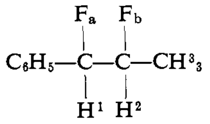
Table III.[a] Nmr Data



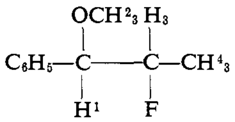
$$C_6H_5\text{—}C(F_a)(H^1)\text{—}C(F_b)(H^2)\text{—}CH^3{}_3$$

	(I) *erythro*	(II) *threo*
$J_{F_aH^1}$	48 cps	48 cps
$J_{F_aF_b}$	~15–16 cps	~15 cps
$J_{F^aH^2}$	~15–16 cps	~15 cps
$J_{F_bH^1}$	~ 14 cps	~14 cps
$J_{F_bH^3}$	~23 cps	~23 cps
$J_{F_aH^3}$	~1.6 cps	<0.5 cps
$J_{H^2H^3}$	~6.5 cps	6.5 cps
δ_{F_a}	ϕ +193.5	ϕ +186.8
δ_{F_b}	ϕ +182.5	ϕ +183.8
δ_{H^1}	−326 cps	−317 cps
δ_{H^2}	−290 cps	−270 cps
δ_{H^3}	−70 cps	−71 cps

[a] Fluorine nmr spectra are reported in units of ϕ = ppm from CCl_3F as internal standard. Proton spectra are reported in cps from tetramethylsilane as internal standard. All spectra were run in CCl_4 as 20% solutions unless otherwise indicated. A Varian HR-40 was used for fluorine spectra and a Varian A-60 for proton spectra.

Dehydrofluorination of I and II. The difluorides (0.1–0.2 g) were treated with 1.0 equiv of potassium *t*-butoxide in *t*-butyl alcohol (~2 ml). The mixture was heated to 75° for 1 hr and then ice-water (1.0 ml) was added. After extraction, washing, drying, and concentration to *ca.* 1 ml, the solution was analyzed by vapor phase chromatography (0.25 in. × 4 ft didecyl phthalate, 129°) and F^{19} nmr. Cumene was added before the reaction to monitor the material balance (usually ~97%). The two isomers were separated by preparative gas phase chromatography for characterization. The fluorine and proton nmr spectra are given in Table V. The infrared spectra are consistent with the assigned structures. *Anal.* Calcd for C_9H_9F: C, 79.39; H, 6.66. Found for *cis:* C, 79.04; H, 6.55. Found for *trans:* C, 79.30; H, 6.75.

Table IV. Nmr Data[a]

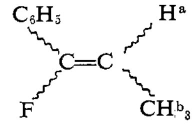


$$C_6H_5\text{—}C(OCH^2{}_3)(H^1)\text{—}C(H_3)(F)\text{—}CH^4{}_3$$

J_{FH^1}	8 cps	δ_F	ϕ +178.5
J_{FH^2}	<0.5 cps	δ_{H^4}	−78, −62 cps
J_{FH^3}	47 cps	δ_{H^3}	−284 cps
J_{FH^4}	24 cps	δ_{H^1}	−242 cps
		δ_{H^2}	−193, −194 cps

[a] See footnote *a*, Table III.

Table V. Nmr Data[a]



	cis	*trans*
J_{FH^a}	22 cps	36 cps
J_{FH^b}	2.2 cps	2.5 cps
$\delta_{H^aH^b}$	7.5 cps	7.0 cps
J_F	ϕ +102.6	ϕ +121.0
δ_{H^a}	−324 cps	−319 cps
δ_{H^b}	−105 cps	−107 cps

[a] See footnote *a*, Table III.

Acknowledgment. I am grateful to Mrs. Carolyn Haney for infrared and nmr spectra and to Mr. Morris Howard for technical assistance.

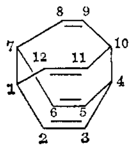
Pyrolysis of Some Bridged Homotropilidene Systems[1]

John N. Labows, Jr.,[2] Jerrold Meinwald, Herbert Röttele, and Gerhard Schröder

Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14850, and the Institut für Organische Chemie, Technische Hochschule Karlsruhe, Karlsruhe, Germany. *Received August 29, 1966.*

Abstract: A new $(CH)_{12}$ hydrocarbon, obtained by pyrolysis of tetracyclo[5.3.2.$0^{2,5}$.$0^{6,8}$]dodeca-3,9,11-triene (**2**), is shown to be tricyclo[5.3.2.$0^{4,8}$]dodeca-2,5,9,11-tetraene (**5**). Its nmr spectrum is similar to that of bicyclo[3.3.2]deca-2,7,9-triene (**10**), characterized as the pyrolysis product of dihydrobullvalene (**14**). Possible pathways for these thermal rearrangements are discussed.

