ether extract was washed with water, dried, and evaporated under vacuum to yield 0.18 g of white solid, which nmr spectroscopy indicated to consist of *ca.* 42% **5c**, 29% **2c**, and 29% **10**.

Acknowledgment. We thank Miss Jill H. Paul and Mr. Jack Landis for their kind assistance.

Registry No. 2b, 18734-98-0; **2c**, 18735-02-9; **4b**, 20023-76-1; **4c**, 42806-98-4; **5b**, 17207-15-7; **5c**, 17207-20-4; **6b**, 19510-15-7; **7b**, 42807-02-3; **7c**, 26157-90-4; **8b**, 42807-04-5; **10**, 42807-05-6; **11**, 6386-41-0; 3,5-di-*tert*-butyl-4-hydroxyphenylacetic acid, 1611-03-6.

References and Notes

(1) This work was supported in part by an American Chemical Society Petroleum Research Fund Graduate Fellowship, 1969–1970.

(2) (a) American Chemical Society Petroleum Research Fund Graduate Fellow, 1969–1970; (b) National Science Foundation Undergraduate Research Participant, 1970–1971.

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(11) V. V. Ershov, A. A. Volod'kin, and V. I. Volod'kina, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 688 (1970).

(12) (a) See ref 3 and 5. We have come to a dead end on this point. Reference 12 within ref 3 was claimed to contain the necessary melting point data. This reference does not appear to exist, and we have not been able to locate this data in the literature. (b) Our melting points for alcohols **2b** and **6b** differ by 35°. (c) Our melting points for alcohols **2c** and **6c** differ by 55°.

(13) Nmr spectra were determined in $CDCl_3$ solution using a Varian A-60 spectrometer. Melting points are corrected. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Mass spectra were determined using a Varian CH5 spectrometer at 70 eV with direct sample inlet and linear mass scan.

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The Course of the Dehydration of 5-Hydroxytetrahydro-*exo*-dicyclopentadiene with Acid

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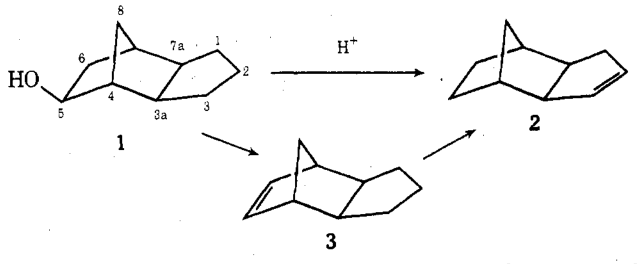
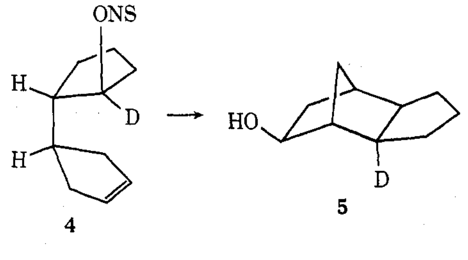
A study of the dehydration of 3a-deuterio-5-hydroxytetrahydro-*exo*-dicyclopentadiene with acid suggests that the formation of 5,6-dihydro-*exo*-dicyclopentadiene proceeds through 2,3-dihydro-*exo*-dicyclopentadiene or the equilibrating ions formed from the latter by protonation followed by a 1,3-hydride shift, a 1,2-hydride shift, and proton loss.

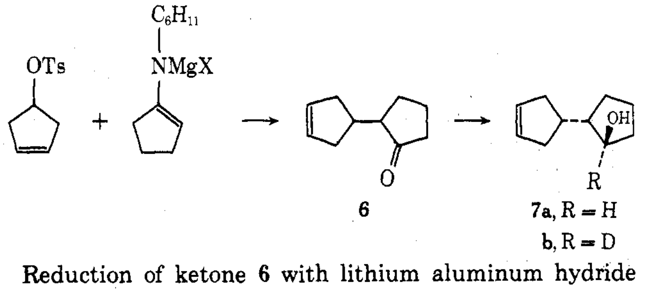
Some years ago it was conclusively shown by Schleyer and Donaldson[2] and simultaneously by Wilder and Youngblood[3] that the dehydration product of 5-*exo*-hydroxytetrahydro-*exo*-dicyclopentadiene[4] (**1**) with 85% phosphoric acid was not the previously suggested[5] 2,3-dihydro-*exo*-dicyclopentadiene (**3**) but 5,6-dihydro-*exo*-dicyclopentadiene (**2**).



