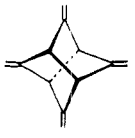
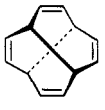
Success was achieved upon reaction of a suspension of **6** in water containing sodium hydroxide with 3 equiv of potassium permanganate at 0 °C for 1 h and at room temperature for 15 h. After filtration, acidification with hydrochloric acid, and freeze drying, the crude carboxylic acid was esterified with diazomethane in ether. After separation of the inorganic salts, **7** was obtained in 51% yield. Structural identification is based on the simplified ^{1}H NMR spectrum which consists of singlets at δ 3.85 (2 H) and 3.57 (12 H), a multiplet of area 4 at δ 3.24, and a two-proton doublet (J = 2 Hz) at δ 2.75. The five-line ^{13}C NMR spectrum was particularly confirmatory of the molecule's C_{2v} symmetry.

No epimerization occurred when **7** was treated with sodium hydroxide in anhydrous methanol (reflux, 6 h) or with catalytic amounts of sodium methoxide in the same solvent (25 °C, 12 h). Whereas equimolar amounts of sodium methoxide in hot methanol (reflux, 3 h) led to decomposition and/or polymerization, catalytic quantities of the same base (reflux, 6 h) resulted in complete conversion to **8**. After silica gel chromatography, the colorless crystalline solid was found to exhibit a ^{1}H NMR spectrum consisting of three peaks at δ 3.59 (s, 12 H), 2.97 (m, 4 H), and 2.46 (m, 4 H). In agreement with the S_4 symmetry of this tetraester, its ^{13}C NMR spectrum is characterized by only four signals.

Many attempts to achieve the reduction of **8** were made with Red-Al, lithium aluminum hydride, or diisobutylaluminum hydride. None proved successful in delivering the tetraol; nor was **8** recovered in most cases. The apparently high sensitivity of the intended product has precluded us from proceeding with the elaboration of tetraenes **9** and **10**[10] until alternative workable procedures are devised.



9



10

Experimental Section

2,4,6,8-*syn,syn*-Tricyclo[3.3.0.0^{3,7}]octanetetracarboxylic Acid. To a suspension of **6** (0.029 g, 0.186 mmol) in 10 mL of water containing 41 mg of sodium hydroxide was added potassium permanganate (0.164 g, 1.038 mmol) at 0 °C with stirring. After 1 h, the reaction mixture was allowed to warm to room temperature where it was stirred for 15 h. The mixture was filtered and the manganese dioxide cake was washed with 20 mL of hot water. The combined filtrate and washing was acidified to pH 1-2 with concentrated hydrochloric acid. After the removal of water by freeze-dry techniques, the white solid which remained was used for further reaction without purification.

2,4,6,8-*syn,syn*-Tetrakis(carbomethoxy)tricyclo[3.3.0.0^{3,7}]octane (7). The crude tetracarboxylic acid from above was treated with excess diazomethane in ether. Since the resulting tetramethyl ester is soluble in ether, the inorganic salts were removed by filtration. After concentration of the filtrate, there remained 0.032 g (51%) of **7** which was recrystallized from methanol: mp 206.0-207.0 °C; ^{1}H NMR ($CDCl_3$) δ 3.85 (s, 2 H), 3.57 (s. 12 H), 3.24 (m, 4 H), 2.75 (d, J = 2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) 171.84, 59.01, 51.80, 43.57, 42.92 ppm.

Anal. Calcd for $C_{16}H_{20}O_8$: C, 56.47; H, 5.92. Found: C, 56.88; H, 6.35.