We have been interested in the possibility of synthesizing the theoretically interesting $(CH)_{12}$ hydrocarbon tricyclo[5.5.0.$0^{4,10}$]dodeca-2,5,8,11-tetraene (**1**). In connection with another problem, it had been noted that the readily accessible isomeric $(CH)_{12}$ hydrocarbon, tetracyclo[5.3.2.$0^{2,5}$.$0^{6,8}$]dodeca-3,9,11-triene (**2**),[3] undergoes a thermal rearrangement to give a new, crystalline $C_{12}H_{12}$ product, A, of unknown structure.[4] Because of the possibility that this unknown might be the desired **1**, and because of the current interest in related thermal rearrangements, we have examined this reaction in greater detail.



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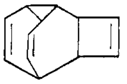

2

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[1] Partial support of this study by a National Science Foundation research grant (GP 4128) is acknowledged with pleasure. We are grateful to Badische Anilin und Soda Fabrik for a generous gift of cyclooctatetraene.

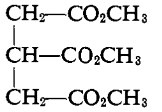
[2] National Institutes of Health Predoctoral Fellow, 1964–1967.

[3] G. Schröder, *Chem. Ber.*, 97, 3131 (1964).

[4] H. Röttele, Diplomarbeit, Technische Hochschule Karlsruhe, Jan 1965.

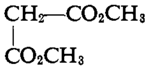
Tricyclo[5.3.2.0^{4,8}]dodeca-2,5,9,11-tetraene (5). A solution of **2** in pentane was passed through a glass-bead-packed column at 480° to yield a single product, as shown by glpc analysis. This product was obtained as colorless crystals, mp 78°, after removal of the solvent, crystallization from ethanol, and sublimation. The ultraviolet spectrum of A showed only end absorption, while its nmr spectrum showed complex absorptions centered at τ 4.1 (8 H) and 7.0 (4 H), indicating a nonconjugated tetraene structure. The mass spectra of both **2** and A were identical (parent peak, *m/e* 156), suggesting that the isomerization may also occur within the injection port (*ca.* 200°). On catalytic hydrogenation, A absorbed 4 moles of hydrogen.

In order to gain further insight into the structure of this rearrangement product, oxidative degradations were examined. Lemieux oxidation failed to give any characterizable products. However, ozonolysis followed by performic acid treatment and diazomethane esterification gave a mixture of esters. Chief among these were the trimethyl ester of propane-1,2,3-tricarboxylic acid (**3**) (35%) and the dimethyl ester of malonic acid (**4**) (36%), accompanied by smaller amounts of the esters of succinic acid (11%), ethanetricarboxylic acid (10%), and propane-1,1,2,3-tetracarboxylic acid (7%).



$$\begin{array}{l}CH_2{-}CO_2CH_3\\ |\\ CH{-}CO_2CH_3\\ |\\ CH_2{-}CO_2CH_3\end{array}$$

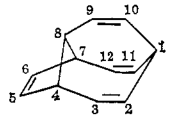
3



$$\begin{array}{l}CH_2{-}CO_2CH_3\\ |\\ CO_2CH_3\end{array}$$

4

These esters were identified on the basis of glpc and mass spectral comparisons with authentic samples. The degradation of A to give chiefly **3** and **4** excludes structure **1** from further consideration, since **1** has its only four saturated carbon atoms arranged as two >CHCH< pairs. It is best reconciled with structures **5** or **6**, which represent the only remaining reasonable structural possibilities.[5] It may be noted that both **5** and **6** have three contiguous, saturated >CH groups; the expected, *immediate* ozonolysis products from each would be, therefore, propane-1,1,2,3,3-pentacarboxylic acid (**7**) and methanetricarboxylic acid (**8**). The partial decarboxylation of **7** and **8** during work-up to give the observed esters would be unexceptional.[6]



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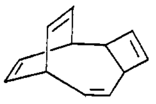

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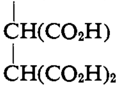


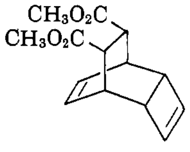
$$\begin{array}{l}CH(CO_2H)_2\\ |\\ CH(CO_2H)\\ |\\ CH(CO_2H)_2\end{array}$$