We sought to gain some understanding of the course of this remarkable and deep-seated rearrangement by a study of the dehydration of samples of **1** suitably substituted by deuterium, and chose the corresponding 3a-deuterio compound **5** as likely to be illuminating. This substance should be readily available by the π-route solvolysis[6] of a *trans*-2-(3′-cyclopentenyl)cyclopentanol sulfonate (**4**) bearing deuterium at the 1 position.

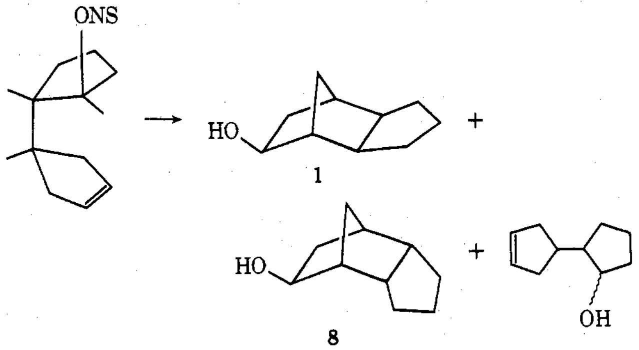


Several approaches to the formation of 2-(3′-cyclopentenyl)cyclopentanone (**6**), from which **4** could easily be made, were explored. The most efficient proved to be the alkylation by 3-cyclopentenyl tosylate of the magnesium salt of the Schiff base formed from cyclohexylamine and cyclopentanone, the procedure of Stork;[7] neither 2-carbethoxycyclopentanone nor the pyrolidine enamine of cyclopentanone could be alkylated successfully with 3-cyclopentenyl tosylate.



Reduction of ketone **6** with lithium aluminum hydride in refluxing ether gave a 1:1 mixture of the two epimeric alcohols, and this ratio was not altered by refluxing the epimeric mixture with aluminum isopropoxide in isopropyl alcohol, a procedure we had hoped would maximize the trans isomer. It was found, however, that by conducting the reaction at low temperatures the trans isomer could be made to predominate, and in tetrahydrofuran at −70° the reduction of **6** with lithium aluminum hydride yields an epimeric mixture with a trans/cis ratio of 5.7:1. In contrast, hydrogenation of **6** over platinum yields a mixture of saturated epimeric alcohols in which the cis isomer predominates (2.2:1).[8]

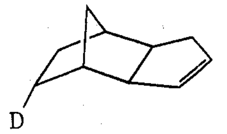
Treatment of mixtures of epimeric alcohols so produced with *p*-nitrobenzenesulfonyl chloride in pyridine at low temperatures gave an unstable, crystalline, sharply melting *p*-nitrobenzenesulfonate, and solvolysis of this substance at 50° in 97% formic acid containing a small amount of sodium formate followed by treatment with lithium aluminum hydride gave **1** in 29% yield along with both cis and trans isomers of 2-(3′-cyclopentenyl)cyclopentanol, and traces (1–5% estimated) of 5,6-dihydro-*exo*-dicyclopentadiene (**2**) and 5-hydroxytetrahydro-*endo*-dicyclopentadiene (**8**), the endo isomer of **1**. The *cis*- and *trans*-2-(3′-cyclopentenyl)cyclopentanols reflect the extent of nonassisted solvolysis[9] and the high ratio of exo isomer to endo isomer **8** is in accord with the observations of Schleyer and Donaldson.[10,11]



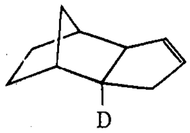
Repetition of this sequence on ketone **6** but using lithium aluminum deuteride for its reduction gave successively a mixture of epimeric alcohols in which **7b** predominated, the *p*-nitrobenzenesulfonate **4**, and finally **5**. A sample of **5**, prepared from **4** containing 98.2% of one deuterium atom per molecule by analysis,[12] also contained 98.2% of one deuterium.

