C, 85.46; H, 8.84.

As indicated by the elemental analyses, **3** is very susceptible to air oxidation, the product being a nonsublimable, friable solid which exhibits an IR spectrum very similar to that of pure **3**, but with enhanced absorption at 1030, 760, and 680 cm^{-1}.

The mass spectra of **1** and **3** showed the peaks of significant intensities (%) given in Table I.

Table I

m/e	159	158	143	129	128	117	115	104	93	92	91
1	13.1	100.0	7.3	12.7	12.2	13.3	15.7	8.2	32.0	72.0	30.9
3	13.4	100.0	11.1	19.5	20.1	20.2	26.0	123	43.8	96.9	44.6
	80	79	78	77	67	66	65	51	39	27	
	31.9	48.3	4.3	19.2	13.4	10.1	10.5	10.7	21.3	12.9	
	44.5	69.2	23.8	25.2	18.9	13.2	14.2	17.1	24.3	20.0	

C. The pyrolysis tube and setup were as described for preparative pyrolysis of **1**. The packing was 4–14 mesh 5% Pt/C which was shown to be active for the dehydrogenation of cyclohexane to benzene at <400 °C.

Birdcage hydrocarbon **1** (1.00 g) was vaporized from the vapor feeder at a temperature of 140 °C, and pyrolyzed at a tube temperature of 550 °C in a nitrogen flow of 176 ml/min. The pyrolysate was a feathery, white solid which in GLC exhibited the same retention time as naphthalene. Sublimation of this pyrolysate yielded naphthalene (0.10 g, 1.2%) as a white solid, mp 78.5–80.0 °C, identical with an authentic sample based on mixture melting point and infrared spectral comparison.

***all-cis*-Tetracyclo[7.2.1.$0^{4,11}$.$0^{6,10}$]dodecane (5).** A solution of **3** (1.27 g, 8.04 mmol) in glacial acetic acid (30 ml) was hydrogenated at atmospheric pressure over 10% Pd/C catalyst (0.30 g), 16.62 mmol of hydrogen (103% of theory for 2 mol) being absorbed over a period of 140 min. The solution was filtered, diluted with water (125 ml), and extracted in succession with 50, 25, and 25 ml of pentane. The combined pentane extracts were washed with water (125 ml) and saturated aqueous sodium bicarbonate (125 ml) and dried over sodium sulfate. Filtration and evaporation of the filtrate at the water pump (room temperature) afforded 1.36 g (104%) of **5** as a white, tacky solid with an IR spectrum nearly identical with that of the analytical sample.

An analytical sample of **5** was obtained as an excessively tacky, white solid, mp 94.7–96.0 °C (sealed capillary), by recrystallization from methanol–water (ice bath) followed by sublimation at room temperature and <0.05 mm. In the IR, **5** absorbed at 2990, 2880, 1475, and 1450 cm^{-1}. The NMR spectrum of **5** exhibited unresolved multiplet absorption between δ 0.5 and 2.8.

Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18; mol wt, 162.26. Found: C, 88.84; H, 11.41; mol wt, 162 (mass spectrum), 156 (cryoscopic, benzene).

***all-cis*-Tetracyclo[7.2.1.$0^{4,11}$.$0^{6,10}$]dodec-2-en-7-one (6). A.** A solid sample of **2** and its methylene chloride solution were pyrolyzed and assayed on a 3 ft × 0.25 in. o.d. copper column packed with 25% neopentyl succinate on 35–48 mesh Chromosorb P at 205 °C and 100 ml/min helium flow. The pyrolysis results are summarized in Table II.

The 5.4- and 6.9-min peaks were **2** and **8**, respectively. The 8.4-min peak showed IR, NMR, and mass spectra practically identical with those of an analytical sample of **6**. The half-cage ketone **11**, which

Table II

Pyrolysis temp, °C	Sample	Pyrolysate composition, %			
		5.4 min 2	6.9 min 8	8.4 min 6	Fragmentation products
255	Solid	~0	Trace	>95	Trace
	Solution	80	Trace	20	Trace
300	Solid	~0	Trace	>95	Trace
	Solution	80	Trace	20	Trace
400	Solid	~0	Trace	>95	Trace
	Solution	20	Trace	80	Trace
500	Solid	~0	30	70	Trace
	Solution	Trace	25	75	Trace
600	Solid	~0	40	20	40
	Solution	~0	60	25	15
700	Solid	~0	~0	~0	>95
	Solution	~0	~0	~0	>95

should appear at 7.8 min, was not detected.

