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$C_{11}H_{12}$ HYDROCARBONS—I

REACTION OF CYCLOOCTATETRAENE DIANION WITH SUBSTITUTED 1,3-DICHLOROPROPANES. PREPARATION OF TRICYCLO[5.4.0.$0^{2,6}$]UNDECA-3,8,10-TRIENE*

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Abstract—Cyclooctatetraene dianion was condensed with 1,3-dichloro-2-tetrahydropyranyloxypropane to afford tricyclic ether **8a**, which was converted in three steps to the $C_{11}H_{12}$ hydrocarbon **4a**. The latter fragments readily to benzene and cyclopentadiene upon thermolysis and upon direct or sensitized photolysis. The dianion reacted with 1,2,3-trichloropropane in a surprising way to afford the cyclobutane derivative **13**.

INTRODUCTION

Interest continues to be centered around the preparation and study of $(CH)_n$[1–3] isomers experimentally or theoretically interrelated by valence bond transformations. Of especial interest are the observations that physical and chemical properties which characterize $(CH)_n$ hydrocarbons do not necessarily vanish completely by interpolating a methylene group into $(CH)_n$, as in $(CH)_nCH_2$.[4–6] Thus, the homotropylium ion, $(CH)_7CH_2^+$, appears to be aromatic as does the tropylium ion, $(CH)_7^+$,[7] and both homocyclooctatetraene, $(CH)_8CH_2$, and cyclooctatetraene, C_8H_8, are reducible to dianions, which also appear aromatic.[8] In purely sigma-bonded compounds, as in homocubane,[9a] the relationship, if any, between $(CH)_n$ and $(CH)_nCH_2$ is not clear.

The transformations between the various $(CH)_nCH_2$ and the various $(CH)_n$ isomers are of theoretical interest with regard to the tenets of orbital symmetry factors expounded upon by Woodward and Hoffmann and others.[10] A large number of $(CH)_{10}$ hydrocarbons, species particularly well studied by an international group of workers, have been characterized.[2] In this regard, we wish to describe the results of a study directed towards preparing and examining the behavior of $C_{11}H_{12}$ hydrocarbons,[11] formally derived by inserting "CH_2" into $C_{10}H_{10}$. At least one other goal of this work is the synthesis of the parent monocycle, cycloundeca-1,3,5,7,9-pentaene.

Cyclooctatetraene (1),† cycloheptatriene (2), and *cis*-bicyclo[6.1.0]nona-2,4,6-triene (3)[12] were considered as possible starting materials for synthesizing various

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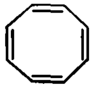
$C_{11}H_{12}$ hydrocarbons. These candidates were considered because they already contain a higher degree of unsaturation ultimately necessary for synthesizing the $C_{11}H_{12}$ formula, thus minimizing double-bond introduction steps. The ready availability of the polyenes **1**, **2**, and **3** was also an important consideration. In an earlier attempt, we found that a two-carbon fragment could readily be added to **3** by thermal cycloaddition,[13] but the derived adducts have thus far not been successfully converted into a $C_{11}H_{12}$ hydrocarbon. In this report, we describe a synthesis of a $C_{11}H_{12}$ hydrocarbon, tricyclo[5.4.0.0^{2,6}]undeca-3,8,10-triene (**4**), resulting from a study of the reactions of the dianion of **1**, namely **5**,[8b] with substituted 1,3-dichloropropanes. We also describe a brief inquiry into the behavior of **4**.



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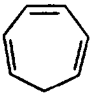

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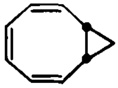

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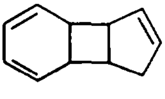

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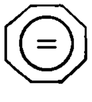

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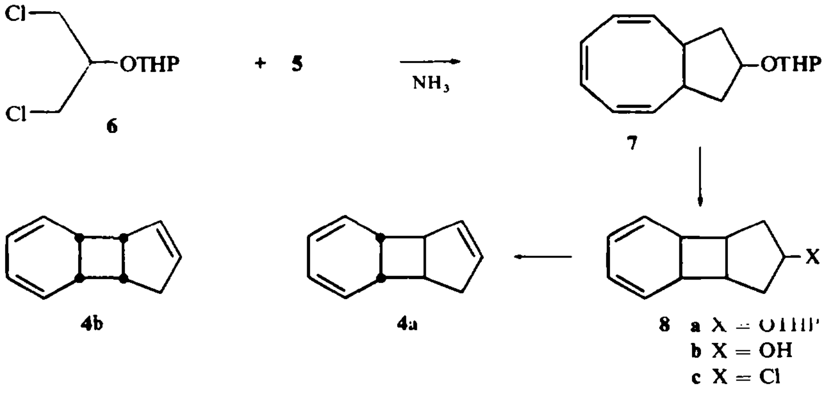
RESULTS