The dehydration of **1** as originally carried out by Bruson gives only moderate amounts of **2**; we found after much experimentation that a much more satisfactory yield is obtained by passing vaporized **1** over a column of glass helices coated with 85% phosphoric acid heated to 180°. Under these conditions three major products, separable by preparative glpc, are formed in ratio of 20:4:1. The major component was **2**, the minor tetrahydro-*endo*-dicyclopentadiene. The remaining component was not identified, but was shown not to be either tetrahydro-*exo*-dicyclopentadiene or adamantane. Yields of purified **2** ranged between 20 and 45%. Under less vigorous conditions appreciable amounts of **3** are formed.

When another sample of monodeuterated alcohol **5** (98.7% of one deuterium, characteristic C–D absorption at 2150 cm^{-1}) was dehydrated in the same way, the olefin **2** obtained had 91.3% of one deuterium per molecule and exhibited infrared absorption at 2178 cm^{-1} with a shoulder at 2152 cm^{-1}.[13] Although the 60-MHz nmr spectra of the product and of undeuterated **2** are poorly resolved, it is possible to infer from a comparison of the two plus some mechanistic assumptions that the product contains 38% of **2a** and 52% of **2b**.



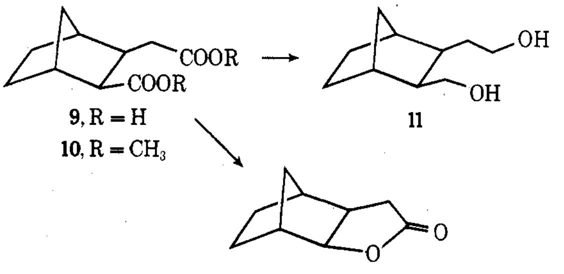
2a



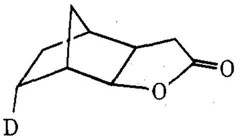
2b

Thus the spectrum of undeuterated **2** exhibits signals centered at δ 5.35 (2 H, olefinic protons), 3.30–1.8 (5.87 H, allylic and methine protons), and 1.8–0.7 (6.23 H, methylene protons), total 14.10 H, whereas **2** produced from **5** (monodeuterated) showed signals in the same ranges whose relative integrations were 2:5.35:5.85, total 13.2 H, respectively. The reduction in absorption in the region δ 1.8–0.7 indicates that 0.38 (6.23 − 5.85) of one deuterium atom occurs in the methylene region and that 0.52 (5.87 − 5.35) of one deuterium occurs in the methine region. Furthermore, within the methylene envelope, the integrated absorption from δ 1.8 to 1.35 is substantially unchanged (2.05 H *vs.* 2.13 H), and it is in this region that Nickon[13] has shown the exo protons of norbornane to absorb (δ 1.4). The reduction in methylene protons thus occurs in the region associated either with the endo 5 (or 6) protons or the bridge methylene protons on carbon 8. A rational set of Wagner–Meerwein rearrangements and hydride shifts will not give rise to deuterium substitution at C$_6$ or C$_8$ of **2** and we therefore conclude that this deuterium is endo at C$_5$.

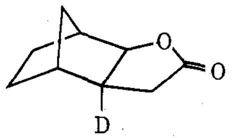
The conclusion that dehydration of **5** gives rise to a mixture of **2a** and **2b** is supported by degradative studies on the dehydration product. On oxidation with permanganate, olefin **2** yields the diacid **9**, readily convertible into the corresponding dimethyl ester **10**, diol **11**, and, following oxidative decarboxylation with lead tetraacetate, into the lactone **12**. This series of reactions, when applied to the dehydration product of **5**, gave diacid **9** containing 86.8% of one deuterium[14] and diester **10** showing C–D stretching absorption at 2183–2188 cm^{-1} with an apparent molar extinction coefficient of 7.3.[15] The absence of an appreciable absorption at 2200 cm^{-1}, the observed[16] C–D absorption of 1-deuterionorbornane, strongly suggests that there is no deuterium at the bridgehead positions. The corresponding diol **11** contained 87.4% of one deuterium and absorbed at 2174 cm^{-1} with an apparent molar extinction coefficient of 8.0. Since there is no significant increase in C–D absorption in going from the diester **10** to the diol **11**, deuterium cannot be located α to either of the carbonyl grounds of **10** and hence not at either 1 or 3a of **2**, since Jones[17] has shown that deuterium substituted α to an ester carbonyl function does not absorb in the region 2100–2200 cm^{-1}. That deuterium cannot be at 3a of **2** is also clear from the nmr spectrum of lactone **12** from the deuterated series, which showed absorption corresponding to one proton as a broadened doublet centered at δ 4.1 and thus must have hydrogen at this position. This spectrum, when compared with that of undeuterated lactone **12**, allows the further conclusion that 43%[14] of one deuterium is present in the group of atoms responsible for absorption between δ 3.82 and 1.70 (the two protons α to the carbonyl and the methine protons) and 32% of one deuterium atom is present in the group responsible for absorption between δ 1.70 and 0.6 (the methylene protons). By elimination, the deuterium in the former group can be assigned to the position β to the carbonyl, since the infrared and nmr evidence adduced earlier has shown that deuterium cannot be α to the carbonyl or at the bridgeheads.