B. A solution of the birdcage alcohol **2** (15.0 g) in ethanol was placed in the dropping funnel and dropped through the pyrolysis tube, maintained at 500 °C, at the rate of ca. 10 drops/min in a nitrogen flow of 60 ml/min. The pyrolysate was evaporated at the water pump and the residue was taken up in benzene (100 ml) which was removed in the same way. The residue was chromatographed on silicic acid (300 g) with 5% ethyl acetate in methylene chloride as the eluting solvent. After passage of the column volume of solvent, 50-ml fractions were collected and assayed by thin layer chromatography (silica/methylene chloride). Fractions 10–23 contained the desired ketone and fractions 25–30 contained starting material. From the latter fractions there was isolated, by evaporation of solvent, 2.0 g (13% recovery) of unreacted birdcage alcohol **2** as a white solid. From the former fractions there was isolated, by evaporation of solvent, 11.9 g (79%) of ketone **6** as a pale yellow solid; their spectra were identical with those of analytical samples.

The analytical sample of **6** was obtained as a tacky, white solid, mp 182–206 °C, by crystallization from ethanol–water followed by sublimation at 80 °C and 0.02 mm: ν_{max} 3040, 2940, 1735, and 698 cm^{-1}; λ_{max} 290 nm (ϵ 15) and 212 (ϵ 900); NMR δ 5.37 (2 H, quartet, J = 5.5 Hz, olefinic), 3.24 (4 H, br s) 1.85–2.8 (8 H, m). This material proved susceptible to air oxidation, and for preservation, **6** was dissolved in ethanol directly from the chromatography column.

Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found (after 1 day): C, 82.10; H, 8.07; mol wt, 174 (mass spectrum). Found (after 1 week): C, 80.29; H, 7.99.

At 400 °C the pyrolysis of **2** was slight; above 550 °C the pyrolysis proceeded more completely than at 500 °C but the desired ketone **6** was contaminated with significant quantities of isomeric material, probably **9**, which could not be removed by chromatography.

***all-cis*-Tetracyclo[7.2.1.0^{4,11}.0^{6,10}]dodecan-2-one (7).** A solution of ketone **6** (ca. 3.5 g, 20 mmol, directly from chromatography) in ethanol was evaporated at the water pump. The residue was then taken up in glacial acetic acid (75 ml) and was hydrogenated over 10% Pd/C analyst (0.5 g) at atmospheric pressure. Hydrogen uptake corresponded to 16.2 mmol (81% of theory for 1 mol) and ceased after 100 min. The reaction mixture was filtered and the filtrate was evaporated at the water pump to yield a white residue of **7** (3.55 g, ca. 100%) which exhibited an infrared spectrum very similar to that of an analytical sample.

The analytical sample was obtained as a tacky, white solid, mp 119.5–121.0 °C, by two crystallizations from methanol–water followed by sublimation at 80 °C and <0.05 mm: ν_{max} 2930, 2870, and 1730 cm^{-1}; λ_{max} 290 nm (ϵ 16). The NMR spectrum of **7** exhibited unresolved multiplet absorption between δ 0.8 and 3.5.

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H. 9.15. Found: C, 81.83; H, 8.89.

Oxime of 6. A solution of **6** (1.74 g, 10.0 mmol, directly from chromatography) in ethanol (8.7 g of solution) was diluted with ethanol (10 ml) and water (10 ml) and to the mixture were added hydroxylamine hydrochloride (0.83 g, 12.0 mmol) and sodium acetate (1.6 g, 20 mmol). The reaction mixture was stirred at room temperature and was assayed by thin layer chromatography (silica/methylene chloride). After 18 h, when all starting material had been consumed, the reaction mixture was diluted to 200 ml with water and extracted, in succession, with 50, 25, and 25 ml of methylene chloride. The combined methylene chloride extracts were washed with two 250-ml portions of water, dried over sodium sulfate, and evaporated at the water pump to yield a white solid residue of oxime (1.72 g, 91%) which exhibited an IR spectrum identical with that of an analytical sample.