2,4,6,8-*anti,anti*-Tetrakis(carbomethoxy)tricyclo[3.3.0.0^{3,7}]octane (8). A solution of sodium methoxide was prepared by dissolving 0.1 g of sodium metal in 25 mL of dry methanol under an argon atmosphere. To a solution of **7** in 15 mL of methanol was added a few drops of the sodium methoxide solution and the mixture was heated to the reflux temperature for 6 h. After the reaction mixture was cooled and concentrated, a quantitative yield of **8** was obtained as a colorless solid: mp 203.5-204.5 °C (after sublimation); ^{1}H NMR ($CDCl_3$) δ 3.59 (s, 12 H), 2.97 (m, 4 H), 2.46 (m, 4 H); ^{13}C NMR ($CDCl_3$) 172.49, 55.30, 52.04, 42.63 ppm.

Anal. Calcd for $C_{16}H_{20}O_8$: C, 56.47; H, 5.92. Found: C, 56.28; H, 6.07.

Acknowledgment. This investigation was financed by a research grant from the National Institutes of Health (Grant AI-11490).

Registry No. **6**, 53283-11-7; **7**, 75599-73-4; **8**, 75658-51-4; 2,4,6,8-*syn,syn*-tricyclo[3.3.0.0^{3,1}]octanetetracarboxylic acid, 75599-74-5.

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1-Semibullvalenylcarbinyl Cation

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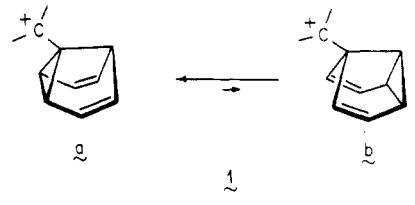
Because the CH_2^+ substituent is simultaneously a powerful σ withdrawer and a very strong π acceptor, cyclopropane rings are capable of exhibiting an intense stabilizing interaction with an adjacent carbocation center if conformationally bisected.[1,2] In their theoretical consideration of the 1(5)-semibullvalenylcarbinyl cation (**1**),



a b

1

Hoffmann and Stohrer showed through calculation that bond order and overlap population changes expectedly favor overwhelming adoption of that valence tautomeric form in which the charge-deficient carbon is bonded to position 1 as in **1a**.[3] Due to the high reactivity of semibullvalene derivatives in general, we considered it unlikely that **1** would persist in solution for any length of time.[4] Nonreversible electronic shifts were anticipated. The nature of these cationic isomerizations were considered of

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Table I. LIS Data for 3 (δ, 60 MHz, $CDCl_3$)

mol % Gu(fod)$_3$	chemical shift, δ									
	H_1	H_2	H_3	H_4	H_5	H_6	H_7	H_9	H_9'	OH
0	3.63	4.32	5.25	6.40	2.94	6.73	5.95	4.57	4.49	1.80
6.3	4.67	*a*	*a*	*a*	3.36	*a*	*a*	4.78	4.70	10.5
11.9	5.67	5.03	*a*	7.45	3.78	*a*	*a*	5.00	4.93	*b*
17.0	6.63	10.20	9.32	7.90	4.17	8.20	8.81	5.20	5.13	*b*
22.8	7.69	12.30	10.80	8.42	4.69	8.70	9.85	5.39	5.35	*b*
33.0	9.49	15.55	12.80	*a*	5.24	*a*	11.40	5.73[c]		*b*
42.8	10.57	18.10	14.32	9.75	5.69	10.00	12.41	5.94[c]		*b*

[a] Not discernable due to overlap. [b] Not observed. [c] Overlap.

Table II. LIS Data for 4 (δ, 60 MHz, $CDCl_3$)