Thus lactone **12** derived from deuterated **2** appears to be a mixture of **12a** and **12b**.



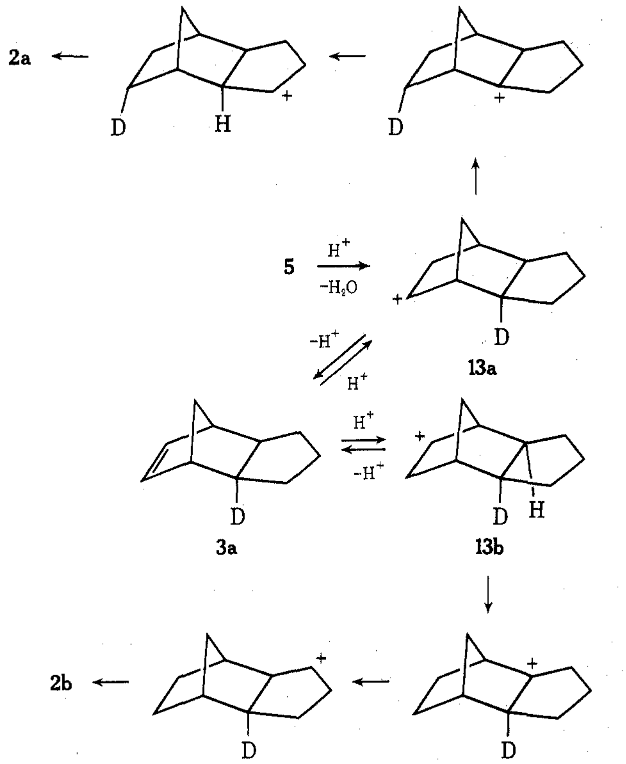
12a



12b

By nmr integration, the ratio of **12a** to **12b** is 1:1.34 and that of **2a** to **2b** is 1:1.37; in view of the uncertainties associated with these nmr integrations, the agreement is perhaps fortuitous.

These data can be accommodated by a reaction course involving a 1,3-hydride shift from position 3a to 5 in the carbonium ions derived from **1**, followed by a 1,2-hydride shift, the final product arising by proton loss.



To the extent that the observed ratio of **2b** to **3a** (1.37) can be relied on, it is consistent with a small positive isotope effect. This value is much smaller than the maximum effect.[18a,b] It may indicate the extent of this hydride transfer in the transition state, although any formation of olefin **2** directly from ion **13a** without equilibration to ion **13b** or conversion to olefin **3a** would lower the ratio of **2b** and **2a** and thus produce an apparent reduction in isotope effect.

A measure of the extent of conversion of **13** directly to olefin **2** without the intermediacy of olefin **3** or equilibration of ions **13a** and **13b** could in principle be obtained by using optically active alcohol **1**. Alcohol **2** derived directly from **1** though ion **13** should retain activity, whereas **2** derived from olefin **3** or subsequent to the equilibration of **13a** and **13b** would, of course, be racemic.