The analytical sample was obtained as white cubes, mp 159.9–161.1 °C, by two crystallizations from benzene–hexane: ν_{max} 3270, 3170, 3060, 2940, 1680, 1640, 1620, and 697 cm^{-1}; λ_{max} 225 nm (ϵ 2200). The NMR spectrum exhibited an exchangeable singlet at δ 9.2 ppm (0.8 H), an AB quartet centered at δ 5.58 (J = 5 Hz, 2.0 olefinic H), and unresolved peaks between δ 2.13 and 3.26 (12.2 H) due to the remaining protons.

Anal. Calcd for $C_{12}H_{15}NO$: C, 76.15; H, 7.99; N, 7.40. Found: C, 76.22; H, 8.15; N, 7.37.

Tosylhydrazone of 6. A mixture of **6** (6.84 g, 39 mmol, directly from chromatography) and tosylhydrazide (7.3 g, 39 mmol) in ethanol (70 ml) was stirred at room temperature for 25 h. The reaction mixture was heated to boiling, clarified with decolorizing carbon, filtered, and cooled to yield the tosylhydrazone (7.8 g, 58%) as a white solid, mp 171.8–174.0 °C, which possessed an IR spectrum identical with that of an analytical sample.

The analytical sample was obtained as white needles, mp 176.6–179.0 °C, by an additional crystallization from ethanol–water: ν_{max} 3240, 3090, 2970, 2930, 1660, 1610, 1350, and 1167 cm^{-1}; λ_{max} 274 nm (ϵ 930), 221 sh (12 400). The NMR spectrum exhibited an AB quartet centered at δ 7.84 (J = 8 Hz, aromatic) overlapping with a sharp singlet at δ 7.53 (NH, total 5.0 H), a pair of doublets (J = 6 Hz) at δ 5.34 (0.9 olefinic H) and 4.44 (0.9 olefinic H), and unresolved multiplet absorption between δ 1.9 and 3.2 (15.1 H).

Anal. Calcd for $C_{19}H_{22}N_2SO_2$: C, 66.64; H, 6.48; N, 8.18; S, 9.36. Found: C, 66.74; H, 6.44; N, 8.01; S, 9.56.

Conversion of the Tosylhydrazone to 3. *A mixture of the above* tosylhydrazone (6.84 g, 20 mmol), 2 N sodium hydroxide (10.0 ml), and ethanol (100 ml) was evaporated under reduced pressure. Ether (100 ml) was added to give, after filtration, 7.4 g (101%) of the sodium salt as a nonhygroscopic, white powder: ν_{max} 1230, 1140, 1125, and 817 cm^{-1}. The finely pulverized salt (1.57 g) was placed in a U tube which was directly connected to another U tube. The latter was immersed in a dry ice bath and a gentle stream of nitrogen was passed through the system while the sample was heated in an oil bath. At 140 °C the salt decomposed vigorously. The products in the dry ice trap were taken up in pentane and dried over sodium sulfate. The solvent was evaporated at room temperature under reduced pressure to yield **3** (0.18 g, 26%) as a waxy, white solid which was identical with authentic **3** by comparison of IR and NMR spectra.

Hexachloro-Birdcage Hydrocarbon 1b, 1,5,6,6,6a,7-Hexachlorodecahydro-1,5,2,4-ethanediylidenecyclopenta[*cd*]pentalene.[1a] A solution of Isodrin, 1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-*endo,endo*-1,4:5,8-dimethanonaphthalene (197 g, Shell Chemical Co., technical) and iodine (2.0 g) in carbon tetrachloride (600 ml) was placed in a tightly stoppered, 1-l., round-bottomed Pyrex flask which was put on the roof in a position where it was exposed to direct (January) sunlight for most of the day. Solid began to appear after a few hours, but the flask was maintained in position for 5 days when thin layer chromatography (alumina, pentane) indicated the total absence of isodrin. The contents of the flask then were transferred to an evaporating dish which was placed on the steam bath under a gentle stream of nitrogen. The contents were stirred occasionally until the solvent and the bulk of the iodine had evaporated. The residue, 196 g (99.5%) of hexachloro-birdcage hydrocarbon, was an off-white solid, mp 295–296 °C dec, which exhibited an IR spectrum identical with that of the analytical sample, mp 299–301.5 °C dec.