7

$CH(CO_2H)_3$

8

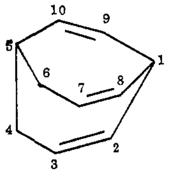
In an effort to distinguish between **5** and **6**, the unknown was subjected to hydroboration followed by chromic acid oxidation. In a model experiment using 7,8-dicarbomethoxytricyclo[4.2.2.0^{2,5}]deca-3,9-diene (**9**),[7] this technique gave rise to ketonic absorption



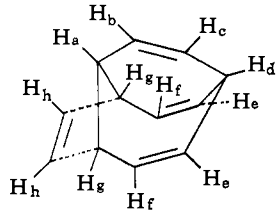
9

at 5.6 μ, characteristic of the cyclobutanone moiety. In the case of A, however, a mixture of three ketones (tlc analysis) showing infrared absorption at 5.75 and 5.85 μ was obtained. There was thus *no* indication of the formation of a cyclobutanone, and on this basis structure **5** appeared preferable to structure **6**.

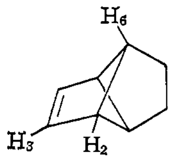
Support for the assignment of structure **5** to A was obtained from a comparison of its nmr spectrum with that of bicyclo[3.3.2]deca-2,7,9-triene (**10**), the synthesis of which will be described below. The close relationship between structures **5** and **10** is shown in formula **11**, in which it can be seen that the formal joining of an ethylene bridge across the 4,6 positions of **10** transforms it into **5**. In comparing the olefinic regions of the spectra of **10** and A, the chief discernible difference may be attributed to the two additional olefinic protons, which appear as a doublet (τ 4.1, $J \cong$ 1 cps). Analogy for this somewhat unexpected splitting pattern can be found in the nmr spectrum of tricyclo[3.3.0.0^{2,6}]oct-3-ene (**12**),[8] in which the olefinic protons (H_3) appear to be coupled with the homoallylic protons (H_6), $J_{2,6} \cong$ 2 cps, much more strongly than with the allylic protons (H_2). A similar splitting of the olefinic protons H_h in **11** by H_a, and negligible splitting by H_g, may therefore not be unreasonable.



10



11



12

It may also be noted that both nmr spectra possess a single, low-field absorption at τ 3.7, attributable to the *unique* olefinic proton, H_c, which appears as a triplet ($J_{bc} \cong J_{cd} \cong$ 9 cps). Over-all, the close similarity of these spectra favors the choice of structure **5** over structure **6**, in agreement with the chemical evidence.

Synthesis of Bicyclo[3.3.2]deca-2,7,9-triene (10). The model hydrocarbon **10** was prepared from bullvalene (**13**) by the sequence outlined below.

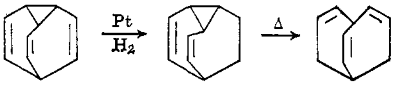
---

(5) We are indebted to R. Hoffmann, Cornell University, and J. Lederberg, Stanford University, for making available their systematic surveys of all theoretically possible $(CH)_{12}$ isomers. Other $C_{12}H_{12}$ structures appear unlikely on the basis of the nmr spectrum.

(6) In fact propane-1,1,2,3-tetracarboxylic acid, which was identified by mass spectral and glpc analysis as one of the products (7%), was shown to fragment under the oxidative ozonolysis work-up conditions to give the observed esters.

(7) W. Reppe, *et al.*, *Ann. Chem.*, **560**, 1 (1948).

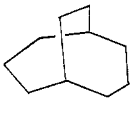
(8) B. Kaplan, Ph.D. Thesis, Cornell University, June 1966.



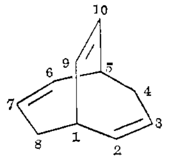
13 **14** **10**

Controlled catalytic hydrogenation of **13** gave a mixture of products comprising unchanged **13** (40%), dihydrobullvalene **14** (25%), tetrahydrobullvalene (15%), and hexahydrobullvalene (15%). These products were collected gas chromatographically, and identified on the basis of their nmr spectra and mass spectra.[9]

Pyrolysis of **14** at 420°[10] yielded an isomeric hydrocarbon assigned structure **10** on the following basis. Ultraviolet end absorption and nmr absorptions at τ 4.2 (6 H), 7.1 (2 H), and 7.5 (4 H) point to a nonconjugated triene. The mass spectral parent peak at m/e 132 confirms the molecular formula $C_{10}H_{12}$. Upon catalytic hydrogenation, **10** absorbs 3 molar equiv of hydrogen to give bicyclo[3.3.2]decane (**15**), identified by direct comparison with an authentic sample prepared *via* exhaustive catalytic hydrogenation of bullvalene.[12]