Experimental Section

2-(3′-Cyclopentenyl)cyclopentamone (6). A solution of ethylmagnesium bromide prepared from 27.0 g (0.26 mol) of ethyl bromide and 6.6 g (0.275 mol) of magnesium turnings in 140 ml of dry tetrahydrofuran was added dropwise to 41.4 g (0.25 mol) of the cyclohexylimine of cyclopentanone[19] over a period of 1.5 hr. The reaction mixture was refluxed for 1 hr, cooled to room temperature, and added dropwise over a period of 5 hr to a solution of 62.3 g (0.26 mol) of Δ^3-cyclopentenyl tosylate[20] in 300 ml of dry tetrahydrofuran. The reaction mixture was then refluxed for 18 hr, at which time the pH of the heterogeneous solution was 8–9. The cooled solution was treated with 0.5 equiv of 10% sulfuric acid, refluxed for an additional 3 hr, cooled to room temperature, and extracted with 2 l. of ether. The ethereal solution was washed with 10% hydrogen chloride, 5% sodium bicarbonate, and brine, and dried over anhydrous sodium sulfate. The ethereal extracts, on concentration, afforded a deep-red, viscous liquid, which was distilled under reduced pressure to give 10 g (27%) of a light-yellow liquid, bp 54° (0.5 mm). The pot residue was polymeric.

The uv spectrum of this distillate indicated the presence of cyclopentylidenecyclopentanone. Analysis by glpc (20 ft × 0.375 in. 25% UCON Polar or Anakrom, column temperature 165°, flow rate 100 cc/min) showed two major components with retention times of 32 and 53 min. The two components were collected and examined by infrared analysis. The first component had absorptions characteristic of a cyclopentanone, of a double bond, and of unsaturation in a strainless five-membered ring (1740, 3044, and 1625 cm^{-1}, respectively), while the second component had characteristic absorption frequencies at 1710 and 1640 cm^{-1} which were assinged to the α,β-unsaturated cyclopentylidenecyclopentanone system.

The first component yielded a semicarbazone, mp 180–181° dec.

Anal. Calcd for $C_{11}H_{17}N_3O$: C, 63.77; H, 8.21. Found: C, 63.50; H, 8.25.

2-(3′-Cyclopentenyl)cyclopentanol (7a). A solution of 200 mg (1.33 mmol) of 2-(3′-cyclopentenyl)cyclopentanone in 20 ml of anhydrous ether was added to a threefold excess of lithium aluminum hydride in 20 ml of anhydrous ether at such a rate as to maintain gentle refluxing. Following the addition, the heterogeneous reaction mixture was refluxed for an additional 6 hr. The cold reaction mixture was taken up in additional ether and carefully washed with 5% sodium hydroxide and water. The solution was dried over magnesium sulfate, filtered, and concentrated to give 182 mg of a light-yellow liquid (90%). A thin film infrared analysis indicated the presence of an unsaturated alcohol and the absence of any ketone. This material was shown by glpc (10 ft × 0.125 in. 20% UCON Polar, column temperature 165°, flow rate 26 cc/min) to consist of two major components in equal amounts (retention times 24 and 27.5 min), presumed to be the cis and trans isomers. A 1.46-g sample of a similar mixture was dissolved in 6 ml of isopropyl alcohol containing 13 mg of starting ketone **6** and 0.93 g of freshly distilled aluminum isopropoxide. Refluxing for a period of 1 week failed to change the isomeric ratio as indicated by glpc. The components were identified as cis (retention time 24 min) and trans (27.5 min) by the following observation. A 200-mg neat sample of ketone **6** was shaken with 100 mg of platinum oxide under 2.7 atm of hydrogen for 17 hr. The filtered reaction mixture gave 190 mg of a light-yellow oil, which was shown by infrared analysis to contain ketonic as well as alcoholic material. Three components were present with retention times of 17, 20.5, and 23.5 min (glpc conditions as already described). The first component had the same retention time as the dihydro derivative of ketone **6**. The ratio of the latter two components to one another was 2.2:1. Since these reduction conditions in other instances[8] have given rise to a greater amount of cis product, we assign the cis configuration to the component with the retention time of 20.5 min.

An ethanolic solution of 100 mg of the cis and trans alcohols resulting from the lithium aluminum hydride reduction of ketone **6** was quantitatively reduced over platinum oxide in 5 min at 760 mm. The solution was filtered and concentrated to give 95 mg of a saturated alcoholic mixture as indicated by infrared analysis. Glpc analysis under identical conditions as those previously described showed two components to be present in equal amounts with retention times of 20.5 (cis) and 23.5 min (trans).