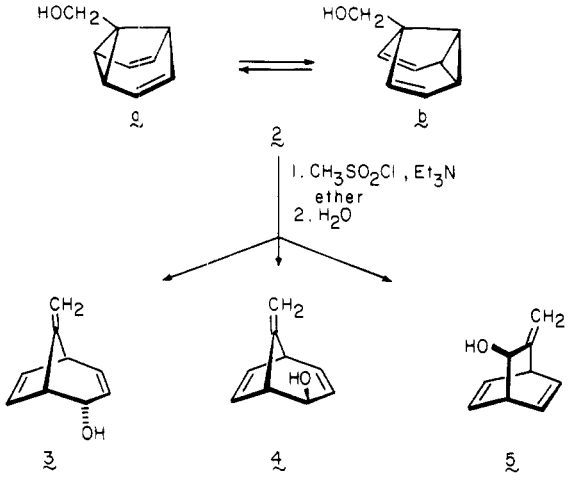
mol % Gu(fod)$_3$	chemical shift, δ								
	H_1	H_2	H_3	H_4	H_5	H_6	H_7	H_9	H_9'
0	3.03[a]	4.03	5.30	6.37	3.03	6.68	6.10	4.62[b]	4.65
4.7	4.32	5.97	*c*	*c*	3.48	*c*	6.38	5.37	5.20
9.1	5.55	*c*	*c*	*c*	3.94	*c*	6.60	6.02	5.64
13.4	6.67	9.40	8.77	7.85	4.33	7.50	6.93	6.63	6.05
18.7	7.97	11.45	10.10	8.42	4.82	7.81	7.24	7.32	6.57
29.0	10.32	15.10	12.30	9.40	5.66	8.38	7.84	8.72	7.42
39.3	12.10	18.15	13.90	10.06	6.23	8.80	8.25	9.34	7.97
49.5	13.10	20.10	14.70	10.43	6.52	9.06	8.53	9.69	8.21

[a] Overlap with H_5. [b] Could be interchanged. [c] Not discernable due to overlap.

sufficient interest to warrant examination. This note presents our findings on this subject.

All attempts to isolate or observe (by ^1H NMR) the mesylate of known carbinol **2**[5] from its reaction with sulfene[6] were thwarted by its lability. Instead, three rearranged alcohols were obtained upon aqueous workup. These difficultly separable substances were ultimately purified by tandem VPC techniques and shown to share the common $C_9H_{10}O$ formula by mass spectrometry.

Major alcohol **3** (52%) could be isolated in pure form by preparative VPC on a 5% XF-1150 column at 120 °C. Whereas **4** and **5** were co-eluted under these conditions, their separation was effected with 15% FFAP. In this manner, sufficient quantities of **3** and **4** were obtained to allow them to be subjected individually to a lanthanide-induced shift (LIS) study using Eu(fod)$_3$.



All three products exhibited ^1H NMR absorptions characteristic of *exo*-methylene protons. In addition, **3** and **4** showed the same type of olefinic pattern as observed for other bicyclo[3.2.1]octa-2,6-dienes.[7] The stereochemistry

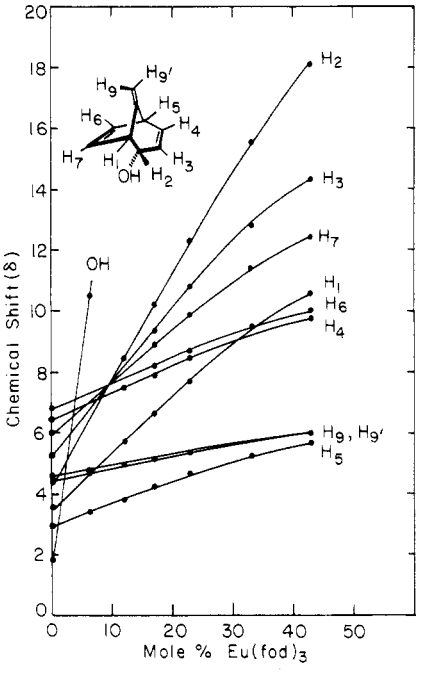


Figure 1. Plot of chemical shift vs. mol % Eu(fod)$_3$ for **3**.