Birdcage Hydrocarbon 1. A 12-l. four-necked round-bottom flask was equipped with a Hershberg stirrer, an efficient condenser with a large-bottom bore, a nitrogen inlet tube, and a thermometer. The exit from the condenser was connected through a Drierite drying tube to a bubbler containing mineral oil. The system was flushed with nitrogen and 207 g of hexachloro-birdcage hydrocarbon was dissolved in 510 g of *tert*-butyl alcohol and 3 l. of dry THF. To the stirred solution was then added 32 g of lithium ribbon ($\frac{1}{4} \times \frac{1}{16} \times 2$ in.) in a countercurrent of nitrogen. Within 5 min an exothermic reaction set in with evolution of hydrogen. The reaction temperature was maintained at 69–71 °C (intermittent cooling is necessary) for approximately 20 min, when the initial vigorous reaction ceased. The cooling bath was removed and the mixture was allowed to cool to 50 °C. It required about 1 h. To the mixture was then added 63 g of lithium ribbon and the reaction was again similarly controlled. When the temperature dropped to 50 °C, the mixture was refluxed on a steam bath for 1 h, cooled to 50 °C, and poured into 15 kg of ice water through a large Büchner funnel to remove the unreacted lithium ribbons. If the reaction mixture was cooled below 45 °C, it turned to a gel. The aqueous mixture was extracted with three 2-l. portions of hexane. The dried ($MgSO_4$) hexane solution was evaporated and the residual solid was sublimed at water-pump pressure on a steam bath to yield 68.5 g (76.4%) of the birdcage hydrocarbon **1**, mp 159–164 °C, ca. 92% pure. Purification by GLC gave a pure sample: mp 167–168 °C (reported mp 165–167 °C[17]); NMR (220 MHz) δ 1.40 (d, J = 10 Hz, 2 H), 1.78 (d, J = 10 Hz, 2 H), 2.28 (s, 4 H), 2.41 (s, 2 H), 2.54 (s, 4 H).

Hexachloro-Half-Cage Ketone 13. A solution of boron trifluoride etherate (4 ml) in toluene (200 ml) was placed in a 2-l. Erlenmeyer flask which was fitted with a magnetic stirrer, a thermometer, and a dropping funnel. The solution was stirred vigorously, and to it was added, from the dropping funnel, a solution of endrin, 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-*endo,endo*-1,4:5,8-dimethanonaphthalene (Shell Chemical Co., technical, 800 g) in toluene (1500 ml), the rate of addition being adjusted so as to maintain the temperature of the reaction mixture at ca. 70 °C. At the end of the addition, two 1-ml aliquots of boron trifluoride etherate were added in succession. The first aliquot produced a significant temperature rise; the second, added after the temperature of the reaction mixture had cooled to ca. 55 °C, did not. The reaction mixture was allowed to cool to room temperature and was then filtered. The precipitate, after being washed with a little toluene and being sucked dry, amounted to 415 g (52%) of hexachloro-half-cage ketone, **13**, mp 289–291 °C (reported mp 285 °C dec).[1b]

Hexachloro-Birdcage Alcohol 14. A solution of 122.7 g of **11** in 700 ml of pyridine was refluxed for 24 h. Evaporation of the solvent followed by a recrystallization from carbon tetrachloride yielded a pyridine complex of **12**, mp 130–132 °C, resolidified at 170 °C and melted at 320 °C dec. The complex was dissolved in chloroform, washed with 2 N sulfuric acid several times, and dried ($MgSO_4$). Evaporation of the solvent gave 122.5 g of **14** as colorless crystals, mp 320 °C dec (reported mp 285 °C dec[1b]).

Birdcage Alcohol 2. Dechlorination of **14** was carried out in the manner described for the preparation of **1**, using 133 g of **14**, 520 g of *tert*-butyl alcohol, 3 l. of THF, and lithium ribbon (32 g, then 65 g). Crude products extracted with methylene chloride from two identical runs were combined and recrystallized from hexane to yield 87.7 g (72%) of **2** as colorless crystals, mp 181–192 °C, which were sublimed at water-pump pressure on a steam bath to give an analytical sample: mp 207–208 °C (reported mp 207–208 °C[1b]); NMR (220 MHz) δ 1.45 (d, J = 10 Hz, 1 H), 1.70 (s, 2 H), 1.77 (d, J = 10 Hz, 1 H), 2.12 (br s, 1 H), 2.4 (m, 5 H), 2.5 (m, 3 H), 3.90 (br s, 1 H, –OH).

Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.45; H, 8.05.

Methoxy-Birdcage Hydrocarbon 12a. To a solution of dimsyl sodium prepared from 3 g of 53.5% sodium hydride and 40 ml of Me_2SO was added a solution of 8.7 g of **2** in 40 ml of THF at 10 °C followed by 25 ml of methyl iodide at 20 °C. The mixture was stirred at 25 °C overnight, poured into 300 ml of ice–water, and extracted with ether twice. The combined extracts were washed with water, then saturated sodium chloride solution, dried ($MgSO_4$), and evaporated. The pale yellow, oily residue was distilled to give 9.13 g (97%) of a colorless oil, bp 86–91 °C (1.6 mm). The center cut, bp 86 °C (1.6 mm), $n^{24.5}{}_D$ 1.5252, was analyzed: NMR δ 3.20 (s, 3 H, OCH_3), 1.65 (AB, J = 10.2 Hz, 2 H), 1.63 (s, 2 H), 2.1–2.6 (m, 9 H).

Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.64; H, 8.80.

Cyanate 12d. To a solution of 17.4 g of **2** in 400 ml of THF was added 60 ml of 1.7 M *n*-butyllithium in hexane at 23 °C. Gaseous cyanogen chloride was introduced through a tubing extended below the surface of the suspension at 0–3 °C. When 14 g of the reagent was added the mixture became a clear solution which was stirred at room temperature overnight. The low boilers were evaporated and the oily residue was distilled to give 13.9 g (70%) of **12d** as a colorless oil, bp 110–127 °C (0.5 mm), which solidified at room temperature. Sublimation at 60 °C gave a crystalline solid, mp 71–73 °C (sinter at 68 °C): ν_{max} (neat) 2260, 2210, 1120 cm^{-1}. The analysis of this sample indicated contamination by **2**.

Anal. Calcd for $C_{13}H_{13}NO$: C, 78.36; H, 6.57; N, 7.03. Found: C, 78.57; H, 6.81; N, 6.11.

Distillation of **12d** at atmospheric pressure over a free flame with or without catalytic amounts of Lewis acids caused no reaction. Refluxing **12d** in toluene in the presence of boron trifluoride for 17 h followed by methanol treatment afforded a complex mixture; the desired methyl urethane could not be isolated.

***p*-Bromobenzenesulfonate 12b.** This ester was prepared from **2** and *p*-bromobenzenesulfonyl chloride in pyridine in 68% yield, mp 82–84 °C (from benzene).

Anal. Calcd for $C_{18}H_{17}SO_3Br$: C, 54.97; H, 4.63; Br, 20.30. Found: C, 54.73; H, 4.59; Br, 20.08.

***p*-Dimethylaminobenzenesulfonate 12c.** A mixture of 5.9 g of **12b** and 15 ml of dimethylamine was heated in a sealed tube at 200 °C for 24 h. The cold mixture was diluted with methylene chloride, washed successively with water and saturated sodium chloride, and dried. The solvent was evaporated and the solid residue was recrystallized from benzene–hexane to give 4.80 g (90%) of **12c** as colorless crystals, mp 116–119 °C. An analytical sample, mp 118.0–119.5 °C, was prepared by two recrystallizations from hexane: ν_{max} (Nujol) no peak above 3100, 1620 (aromatic), 1330, 1180 (sulfonate), 1350 cm^{-1} (tertiary aromatic amine).

Anal. Calcd for $C_{20}H_{23}NSO_3$: C, 67.19; H, 6.49; N, 3.92; S, 8.97. Found: C, 67.33; H, 6.58; N, 4.00; S, 9.08.