Table I indicates the stereospecificity obtained by varying the lithium aluminum hydride reduction conditions.

2-(3′-Cyclopentenyl)cyclopentyl *p*-Nitrobenzenesulfonate. A 17.7-g (0.115 mol) solution of 2-(3′-cyclopentenyl)cyclopentanol, whose trans to cis ratio was 4:1, in 40 ml of anhydrous pyridine was cooled to −24° and treated with three 8.5-g (0.115 mol) portions of recrystallized *p*-nitrobenzenesulfonyl chloride over a period of 1 hr. The reaction was maintained at −24° for 48 hr, taken up in ether, and washed successively with cold 10% hydrogen chloride, 5% sodium bicarbonate, and water. The ethereal extract was dried over magnesium sulfate at low temperatures, filtered, and concentrated *in vacuo* to give 37.5 g of a red oil. The oil was triturated with petroleum ether (bp 30–60°) and a small amount of anhydrous ether to give a murky, heterogeneous solution. From this solution 30 g of a light-yellow powder, mp 58.5-60°, was isolated after cooling to −70°. Further recrystallizations failed to alter the melting point of a small sample. An infrared spectrum showed λ_{max} ($CHCl_3$) 3050, 1375-1350, 1180, and 680 cm^{-1}. An analysis for this compound was not obtained owing to its facile decomposition at room temperature. Many attempts to prepare the above mentioned solid *p*-nitrobenzenesulfonate fail when higher reaction temperatures were employed. Furthermore, a crystalline tosylate could not be obtained by this procedure.

5-Hydroxytetrahydro-*exo*-dicyclopentadiene (1). A. A solution of 50 g (0.27 mol) of 5-formoxydihydro-*exo*-dicyclopentadiene[21] in 250 ml of absolute ethyl alcohol was shaken with 100 mg of platinum dioxide under 2.7 atm of hydrogen for 12 hr. The solution was treated with Norit, filtered through a cake of Celite, diluted with enough ethyl alcohol to bring the total volume to 400 ml, and added to 200 ml of water containing 60 g of sodium hydroxide. This heterogeneous mixture was refluxed for 2 hr, salted with a large volume of saturated sodium chloride, and extracted with ether. The ethereal extracts were washed with saturated sodium chloride and dried over magnesium sulfate. The light-yellow liquid, 39.0 g, obtained from the dried ethereal extracts, was distilled at 71° (0.3 mm) to give 32 g of a colorless, viscous liquid. Two recrystallizations from nitromethane gave 25 g (61%) of a colorless solid, mp 53-55° (reported[22] mp 53-54°). Its phenylurethane melted at 105-106° (reported[22] mp 107-108°).

B. A 1.1-g sample of an oily mixture containing 80% by weight of 2-(3′-cyclopentenyl)cyclopentyl *p*-nitrobenzenesulfonate and 20% of the corresponding alcohol was dissolved in 145 ml of 0.04 *M* sodium formate in 97% formic acid, which had been preheated to 50 ± 2°. The reaction mixture was stirred for 20 hr at this temperature, cooled, and extracted with technical pentane. The pentane extracts were washed with 10% sodium carbonate and water. The sodium sulfate dried extracts yielded 0.681 g of a sweet-smelling yellow oil containing formates and alcohols, λ_{max} (neat) 1735 and 3350 cm^{-1}, respectively, which was reduced with 0.250 g of lithium aluminum hydride in 25 ml of anhydrous ether to give 0.394 g of neutral material. Glpc analysis showed this reaction mixture to contain alcohol 1 (retention time 30 min) as 41% (0.163 g) of the total mixture (10 ft × 0.125 in. UCON Polar on Anakrom, column temperature 165°, flow rate 26 cc/min). The retention time of authentic alcohol 1 was 30 min under these conditions. Trace amounts of 5,6-dihydro-*exo*-dicyclopentadiene (2) and 5-hydroxytetrahydro-*endo*-dicyclopentadiene (8) were detected by comparison with the retention times of authentic samples of each.[2,3,23] In that the sulfonate used in this solvolysis was prepared from a 0.549-g mixture of *cis*- and *trans*-2-(Δ^3-cyclopentenyl)cyclopentanol containing 60% trans by weight, and that complete esterification of the trans alcohol seemed to be a reasonable assumption, the theoretical yield of alcohol 1 was 0.329 g. The observed yield of alcohol 1 was 29% overall or 49% based on trans alcohol.