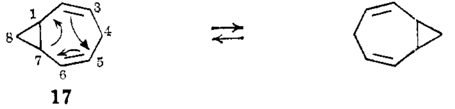
15



16

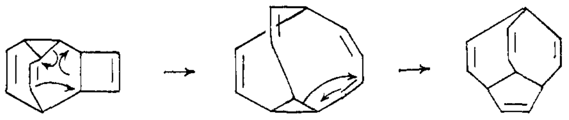
The only other possible triene based on a bicyclo[3.3.2]decane carbon skeleton is bicyclo[3.3.2]deca-2,6,9-triene (**16**),[13] a known compound, an authentic sample of which was prepared by the sodium–liquid ammonia reduction of bullvalene.[12] A direct nmr and glpc comparison of **16** with the rearrangement product of **14** showed the two to differ, thus establishing structure **10** unambiguously.

Mechanistic Consideration. Having established that the thermal rearrangement of **2** leads to **5**, and incidentally that **14** is converted thermally into **10**, it is appropriate to consider what pathways seem likely for these transformations. The report of the discovery of the rapidly reversible, degenerate Cope rearrangement of bicyclo[5.1.0]octa-2,5-diene ("3,4-homotropilidene") (**17**) by Doering and Roth,[14] along with their discussion of the spectacular properties anticipated for bullvalene, is one of the milestones of organic chemistry. These workers were able to show that the half-life of an individual molecule of **17** in a fixed structure must be less than $^{1}/_{250}$ sec at 180°, increasing to 1 sec or longer at −50°. They predicted that the joining of an additional bridge across the 4,8 positions of **17** would give rise to conformationally fixed molecules (such as bullvalene), capable of even more facile rearrangement. This prediction has been confirmed.[15]



17

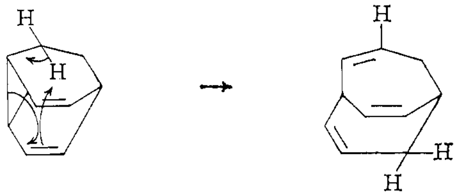
Turning to the case of **2**, we see that it represents a 3,4-homotropilidene system in which the 4,8 positions are bridged by a cyclobutene moiety. As in the case of **17** itself, the simple Cope rearrangement is degenerate. However, the formally analogous process involving the cyclobutene bridge single bond would lead to structure **18**, a vinylog of bullvalene. A subsequent vinylcyclopropane → cyclopentene[16] rearrangement (**18**, see arrows) would then convert **18** to **5**. Doering has invoked a similar vinylcyclopropane rearrangement followed by bond cleavage to account for the pyrolysis products of bullvalene.[11]



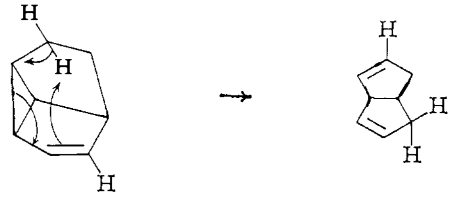
2 **18** **5**

An alternate path from **2** to **18** would involve the direct thermal opening of the cyclobutene moiety. Such an opening should prefer a conrotatory motion.[17] This would lead to an intermediate in which one of the conjugated double bonds would be *trans*, a stereochemistry which would be highly strained within this ring system. The relative thermal stability of **2** is probably related to this fact. (It should be noted, however, that the less favored disrotatory opening, such as that observed in the transformation of bicyclo[3.2.0]hept-6-ene into 1,3-cycloheptadiene[18] may occur at the relatively high temperature used here.)

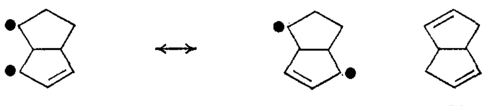
The conversion of **14** to **10** can be formulated as a 1,5-homodienyl hydrogen shift,[19,20] analogous to the conversion of tricyclo[3.3.0.0^{4,6}]oct-2-ene (**19**) to bicyclo[3.3.0]octa-2,7-diene (**20**).[20] These reactions appear to be concerted, since in both cases a single isomer is produced. (Were the diradical **21** an intermediate in the cleavage of **19**, formation of **22** along with **20** would probably have been expected.)



14 **10**



19 **20**



21 **22**

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(9) *Cf.* ref 12.