Iso-Half-Cage Ketone 8. A mixture of 10.5 g of half-cage ketone **11**[1d,18] in a potassium *tert*-butoxide solution prepared from 3.6 g of potassium and 210 ml of *tert*-butyl alcohol, was heated in a 1-l. stainless steel bomb under nitrogen at 250 °C for 4 h. The cooled mixture was poured into 250 ml of ice water and extracted with ether three times. The combined extracts were washed with water, dried ($MgSO_4$), and evaporated. The slightly colored waxy residue was a ca. 96:4 mixture of **8** and **11** by GLC. A recrystallization from hexane–pentane followed by sublimation afforded 9.2 g (88%) of **8** as a colorless wax, mp 215–224 °C. An analytical sample was obtained by another recrystallization from hexane followed by sublimation at 80 °C (0.05 mm): mp 232–234 °C; ν_{max} 1733 and 1742 cm^{-1}; NMR (220 MHz) δ 1.23 (d, J = 12.5 Hz, 1 H), 1.77–2.04 (m, 5 H), 2.34–2.57 (m, 6 H), 2.61–2.80 (m, 2 H).

Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.74; H, 8.11.

Endo-Half-Cage Alcohol 15a. A solution of 26 g of half-cage ketone **11** in 200 ml of ether was added to a stirred suspension of 2.5 g of lithium aluminum hydride in 500 ml of ether over a 30-min period. The resulting mixture was refluxed for 1 h, cooled, and treated successively with 25 ml of water and 150 ml of 2 N sulfuric acid. The ether layer was separated, washed once with saturated sodium chloride solution, and dried ($MgSO_4$). The solvent was evaporated and the slightly colored waxy residue was sublimed at 0.15 mm on a steam bath to yield 25.2 g of crude **15a** as a colorless wax, mp 173–192 °C, which was recrystallized from hexane and resublimed. This material, mp 182–192 °C, may possibly be contaminated with its epimeric alcohol (mp 130–131 °C), and was recrystallized three times from hexane and resublimed to give an analytical sample: mp 192–194 °C; ν_{max} (CCl_4) 3636, 3343, 3083 cm^{-1} (sterically opposing C–H_{endo} stretch[1d]); NMR (220 MHz) δ 0.93 (dd, J = 12.3, 7.6 Hz), 1.36 and 1.39 (d and s, 3 H), 1.42 (d, J = 10 Hz), 2.23 (s, 1 H), 2.11 (s, 1 H), 2.13–2.41 (m, 7 H, including OH), 3.54 (dt, J = 12.3, 2.6 Hz, 1 H), 4.02 (d, J = 5 Hz, 1 H, >CHO).

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.81; H, 8.97.

Oxidation of a **15a** sample, mp 174–182 °C, with chromium trioxide in pyridine afforded **11** in quantitative yield.

Reactions of Half-Cage Ketone 11 with Butyllithium. To a solution of 1.74 g of **11** in 40 ml of THF was added 6.0 ml of 1.7 M *n*-butyllithium in hexane. After the pale yellow solution was refluxed under nitrogen for 24 h, 5 ml of methanol was added and the solvents were evaporated. The residue was taken up in water and extracted with ether three times. The combined ether extracts were washed with saturated sodium chloride solution and dried ($MgSO_4$). The solvent was evaporated to give 2.28 g of slightly colored crystals which consisted of ca. 94% **15b** and 6% **11** by GLC. Three recrystallizations from hexane followed by sublimation gave an analytical sample: mp 108–109.5 °C; ν_{max} (CCl_4) 3610 (O–H), 3086 cm^{-1} (C–H).

Anal. Calcd for $C_{16}H_{24}O$: C, 82.70; H, 10.41. Found: C, 82.95; H, 10.40.

A similar reaction of **11** with *tert*-butyllithium gave **15c** as colorless crystals: mp 84–86 °C; ν_{max} (CCl_4) 3600 (O–H), 3080 cm^{-1} (C–H).

Anal. Calcd for $C_{16}H_{24}O$: C, 82.70; H, 10.41. Found: C, 82.93; H, 10.45.

The *tert*-butyl derivative **15c** decomposed on Woelm neutral alumina (activity grade 1) and on GLC columns above 190 °C to a complex mixture of alcohols and hydrocarbons.