A 0.380-g sample of the reduced solvolysis reaction mixture in benzene was chromatographed on 38 g of commercial Fischer alumina, monitoring the eluted material by glpc. When such analysis showed 85% of alcohol 1 to be present in a respective fraction, the column was washed with 9:1 ether-methanol, which gave 0.100 g of a light-yellow oil. Its phenylurethane melted at 105-106°, undepressed on mixture with the phenylurethane of authentic alcohol 1, mp 106-107.5°. The infrared spectra of the two urethanes were identical. However, it was impossible to crystallize the ether-methanol eluted material.

5,6-Dihydro-*exo*-dicyclopentadiene (2). A slow stream of nitrogen was passed into a 10-ml pear-shaped two-neck flask charged with 5.0 g of 5-hydroxytetrahydro-*exo*-dicyclopentadiene (1). The flask was in turn connected to a hot (180 ± 5°) 8 × 0.5 in. horizontal column packed with glass helices, which had previously been coated with 85% phosphoric acid. The column in turn was connected to two traps maintained at 0°.

The charged flask was heated by means of an infrared lamp such that the sample was vaporized over a period of 3 hr. Nitrogen was swept through the system for an additional 2 hr, the trapped material was taken into ether, and the ethereal solution was washed with 5% sodium bicarbonate and water. The magnesium sulfate dried solution afforded 4 g of a colorless liquid, which was chromatographed on 80 g of No. I Woelm alumina to give 3.9 g of petroleum ether eluted material (86% of theoretical), n^{21}D 1.5020 (reported[24] n^{25}D 1.4990). This sample, which was analyzed by glpc on a 150-ft UCON Polar Golay column at 90°, consisted of three major components in the ratio of 20:4:1 (retention times 27, 30, and 33 min). The reaction mixture was separated by preparative glpc (20 ft × 0.375 in. 20% Apiezon L, column temperature 130°, injector temperature 180°, flow rate 100 cc/min, retention times 37, 40.4, and 48 min). The retention time of authentic 5,6-dihydro-*exo*-dicyclopentadiene under these conditions was 37 min. The infrared spectrum of authentic material was identical with that of the material collected.

Table I
Effect of Temperature on the Isomeric Ratio of Cis and Trans Alcohols from Reduction of Ketone 6

Medium	Temp, °C	Trans:cis
$LiAlH_4$–Et_2O	Reflux	50:50
$LiAlH_4$–THF	25	78:22
$LiAl(t\text{-}BuO)_3H_4$–THF	25	65:35
$LiAlH_4$–THF	0	80:20
$LiAlH_4$–THF	−70	85:15

Anal. Calcd for $C_{10}H_{14}$: C, 89.55; H, 10.45. Found: C, 89.27; H, 10.33.

For several runs the overall yield of purified olefin was 20-45%.

The material corresponding to the retention time of 48 min was identified as tetrahydro-*endo*-dicyclopentadiene by comparison with authentic material (retention time 48.5 min) prepared by total hydrogenation of commercial dicyclopentadiene over platinum oxide. The infrared spectra of the two samples were essentially identical. The authentic material melted at 79-81°, while the material collected from the reaction mixture melted at 80-82°, and an admixture melted at 77-80°.

The remaining component was shown not to have a retention time that corresponded with that of authentic samples of tetrahydro-*exo*-dicylopentadiene or adamantane. Because of the poor separation of this component and olefin 2, a sample was not obtained in a sufficiently pure state to permit its positive identification. Although the retention time of 40.4 min corresponds most closely with that of 5,6-dihydro-*endo*-dicyclopentadiene, the nmr spectrum suggests the absence of a bridged system inasmuch as there is only a small contribution to the spectrum at δ 2.