of their hydroxyl functions was assigned on the basis of the LIS results which established the exocyclic methylene protons in **4** to be substantially more affected than those in **3** (Tables I and II, Figures 1 and 2). These data, taken in combination with infrared hydroxyl absorptions at 3350 cm^{-1} (in CCl_4 solution), are strongly supportive of the structural assignments. The ^1H NMR data for **5** include one multiplet at δ 6.72–6.16 arising from four olefinic protons, a second multiplet of area 3 in the δ 4.16–3.74 region, and a doublet (J = 9 Hz) hydroxyl proton signal at δ 1.35, in addition to the exocyclic proton pattern. The appearance in the proton spectrum of the three-proton signal at δ 4.16–3.74 requires that there be six olefinic

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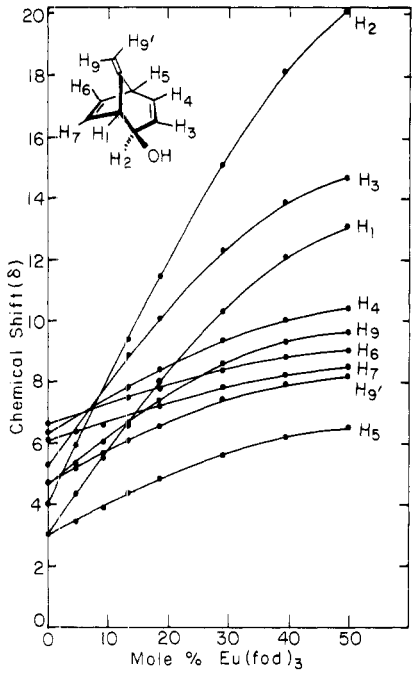
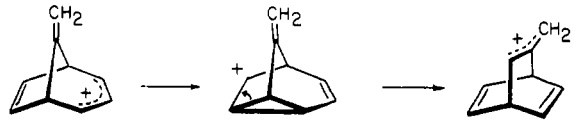


Figure 2. Plot of chemical shift vs. mol % $Eu(fod)_3$ for **4**.

carbon atoms and eliminates all tricyclic structures from consideration. It follows further that the dihydrobarrelene formulation is particularly consistent with the spectral features observed.

A mechanistic rationalization of the formation of **3–5** involves the assumption that **1** experiences initial ring opening to give symmetrical carbocation **6** which can either be captured by a nucleophile (with exo bonding favored by a factor of approximately 2) or experience further isomerization via **7** to **8**. The conversions of **6** to **7** and of **7** to **8** are straightforward homoallyl–cyclopropylcarbinyl rearrangements. While the driving force for conversion to **8** (or its capture by solvent) appears not to be overwhelming, it apparently derives in part from strain release.



6 **7** **8**

Experimental Section

Attempted Preparation of 1(5)-[(Methanesulfonyloxy)]-semibullvalene. Direct Conversion of 2 to 3–5. A mixture of 142 mg (1.06 mmol) of **2**,[5] 0.23 mL (1.65 mmol) of triethylamine, and 5.0 mL of dry ether under argon was cooled in a dry ice–carbon tetrachloride bath (–25 °C). To this solution was added dropwise 90 μL (1.20 mmol) of methanesulfonyl chloride over 2 min; a precipitate immediately started to form. After addition was completed, the cooling bath was allowed to warm gradually to room temperature over approximately 20 min. The reaction mixture, which now contained a large amount of precipitate, was added to a separatory funnel containing 50 mL of water and 25 mL of ether. The ether layer was washed with saturated sodium bicarbonate solution and brine and dried over sodium sulfate. Thin-layer chromatography on silica gel showed only one spot (R_f 0.38, 20% ether/carbon tetrachloride). Gas chromatographic analysis on a 6 ft × 0.25 in. 5% XF-1150 on 60/80-mesh Chromosorb W column (120 °C) showed two peaks: t_R 5.1 and 8.0 min, with relative areas of 48:52. These two components were separated to give 16 mg of the 5.1-min component, a solid, and 19 mg of **3**, a liquid. These samples were identified as $C_9H_{10}O$ isomers by their mass spectra: calcd m/e 134.0732, found 134.0733. Their ^1H NMR spectra and LIS studies [$Eu(fod)_3$] indicated that the 5.1-min component was a mixture of two compounds and that the 8.0-min component was pure. Resolution of the 5.1-min mixture into its components was accomplished on a 12 ft × 0.25 in. 15% FFAP on 60/80-mesh Chromosorb W column (120 °C): t_R 26.1 and 27.9 min, with relative areas of 61:39. Isolation of these two components gave 2.3 mg of **4** and 1.4 mg of **5**, respectively.