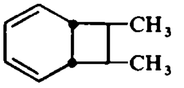
The addition of an ether solution of 1,3-dichloro-2-tetrahydropyranyloxypropane (**6**) to the dilithium salt of (**5**)‡,[12b] in ammonia afforded, after work-up and distillation, a 65% yield of the tricyclic ether **8a**. An intermediate precedes the formation of **8a** since examination of the NMR spectrum of the crude material from the reaction



‡ We thank Professor Stuart Staley, the University of Maryland, for experimental details.

between **5** and **6** shows the presence of another olefinic substance, presumably **7**, with resonances centered at τ 4·3. When the same NMR sample was heated (~30 min at 75°), the spectrum of the intermediate was replaced by that of **8a** (olefinic resonances centered at τ 4·5). The crude ether **8a** was converted by acid treatment to alcohol **8b**, which upon attempted dehydration with phosphorous oxychloride-pyridine, afforded instead the chloride **8c** in 55% yield.[14] When the intermediates were used without purification, the overall yield of **8c** was 50% (based on **1**). Reaction of **8c** with potassium t-butoxide in dimethyl sulfoxide-ether gave the desired $C_{11}H_{12}$ hydrocarbon **4** in 76% yield.

Both **8c** and **4**, like other *cis*-bicyclo[4.2.0]octa-2,4-dienes,[15] possess UV maxima at ~275 nm (Table I). The NMR spectrum of chloride **8c** (crude or purified), which appears to be a single substance, reveals that the molecule possesses a plane of symmetry. Absorptions appear at τ 4·42 (olefinic), 5·65 (CHCl), 6·94 (allylic cyclobutane protons), 7·24 (non-allylic cyclobutane protons), and 7·83 (CH_2) with relative areas 4:1:2:2;4. The corresponding olefinic and cyclobutane protons reported for *cis*-7,8-dimethylbicyclo[4.2.0]octadiene (**9**) absorb at τ 4·28, 7·25, and 7·44 in a 4:2:2 ratio respectively, while the NMR spectrum of the *trans*-isomer **10** reveals an unsymmetrical



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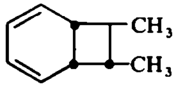

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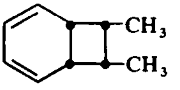
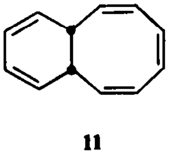


9′

set of ring proton resonances at τ 4·0–4·7 (4H), 6·8–7·2 (1H), and 7·4–7·9 (3H). It should be noted too that the NMR absorption due to the olefinic protons of **8c**, like that of **9** and unlike that of **10**, appears as a broad singlet. Thus, the cyclobutane H atoms of chloride **8c** are *cis*-orientated as in **9** (*cis,anti,cis*) or **9′** (*cis,syn,cis*). Röttele, *et al.*[3a] have firmly established that the *cis*-fused derivative **11** rearranges exclusively to **11′** possessing the indicated *cis,anti,cis* stereochemistry and Huisgen, *et al.* have also



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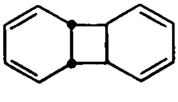

11′

indicated that *cis*-7,8-dimethylcycloocta-1,3,5-triene rearranges to **9** (and not **9′**)[15c] and *cis*-7,8-dichlorocycloocta-1,3,5-triene rearranges in a similar way to the corresponding *cis,anti,cis* compound.[16] It is therefore likely that **8** and **4** possess the *cis,anti,cis* stereochemistry as depicted in structure **4a**.* The development of the *cis* geometry between the 5 and 6-membered rings appears to be governed during the alkylation step **6** + **5** → **7** and the remaining stereochemical feature, presumably of steric origin, governed during the electrocyclization **7** → **8a**.

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* A referee has suggested that we make note of the fact that *cis*-bicyclo[3.2.0]heptyl system is thermodynamically more stable than its *trans*-isomer. [c.f. N. L. Allinger, M. Nakazaki, and V. Zalkow, *J. Amer. Chem. Soc.*, **81**, 4074 (1959) and J. Meinwald, P. Anderson, and J. J. Tufariello, *ibid.*, **88**, 1301 (1966)].