(10) The temperature was chosen in order that the bullvalene present would be converted to the dihydronaphthalenes in less than 10%.[11]

(11) W. von E. Doering and J. Rosenthal, *J. Am. Chem. Soc.*, **88**, 2078 (1966).

(12) G. Schröder, *Chem. Ber.*, **97**, 3140 (1964).

(13) Previously designated as bicyclo[3.3.2]deca-3,7,9-triene.[12]

(14) W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).

(15) For a recent review see G. Schröder, J. F. M. Oth, and R. Merényi, *Angew. Chem. Intern. Ed. Engl.*, **4**, 752 (1965).

(16) C. G. Overberger and A. E. Borchert, *J. Am. Chem. Soc.*, **82**, 1007, 4896 (1960).

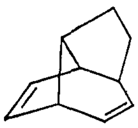
(17) R. Woodward and R. Hoffmann, *ibid.*, **87**, 395 (1965).

(18) O. L. Chapman, D. J. Pasto, G. W. Borden, and A. A. Griswold, *ibid.*, **84**, 1220 (1962).

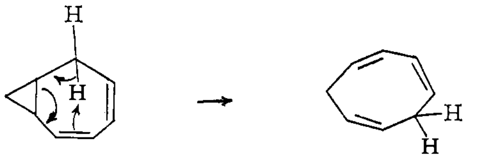
(19) (a) D. S. Glass, J. Zirner, and S. Winstein, *Proc. Chem. Soc.*, 276 (1963); (b) W. Roth, *Ann. Chem.*, **671**, 10 (1964).

(20) W. Roth, *Angew. Chem. Intern. Ed. Engl.*, **3**, 440 (1964).

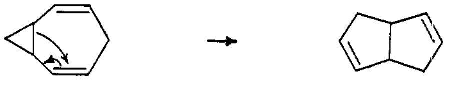
An alternate thermal reaction of **14** might have been a vinylcyclopropyl type rearrangement, which would generate **23**. Since **23** does not appear to be a likely precursor for the observed **10**, however, this mechanism seems not to be preferred over the 1,5-homodienyl hydrogen transfer. The greater ease of this latter process finds analogy in a comparison of the reaction of **24** and **17**. Bicyclo[5.1.0]octa-2,4-diene (**24**) pyrolyses to cycloocta-1,3,6-triene (**25**) at 225°, well below the 305° at which the isomeric bicyclo[5.1.0]octa-2,5-diene (**17**) suffers vinylcyclopropane rearrangement to bicyclo[3.3.0]octa-2,6-diene (**22**).[14]



23



24 **25**



17 **22**

Experimental Section

Nmr spectra were obtained on Varian A-60 and HA-100 spectrometers. Mass spectra were determined on a Consolidated Engineering Type 21-103A mass spectrometer equipped with a heated inlet system. Ultraviolet spectra were recorded on a Cary Model 14 recording spectrophotometer. Glpc determinations were carried out on Aerograph Hy Fl Models 600 and 660, with collections made by use of microcollection tubes. The two columns used were a 5% SE-30 on acid-washed Chromosorb W and a 15% butanediol succinate on acid-washed Chromosorb W.

Pyrolysis of Tetracyclo[$5.3.2.0^{2,6}.0^{6,8}$]dodecatriene (2). A glass tube 30 cm long was filled with glass beads and wrapped with a heating tape containing a thermocouple. The column was equilibrated at 480° under a slow stream of nitrogen, and 0.650 g of **2** in 2 ml of pentane was dropped through the column, followed by 20 ml of additional pentane. The time required for **2** to pass through the column was about 2 min. The product was collected in a cold trap; the pentane was evaporated, and the residue was crystallized from ethanol and then sublimed to yield 0.200 g of a crystalline solid (**5**), mp 78°. In the infrared **5** showed absorption at 3.28, 3.41, 6.05, 10.4, and 10.7 μ; the nmr spectrum showed peaks at τ 4.1 (8) and 7.0 (4); the ultraviolet spectrum showed only end absorption with λ^{EtOH} 230 mμ (ϵ 625) and 202 mμ (ϵ 4400). The mass spectrum showed a parent peak at *m/e* 156. The product was shown to be pure by glpc examination on both 5% SE-30 [145° (18 psi), 4.8 min] and 15% butanediol succinate [175° (19 psi), 6.8 min] columns.

Anal. Calcd for $C_{12}H_{12}$: C, 92.26; H, 7.74. Found: C, 92.02; H, 7.78.