For **3**: ^1H NMR ($CDCl_3$, 90 MHz) δ 6.63 (dd, $J_{6,7}$ = 6.0, $J_{5,6}$ = 3.0 Hz, 1 H, H_6), 6.34 (ddd, $J_{3,4}$ = 9.5, $J_{4,5}$ = 6.0, $J_{2,4}$ = 1.7 Hz, 1 H, H_4), 5.89 (dd, $J_{6,7}$ = 6.0, $J_{1,7}$ = 3.0 Hz, 1 H, H_7), 5.22 (dm, $J_{3,4}$ = 9.5 Hz, 1 H, H_3), 4.67 (s, 1 H, H_9 or $H_{9'}$), 4.48 (s, 1 H, H_9 or $H_{9'}$), 4.32 (m, 1 H, H_2), 3.54 (m, 1 H, H_1), 2.93 (dd, $J_{4,5}$ = 6.0 Hz, $J_{5,6}$ = 3.0 Hz, 1 H, H_5), 2.02 (m, 1 H, hydroxyl).

Anal. Calcd for $C_9H_{10}O$: C, 80.56; H, 7.51. Found: C, 80.36; H, 7.48.

For **4**: ^1H NMR ($CDCl_3$, 90 MHz) δ 6.65 (dd, $J_{6,7}$ = 5.6, $J_{5,6}$ = 3.0 Hz, 1 H, H_6), 6.35 (dd, $J_{3,4}$ = 9.4, $J_{4,5}$ = 6.6 Hz, 1 H, H_4), 6.06 (dd, $J_{6,7}$ = 5.6, $J_{1,7}$ = 3.0 Hz, 1 H, H_7), 5.30 (ddd, $J_{3,4}$ = 9.4, $J_{2,3}$ = 3.4, $J_{1,3}$ = 1.9 Hz, 1 H, H_3), 4.70 (s, 1 H, H_9 or $H_{9'}$), 4.67 (s, 1 H, H_9 or $H_{9'}$), 4.20–3.94 (m, 1 H, H_2), 3.14–2.98 (m, 2 H, H_1 and H_5), 1.72 (br d, 1 H, $J_{2,OH}$ = 9.1 Hz).

For **5**: ^1H NMR ($CDCl_3$, 90 MHz) δ 6.72–6.16 (m, 4 H, H_1, H_2, H_3, and H_4), 4.94 (s, 1 H, H_9 or $H_{9'}$), 4.93 (s, 1 H, H_9 or $H_{9'}$), 4.16–3.74 (m, 3 H, H_5, H_6, and H_7), 1.35 (br d, $J_{6,OH}$ = 9.0 Hz).

Acknowledgment. We thank the National Science Foundation for their financial support of this work.

Registry No. **2**, 54007-60-2; **3**, 75600-62-3; **4**, 75600-63-4; **5**, 75600-64-5.

Cycloaddition Behavior of Heptalene toward Triazolinediones

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Although research in the area of heptalene chemistry lapsed seriously after Dauben and Bertelli's original synthesis of the nonbenzenoid hydrocarbon in 1961,[2] the last five years have witnessed a marked resurgence of interest in the field.[3] The principal underlying factor appears to be the successful development of efficient new synthetic routes both to the parent system[4,5] and to select stable derivatives[6–8] whose three-dimensional characteristics have been determined by X-ray methods.[9] Complementary

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