The NMR spectrum of hydrocarbon **4a** (Fig 1) reveals two complex patterns of equal area attributable to the olefinic and aliphatic protons. Heating a sample of **4a** in a sealed ampoule for 1·5 h at 127° leads predominantly to a mixture of benzene (65%), dicyclopentadiene (29%) and cyclopentadiene (6%). A similarly prepared sample, after being heated for 18 h at 70°, showed that about 85% of **4a** remained. In preliminary photochemical studies, sensitized (benzil, pyrex vessel, 3000 Å lamps using a Srinivasan-Rayonet-Griffin Photochemical Reactor) irradiation of **4a** for ~16 h in cyclohexane at 10° afforded a clean mixture of benzene, cyclopentadiene, and **4a** (~50% completion). Similar results were obtained using acetophenone as sensitizer. Direct irradiation of **4a** (to ~25% completion) through quartz with a medium pressure mercury arc (pentane, <0°) also produced benzene and cyclopentadiene.

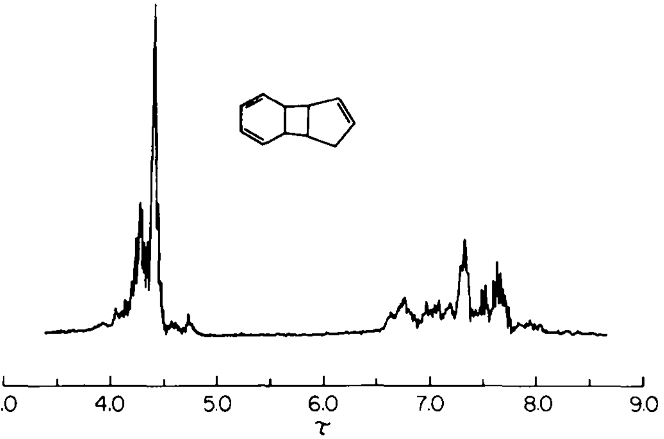
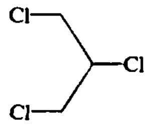


Fig 1. NMR spectrum of **4a** (60 MHz, neat sample)

It seemed reasonable that a synthesis of **8c** could be achieved more simply by reacting **5** with the commercially available 1,2,3-trichloropropane **12**. Reaction of **12** with **5**, in a way similar to the reaction between **6** and **5**, did not afford **8c**, the derivative corresponding to **7**, or **14**, but produced instead the isomeric chloride **13**. The presence of the chloromethylene grouping in **13** was signaled in its NMR spectrum by the appearance of a two proton doublet ($J \sim 6$ Hz) centered at τ 6·49. The chemical shift



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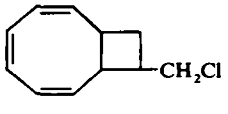

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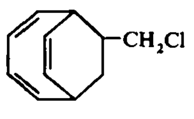

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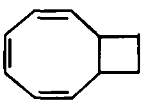

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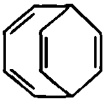
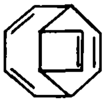
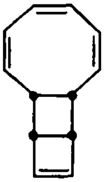
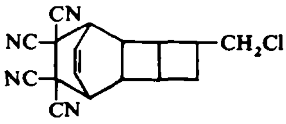
TABLE I. UV SPECTRA

	λ_{max}, nm	ε	Solvent	Ref.
8c	272	3260	hexane	this work
4	275	3100	hexane	this work
cis-Bicyclo[4.2.0]octa-2,4-diene	274	3340	cyclohexane	15*a*
10	278	—	—	15*b*
	274	2500	—	15*c*
9	275	—	—	15*b*

of the chloromethylene protons of n-butyl chloride is τ 6·54. The UV spectrum of **13** consists of a single maximum like that of **15**,[12b] and seemingly unlike that expected for **14** (Table 2). Known derivatives of **14** show a more complex array of absorptions as indicated in Table II. Tetracyanoethylene (TCNE) reacted with **13** to afford what is presumed to be adduct **16** (unknown stereochemistry), formally derived from TCNE and **17**. The formation of **16** is signaled in its NMR spectrum by the presence of only two olefinic protons appearing as a double-doublet characteristic of other TCNE adducts of cyclohexadiene derivative.[18] Diels-Alder reactions of cyclooctatrienes, presumably via their bicyclo[4.2.0]octadiene valence isomers, are well known[13, 15, 19] to give products of this type.