Catalytic hydrogenation (4 moles of hydrogen) with palladium on carbon gave a saturated hydrocarbon, $C_{12}H_{20}$, mp 168–172°.

Anal. Calcd for $C_{12}H_{20}$: C, 87.72; H, 12.27. Found: C, 87.38; H, 12.15.

Ozonolysis of 5. A methylene chloride–methanol solution of **5** (70 mg) was ozonized at −78° until there was no further uptake of ozone. The ozonide was treated with 30% hydrogen peroxide (2 ml), water (2 ml), and formic acid (2 ml) and heated at reflux for 1 hr. The solution was then evaporated to dryness and the residue esterified with an ethereal solution of diazomethane. The infrared spectrum of the microdistilled product (120 mg) had bands at 3.4, 5.75, and 8–9 μ. Glpc analysis on a 5% SE-30 column at 158° showed the presence of five esters, with retention times (min) of 0.5 (36%), 0.7 (11%), 2.3 (10%), 3.7 (36%), and 10.0 (7%). These esters were identified by comparison with synthetic samples of the methyl esters of malonic acid (0.5), succinic acid (0.7), ethanetricarboxylic acid (2.3),[21] propane-1,2,3-tricarboxylic acid (3.7),[22] and propane-1,1,2,3-tetracarboxylic acid (10.0).[23] It was found that treatment of propane-1,1,2,3-tetracarboxylic acid under the work-up conditions yielded the same ester mixture. Malonic acid was observed to be formed by treatment of methanetricarboxylic acid[24] with hydrogen peroxide and formic acid. The esters were also compared with authentic samples by mass spectral examination of glpc collected samples on the basis of major peaks (P-31, P-59, and P-91).

Hydroboration of 5. A solution of 20 mg of **5** in tetrahydrofuran was stirred at 0° for 3 hr with 0.2 ml of a 1 *M* solution of diborane in tetrahydrofuran (Metal Hydrides Inc.). Water (1 ml) was added, and the solution was titrated with 2 *M* chromic acid. The solution was diluted with water and extracted with ether. Thin layer chromatography indicated the presence of three ketones (sprayed with 2,4-dinitrophenylhydrazine reagent) and separation by preparative tlc (silica gel eluted with chloroform) gave two ketones with infrared absorption at 5.75 and 5.85 μ identical with those absorptions observed in the ketone mixture.

Preparation of Tricyclo[$3.3.2.0^{4,6}$]decadiene (14). Bullvalene (200 mg) was catalytically hydrogenated with 1 molar equiv of hydrogen. This resulted in a mixture of unreacted bullvalene (40%), dihydrobullvalene (**14**) (25%), and tetra- (15%) and hexa- (15%) hydrobullvalene. These products were completely separated on a 15% butanediol succinate column and were collected in microtubes and identified by their nmr and mass spectra.

Pyrolysis of 14. The above mixture of hydrogenation products from bullvalene was subjected to pyrolysis at 420° in the manner described for **2**. The conversion of **14** to a new product **10** was followed by glpc analysis. After four passes through the column, complete conversion (>95%) was obtained. A sample of **10** was collected by glpc on a 15% butanediol succinate column [115° (11 psi), 10 min] using a microcollection tube. It gave the following spectral data: the ultraviolet spectrum showed only end absorption with λ^{EtOH} 230 mμ (ϵ 475) and 202 mμ (ϵ 2520); the nmr spectrum showed peaks at τ 4.15 (6), 7.1 (2), and 7.5 (4); the mass spectrum showed a parent peak at *m/e* 132.

Hydrogenation of 10. A glpc collected sample of **10** (3 mg) was subjected to a microhydrogenation over a prereduced platinum oxide catalyst. There was an immediate uptake of 1.8 ml of hydrogen (3 molar equiv). Glpc analysis on two columns showed the product to be identical with bicyclo[3.3.2]decane.[12]

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[21] C. A. Bischoff, *Ann.*, **214**, 38 (1882).

[22] Synthesized from propane-1,1,2,3-tetracarboxylic acid by treatment with hydrogen peroxide and formic acid.

[23] H. T. Clarke and T. F. Murray in "Organic Syntheses," Coll. Vol. I, H. Gilman and A. H. Blatt, Ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p 272.

[24] B. B. Corson and J. L. Sayre in "Organic Syntheses", Coll. Vol. II, A. H. Blatt, Ed., John Wiley and Sons, Inc., New York, N. Y., 1943, p 596.