Iso-Half-Cage Ketoxime 8. A mixture of 34.8 g of **8**, 27.8 g of hydroxylamine hydrochloride, 25 ml of 30% sodium hydroxide solution, 45 ml of water, and 125 ml of ethanol was refluxed for 46 h, poured into 500 ml of water, and extracted three times with ether. The combined ether extracts were dried and evaporated. The colorless, crystalline residue was recrystallized from hexane to yield 34.2 g of **8**, mp 132–136 °C. An analytical sample, mp 134.5–136.0 °C, was obtained by another recrystallization from hexane followed by sublimation.

Anal. Calcd for $C_{12}H_{15}NO$: C, 76.15; H, 7.99; N, 7.40. Found: C, 76.55; H, 8.41; N, 7.33.

Registry No.—**1**, 704-02-9; **1b**, 3212-28-0; **2**, 707-05-1; **3**, 60606-96-4; **5**, 60606-97-5; **6**, 60606-98-6; **6** oxime, 60606-99-7; **6** tosylhydrazone, 60607-00-3; **6** Na salt, 60607-01-4; **7**, 60607-02-5; **8**, 707-83-5; **8** oxime, 1603-18-5; **11**, 7509-41-3; **12a**, 60607-03-6; **12b**, 741-42-4; **12c**, 60607-04-7; **12d**, 60607-05-8; **15a**, 7261-85-0; **15b**, 60607-06-9; **15c**, 60607-07-0; isodrin, 465-73-6; endrin, 72-20-8.

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(18) *We obtained half-cage ketone* **11** *as a by-product in the triquinacene synthesis:*[2] ^{1}H NMR (220 MHz) δ 1.32 (ddm, J = 13, 8 Hz, 1 H), 1.44 (dm, J = 10 Hz, 1 H), 1.56 (dm, J = 11 Hz, 1 H), 1.72–1.89 (m, 3 H), 2.24 (br s, 1 H), 2.30 (br s, 1 H), 2.35–2.65 (m, 6 H).

1-Cycloheptatrienylidene-4-cyclopentadienylidene-2,5-cyclohexadiene System[1,2]

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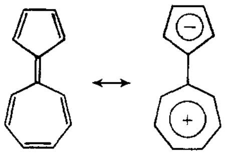
A synthesis of the parent hydrocarbon, 1-cycloheptatrienylidene-4-cyclopentadienylidene-2,5-cyclohexadiene (**4**), was attempted. The approach was based on the dehydrogenation of the dihydro derivative **11.** Hydride abstraction of **11** did not lead to the desired tropylium salt **13.** A synthetic approach to the tetraphenyl derivative **17** involved the tropylium salt **16.** Deprotonation of **16** produced an apparent oligomer of **17.** A stable organoiron derivative **7** of **4** was prepared by a three-step synthesis starting with *p*-ferrocenylphenylmagnesium bromide (**19**).

Sesquifulvalene (**1**) is a cross-conjugated two-ring hydrocarbon of considerable theoretical interest[3] which is expected to have a certain amount of contribution to its structure from the dipolar resonance form. The parent hydrocarbon **1**[4] is unstable and could not be isolated as a solid at low temperature.[5] The tetraphenyl derivative **2** possesses the expected thermal stability.[6] The hydrocarbon **1** can also be stabilized as a ligand in transition metal complexes. This was demonstrated by the synthesis of ferrocenyltropylium fluoroborate (**3**).[7]



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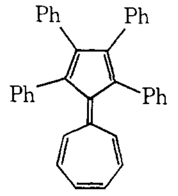

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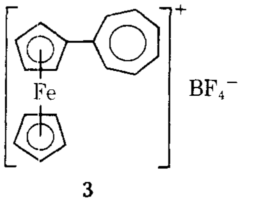

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The system **4** is a cross-conjugated three-ring hydrocarbon having an inserted *p*-phenylene ring between the two aromatic rings of sesquifulvalene in the dipolar structure. It was of interest to study the synthesis of this long conjugated system about which very little is known. The parent hydrocarbon **4** has not yet been synthesized. Only three derivatives, **5**,[8] **6**,[9] and **7**,[2] with strong electron-withdrawing substituents or metal coordination have recently been reported. The present paper describes the preparation of the dihydro derivative **11,** which was a key intermediate in the attempted synthesis of the parent hydrocarbon **4,** and the isolation of an oligomer of tetraphenyl derivative **17.** Also included is a detailed report of the synthesis of π-cyclopentadienyliron derivative **7.**