TABLE II. UV SPECTRA

	λ_{max}, nm	ε	Solvent	Ref.
13	253	1990	hexane	this work
15	250	2090	hexane	12*b*
	280, 268, 258	2900, 4200, 4200	ethanol	2*a*
	280, 268·5, 258·5	2700, 5000, 4600	hexane	17
	258	1300	hexane	17



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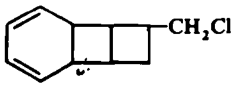
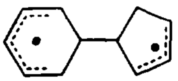


17

In studies directed towards obtaining further sturctural information, dehydrohalogenation of **13** with potassium t-butoxide produced a yellow oil consisting of a mixture of hydrocarbons (apparently one major component by VPC), which analyzed correctly for the $C_{11}H_{12}$ formula. The oil revealed the presence of an equal number of olefinic and aliphatic protons in its NMR spectrum and a weak band at 1563 cm^{-1} characteristic of cyclobutenes in its IR spectrum.[20a] Because of purification problems, however, no further investigations of the yellow oil have been carried out.

DISCUSSION

The ready thermal and photochemical fragmentation of **4a** to benzene and cyclopentadiene is precedented by the even more ready conversion of **11′** to two molecules of benzene.[3a] The two thermal conversions are of some theoretical interest because these processes breach orbital symmetry requirements,[10] the consequence of which leads to our hypothesizing the biradical **18** as a plausible intermediate in the thermal retrogression of **4a**. We have attempted to observe nuclear polarized products by thermolyzing **4a**, but no polarization of resonances was observed in the NMR spectrum.[21] In a recent pertinent study,[11b] the hydrocarbon **19** was observed to fragment both thermally (half-life of 2–3 days at 33°) and photochemically to cyclopentadiene and 1,4-dimethyl-2,3-diphenylbenzene (**20**). The direct photofragmentation of **19** was also suggested to proceed through a biradical intermediate for reasons similar to our proposing **18** as an intermediate. The earlier workers rejected the theoretically allowed pathway, **19** → **21** by a 1,3-sigmatropic shift[22] then **21** → fragments by a reverse 2 + 2 cycloaddition, on the basis that no intermediate, **21**, was observed by NMR during photo-fragmentation of **19**. Clearly, there is no basis for rejecting this last mechanistic pathway since the seemingly related substance **4a** degrades readily. While **4a** and **11′** fragment readily, it is noteworthy that *cis*-bicyclo[4.2.0]octa-2,4-diene appears also to fragment in part to ethylene and benzene, but at considerably higher temperatures.[23]



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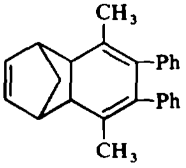

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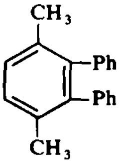

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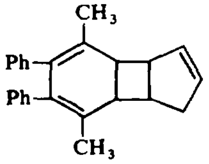
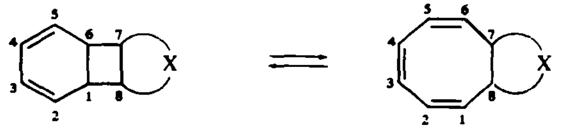


21

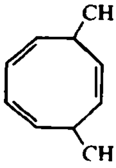
Besides undergoing fragmentation, bicyclooctadienes **22** also show a marked tendency to be in equilibrium with their valence tautomers **23** and the magnitude of the equilibrium constant is known to be a sensitive function of substitution at C_7 and C_8.[19] It is interesting to summarize the effect of ring fusion at these positions.



22 **23**

When X consists of one-carbon atom (**3**) or two carbon atoms (**13**, **15**), the equilibrium lies exclusively to the right (**23**), but when X contains three (**4a**, **8**) or four carbon atoms (**11**),[*] the equilibrium lies to the left (**22**). These observations are simply, but not necessarily, explained by ring strain factors.

The possibility of thermally isomerizing **8c** first then dehydrohalogenating second to afford isomeric $C_{11}H_{12}$ hydrocarbons has been considered. The derivative **8**, which lacks the five membered ring double bond, was expected to show a lesser tendency to fragment since an intermediate like **18** should be less stable. We have observed in a preliminary way that **8c** does indeed isomerize at 180° (10 minutes) without fragmentation. This promising avenue is being further explored as another approach to $C_{11}H_{12}$ hydrocarbons.



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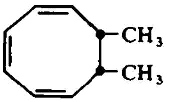

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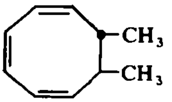

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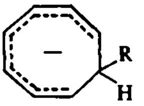

27a: R = CH_3
b: R = $CH_2CHClCH_2Cl$
c: R = $CH(CH_2Cl)_2$
d: R = CH_2CH_2Br

Conrow and Bak[24] have reported that methyl iodide reacts with **5** to produce among other by-products, the 8-membered trienes **24**, **25**, and **26**. The intermediate is presumably **27a** which reacts with a second methyl iodide in at least three ways to give the observed products. There appears no obvious reason, at least by inspection of molecular models, why in our case a similar intermediate **27b**, in the reaction between **5** and **12**, prefers to give **13** rather than **14** or the chloro analog of **7**. The interesting possibility is that the reaction between **5** and **12** might actually involve an electron transfer pathway. Such a scheme could lead to the production of cyclooctatetraene radical-anion and **28**, which could couple to give **27c** (leading to **13**). We hope to test the latter mechanistic possibility. However, we note too that Staley has observed

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[*] The NMR spectrum of **13** remains virtually unchanged to ~150° and that of **4a** to ~100° (for brief periods).

$$\mathrm{ClCH_2—\dot{C}H—CH_2Cl}$$

28

that ethylene bromide reacts with **5** to give **15** in good yield.[12b] The intermediate is presumably **27d** and it is not unreasonable that four membered ring closure is simply faster in the case of **27b**.*

EXPERIMENTAL

General. IR spectra were determined with a Perkin–Elmer 621 Grating Spectrophotometer and UV spectra with a Cary Model 14 Spectrophotometer. NMR spectra were recorded with a Varian 60 MHz spectrometer (A-60, A-60D, or T-60) and unless otherwise indicated, the spectra produced integrals appropriate for the structural assignments. Mass Spectra were taken on a Hitachi–Perkin Elmer Model RMU-60 spectrometer and VPC was carried out on a Varian-Aerograph A90-P apparatus. M.ps and b.ps are uncorrected.

Preparation of 1,3-dichloro-2-tetrahydropyranyloxypropane (**6**). Two drops of conc HCl were added to a soln of commercial 1,3-dichloro-2-propanol (54 g, 0·42 mole) in dihydropyran (100 ml). The initially exothermic mixture was allowed to stand at ambient temp for 20 hr. Solid anhyd K_2CO_3 was added and the mixture was filtered. Concentration of the mixture under vacuum afforded a residual liquid which was distilled giving 86·9 g (97% yield) of ether **6** as a water clear liquid: b.p. 80·0–80·5° (0·2 mm); NMR (CCl_4) τ 5·1–5·3 (broad peak, 1H), 5·9–6·8 (complex m, 7H), and 8·1–8·8 (broad peak, 6H); partial mass spectrum (80 eV) *m/e* (rel intensity, based on ^{35}Cl) 215 (0·4), 214 (0·4), 213 (2·2), 212 (0·8), 211 (3.5), 79 (100). Even after careful re-distillation of this material (b.p. 56°/0·09 mm), a satisfactory microanalysis of **6** was not obtained. The spectral properties and chemical transformation of **6**, however, are in accord with the assigned structure.

Preparation of tricyclo[5.4.0.0^{2,6}]*undeca-8,10-dien-4-ol* (**8b**). A soln of Li (4·58 g, 0·66 g-atoms) in liquid ammonia (~750 ml) at −33° was prepared in a two liter 3-necked round bottom flask equipped with a stirrer, a dry ice condenser protected with a drying tube (KOH), and a pressure equilibrated dropping funnel. Cyclooctatetraene (33·5 g, 0·322 mole) was added as rapidly as possible to the Li soln, then the mixture stirred until the initial deep blue soln was replaced by a light brown to orange suspension of dilithium cyclooctatetraenide. The dichloro compound **6** (70·4 g, 0·311 mole) diluted to 125 ml with ether was added to the stirred dianion suspension over 30 min. After a 4 hr reaction period, the ammonia was allowed to evaporate then sat NH_4Cl aq (200 ml) was added to the residue. The aqueous mixture was extracted with ether (3 × 100 ml) and the combined ether extracts were washed with water (3 × 100 ml), dried over $MgSO_4$, filtered, and concentrated under vacuum. The crude residue (76·9 g, 91%) was distilled (b.p. 122–125°/0·18 mm) to afford 49·2 g (64%) of **8a** as a waxy solid.† The NMR spectrum (CCl_4) revealed a multiplet at τ 4·1–4·8 (olefinic, sharp band centered at τ 4·5) and a complex array of multiplets at τ 5·1–5·8, 5·9–6·9, 6·9–7·7, and 7·7–8·9 (aliphatic) with olefinic/aliphatic integration ratio of 3·9 to 18·4 (calculated for **8a**: 4·0 to 18·0).

In another experiment, when the crude product was isolated at below room temp, the NMR spectrum of the crude material revealed the presence of an intermediate, presumably **7**, possessing olefinic absorption centered at τ 4·3. The spectrum of the intermediate is replaced by that of **8a** on heating (30 min at 75°).

The crude **8a** (50·3 g, 0·192 mole) in MeOH (500 ml) containing 6 drops of conc HCl was refluxed for 1 hr. The cooled mixture was poured into 1000 ml water containing 100 ml sat $NaHCO_3$ aq. The aqueous soln, after saturation with ether, was extracted with ether (3 × 200 ml), dried ($MgSO_4$), filtered, then concentrated under vacuum. The crystalline residue was evacuated (~1 mm) at 30–35° for several hr. The alcohol was obtained in near quantitative yield (31·1 g) based on starting ether.

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* After this manuscript was submitted, the following relevant papers have appeared: T. Mukai, Y. Akasaki, and T. Hagiwara, *J. Am. Chem. Soc.* **94**, 677 (1972); M. J. Goldstein, R. C. Krauss, and S.-H. Dai, *Ibid.* **94**, 680 (1972); F. A. Cotton and G. Deganello, *Ibid.* **94**, 2142 (1972). We thank Professor Mukai for informing us of other studies not yet published.

† Repeated recrystallization and sublimation of this material afforded waxy needles (m.p. 54·5–56·0°) with considerable loss. No further attempts were made to purify this material. The crude, undistilled material was hydrolyzed to **8b** without purification.

The crude alcohol was recrystallized from pentane at −78° to afford 15·9 g (51%) of **8b**: m.p. 73–79°; NMR (CCl_4) τ 4·1–4·9 (m with sharp signal at τ 4·48, 4H, olefinic), 5·2–5·7 (apparent quintet with further splitting, 1H, $J \sim 7$ Hz, $\gt$CH—O—), 6·24 (broad peak, 1H, OH), 7·0–7·6 (m, 4H, cyclobutane), and 7·9–8·8 (m, 4H, CH_2); partial mass spectrum (80 eV) *m/e* (rel intensity) 162 (10), 84 (58), and 78 (100). The sample submitted for analysis was obtained pure by sublimation (70°/1 mm) as colorless needles, m.p. 80·5–83·5°. In view of the broad melting range of this substance, it may consist of a mixture of isomers. (Found: C, 81·39; H, 8·77. Calcd. for $C_{11}H_{14}O$: C, 81·44; H, 8·70%).

Preparation of 4-*chlorotricyclo*[5.4.0.0^{2,6}]*undeca*-8,10-*diene* (**8c**). $POCl_3$ (6·00 ml, ~10·1 g, 0·066 mole) was added dropwise during several min to a stirred, ice-cooled soln of crude **8b** (6.3 g, 0·039 mole) in pyridine (50 ml). An intermediate white ppt formed during the addition. The mixture was allowed to stand at ambient temps for 12 hr, then was heated on a steam bath for 1 hr. Crushed ice was added to the ice-cooled mixture, which was transferred to a separatory funnel and extracted with ether (3 × 100 ml). The combined organic extracts were washed successively with 5% HCl (2 × 100 ml), sat $NaHCO_3$ aq (1 × 100 ml), and water (2 × 100 ml), then dried ($MgSO_4$). After removal of the drying agent by filtration, the soln, upon concentrating under vacuum, left a residue which crystallized (3·85 g, ~55% yield). The crude material possessed spectral properties identical to that of the purified material and was used without further purification. The overall yield of **8c** is 50% (based on cyclooctatetraene) when only crude materials were carried through in each of the preceeding steps. Crude **8c** possessed a NMR spectrum identical to that of the purified material. The crude chloride was recrystallized from pentane, then sublimed (60°/0·1 mm) to afford colorless crystals of **8c**: m.p. 53·5–55·0°; NMR (CCl_4) τ 4·42 (broad singlet, 4H, olefinic), 5·65 (apparent quintet, 1H, $J \sim 4·5$ Hz, −CHCl), 6·8–7·2 (two broad peaks of equal intensity centered at τ 6·94 and 7·24, 4H, cyclobutane), and 7·7–7·9 (m centered at τ 7·83, 4H, CH_2); UV (hexane) λ_{max} 272 nm (ε 3260); partial mass spectrum (80 eV) *m/e* (rel intensity, based on ^{35}Cl) 182 (1·2), 181 (0·6), 180 (3.4), 149 (10), 91 (7·1), 79 (9·1), 78 (100), 77 (5.6), 67 (14), 66 (8·7). (Found: C, 73·35; H, 7·47. Calcd. for $C_{11}H_{13}Cl$: C, 73·10; H, 7·25%).

Preparation of tricyclo[5.4.0.0^{2,6}]*undeca*-3,8,10-*triene* (**4a**). A soln of the crude chloride **8c** (7·2 g, 0·04 mole) in an ether-dimethylsulfoxide mixture (25 ml each) was prepared in a 100 ml round bottom flask equipped with a magnetic stirring bar, a solid addition funnel, and a drying tube. Solid solvent-free t-BuOK (10 g) was added to the cooled (ice bath), stirred soln over a 4 min period. The initial mixture solidifies somewhat on cooling, but becomes homogeneous by the end of the addition of base. The ice bath was removed, then the stirring was continued for 6 additional min at ambient temp. The dark brown mixture was quenched with 50 cc water containing *ca* 50 cc cracked ice. The aqueous suspension was extracted with pentane (5 × 25 ml), then the combined pentane extracts were washed with water (4 × 50 ml). The inorganic phase was dried ($MgSO_4$), filtered, then concentrated under vacuum to afford a residual oil. Vacuum distillation afforded 4·53 g (76%) of **4a** as a yellow oil: b.p. 30–34° (0·25 mm); NMR (CCl_4, see figure I) τ 3·9–4·8 (complex m, 6H, olefinic) and 6·5–8·1 (complex m, 6H, aliphatic); partial mass spectrum (80 eV) *m/e* (rel intensity) 144 (3·6), 143 (2·0), 142 (0·7), 141 (2·0), 129 (7·2), 128 (5·8), 119 (7·1), 117 (7·0), 104 (8·7), 91 (7·5), 79 (9·2), 78 (100), 77 (22), 67 (7·5), 66 (96), and 65 (22); UV (hexane) λ_{max} 275 nm (ε ~ 3100). The sample submitted for analysis was purified by redistillation (b.p. 58–60°/2·4 mm). (Found: C, 91·67; H, 8·35. Calcd. for $C_{11}H_{12}$: C, 91·61; H, 8·39%).

Preparation of 9-*chloromethylbicyclo*[6.2.0]*deca*-2,4,6-*triene* (**13**). Dilithium cyclooctatetraenide was prepared from Li (1·7 g, 0·25 g-atoms) and cyclooctatetraene (13·0 g, 0·125 mole) in liquid ammonia (250 ml) by the procedure described. The trichloride **12** (19·7 g, 0·134 mole) diluted to 25 ml with ether was added dropwise to the stirred dianion suspension (−33°) as rapidly as possible (exothermic). After stirring the mixture for 2 hr, the ammonia was allowed to evaporate (steam bath). Sat NH_4Cl aq (100 ml) was added. The residue was extracted with ether (3 × 100 ml), then the combined ether extracts were washed successively with water (2 × 100 ml) and saturated brine (100 ml). The organic phase was dried ($MgSO_4$), filtered, and concentrated under vacuum. The residue was distilled to afford 12·2 g (54%) of **13**: b.p. 67–68° (0·37 mm); NMR (CCl_4) τ 3·9–4·6 (m, 6H, olefinic), 6·49 (d, 2H, $J \sim 6$ Hz, $-CH_2Cl$), and 6·6–8·3 (complex m, 5H, cyclobutane); UV (hexane) λ_{max} 253 nm (ε 1990). The material, after redistillation, b.p. 57–58° (0·13 mm), afforded the analytical sample as a colorless oil. (Found: C, 73·26; H, 7·39. Calcd. for $C_{11}H_{13}Cl$: C, 73·10; H, 7·25%).

The tetracyanoethyl (*TCNE*) *adduct of* **13**. A mixture of **13** (1·1157 g, 6·20 mmole) and TCNE (1·0133 g, 7·91 mmole) in toluene (10 ml) was refluxed for 18 hr. The residue, after removing the solvent under vacuum, was dissolved in hot benzene (30–35 ml) and filtered. After slowly adding an equal volume of hexane, the cooled mixture was filtered to afford 1·44 g (75·5%) **16** as colorless platelets: m.p. 180–196°; NMR ($CDCl_3$)

τ 3·40 (apparent dd, 2H, $J \sim 3{\cdot}5$ Hz, olefinic) 6·2–6·7 (m with doublet centered at τ 6·59, 4H, $J \sim 7$ Hz, d assigned to —CH_2Cl), and 6·9–8·1 (m, 7H); NMR (acetone-d_6) τ 3·28 (apparent dd, 2H, $J \sim 3{\cdot}5$ Hz, olefinic), 5·9–6·4 (broad m, 2H), 6·48 (d, $J \sim 7$ Hz, —CH_2Cl), and 6·9–8·0 (m, 7H). An additional ~0·5 g (total yield, ~100%) of TCNE adduct **16** was obtained from the mother liquors. The NMR spectra of the crude residue, the first and second crops from the recrystallization, and the sample submitted for microanalysis were nearly identical. Some differences in the shapes of some of the peaks in the NMR spectra of the various samples were noted. M.ps of the samples were broad, suggesting the presence of isomers. A sample was purified (recrystallized from benzene–pentane), then submitted for microanalysis (m.p. 184–192°). (Found: C, 66·15; H, 4·09; Cl, 11·51; N, 18·18. Calcd. for $C_{17}H_{13}ClN_4$: C, 66·13; H, 4·24; Cl, 11·48; N, 18·15%).

Dehydrohalogenation of **13**. A soln of **13** (1·5186 g, 8·39 mmoles) in an ether-dimethylsulfoxide mixture (8 ml of each) was prepared in a 3-necked flask equipped with a magnetic stirrer, solid addition funnel, and N_2 inlet. Solvent-free t-BuOK (~2 g)[25] was added over a 1-min period to the ice-cooled soln. The mixture was stirred at 0° for 4 min (during which the mixture turned from dark yellow, to black, then to green), the ice bath was removed, and the stirring continued at ambient temp for an additional 5 min. The reaction was quenched with a mixture of water (50 ml) and chipped ice (~50 ml) and the resulting aqueous soln was extracted with pentane (5 × 25 ml). The combined pentane extracts were washed with water (4 × 50 ml), dried over $MgSO_4$, filtered, and concentrated under vacuum on a rotary evaporator. The residue was distilled to afford 0·618 g (51%) of a yellow oil: b.p. 44–52° (5 mm); NMR (neat) τ 4·0–4·6 (m with broad peak centered at τ 4·47, 6H, olefinic) and 7·4–8·4 (complex m with overlapping d centered at τ 7·24, $J \sim 6$ Hz, 6H, aliphatic); IR (film) ν_{max} 3025(m), 2995(s), 2950(s), 2905(s), 2840(s), 1728(w), 1653(w), 1633(m), 1603(vw), 1583(vw), 1563(vw), 1461(w), 1443(m), 1313(w), 1218(w), 1158(w), 1033(w), 971(w), 883(w), 861(w), 778(m), 761(m), 731(s), and 693(s) cm^{-1}. Redistillation (b.p. 72–73°/6·5 mm) of the above material afforded the sample submitted for analysis. (Found: C, 91·48; H, 8·52. Calcd. for $C_{11}H_{12}$: C, 91·61; H, 8·39%).

Thermolysis of **4a**. A degassed sample of **4a** (300 mg) was sealed under vacuum (0·05 mm) in a 10 ml ampoule, then was heated at 127° for 1·5 hr. The resulting oil, obtained in essentially quantitative yield, consisted (NMR) mainly of benzene (65%), dicyclopentadiene (29%), and cyclopentadiene (6%). The remainder of the material* appeared to contain starting material and mainly unidentified substances. A similarly prepared sample, after being heated at 70° for 18 hr, showed that about 85% of the starting material remained.

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