5-*endo*-Hydroxydihydro-*exo*-dicyclopentadiene. A solution containing 4.04 g (0.028 mol) of 5-ketodihydro-*exo*-dicyclopentadiene[22] in 100 ml of anhydrous ether was added with external cooling to 0.685 g (0.018 mol) of lithium aluminum hydride in 23 ml of anhydrous ether at such a rate as to maintain the reaction temperature at 0 ± 3°. Following the addition the stirred solution was allowed to come to room temperature and stand for a period of 12 hr. An infrared spectrum of the recovered reduced material (4.10 g) indicated the presence of an alcohol and the absence of starting ketone. A 200-mg sample was further purified by a short-path distillation, bp 75° (1 mm), yielding 190 mg of a colorless liquid. The nmr spectrum (deuteriochloroform with deuterium oxide) showed absorptions at δ 5.58 (2 H), 4.2 (0.85 H), 3.8 (0.15H), and 3.0-0.7 (10 H). A 100-mg (0.66 mmol) sample of the alcoholic distillate was mixed with 80 mg (0.68 mmol) of distilled phenyl isocyanate and heated to 85° for 1 hr. The semisolid reaction mixture was cooled and triturated with petroleum ether to give 130 mg of a colorless solid, mp 85-105°. Two recrystallizations from ethyl alcohol gave 100 mg (60%) of a phenylurethane, mp 118-119.5°.

Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.84; H, 7.06. Found: C, 75.65; H, 7.20.

The nmr spectrum of the endo urethane showed absorptions at δ 7.6-6.6 (6 H), 5.52 (2 H), and 3.4-0.7 (10 H).

A 1.5-g (6 mmol) sample of the endo urethane was refluxed with 400 mg of lithium aluminum hydride in 20 ml of dry tetrahydrofuran for 18 hr. The dried neutral ethereal extracts afforded 890 mg (99% crude) of a light yellow oil, λ_{max} (neat) 3400 (s), 3050, and 1700 cm^{-1} (w).

3-Hydroxy-2-norbornaneacetic Acid Lactone (12). A solution containing 0.300 g (1.5 mmol) of 3-carboxy-2-norbornaneacetic acid (9),[2] 0.24 g (3.0 mmol) of dry pyridine, and 0.800 g (1.8 mmol) of lead tetraacetate in 10 ml of dry benzene was gently refluxed for 1.5 hr, cooled, filtered, and washed successively with 5% sodium carbonate, 10% hydrogen chloride, and water. The sodium sulfate dried extracts afforded 0.131 g (57%) of a slightly yellow oil, λ_{max} (neat) 1765-1760 cm^{-1} with a small shoulder at 1740 cm^{-1}. Glpc analysis on a 150-ft UCON Polar Golay column at 170° indicated that the reaction mixture was at least 95% pure (retention time 2 hr). An analytical sample was prepared by preparative glpc (5 ft × 0.25 in. 20% UCON Polar, column temperature 170°, flow rate 60 cc/min, retention time 15 min).

Anal. Calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: C, 71.49; H, 8.31.

The nmr spectrum showed a poorly resolved quartet centered at δ 4.43 (1 H), and complex absorptions at δ 2.60–0.7 (11.14 H).

2-(3′-Cyclopentenyl)-1-deuteriocyclopentyl *p*-Nitrobenzenesulfonate (4). A 47-g sample of 2-(3′cyclopentenyl)-1-deuteriocyclopentyl *p*-nitrobenzenesulfonate, mp 59–60°, was prepared from 40 g of 2-(3′-cyclopentenyl)cyclopentanone by using those procedures already outlined in the hydrogen series. Thus, the ketone in 2 l. of tetrahydrofuran was reduced with 3.5 g of lithium aluminum deuteride and the resulting 41 g of isomeric alcohols was converted into the sulfonate at −24°.

The 3,5-dinitrobenzoate of the corresponding alcohol was prepared, mp 86°, and analyzed for deuterium by combustion techniques.[25]

Anal. Calcd for $C_{17}H_{17}N_2O_6D$: D, 5.55 atom %. Found: D, 5.45 atom %.

3a-Deuterio-5-hydroxytetrahydro-*exo*-dicyclopentadiene (5). A. A mixture of 1.5 l. of 97% formic acid and 19 g (0.28 mol) of sodium formate was preheated to 50 ± 2° and treated with 47 g (0.14 mol) of 2-(3′-cyclopentenyl)-1-deuteriocyclopentyl *p*-nitrobenzenesulfonate. The resultant black reaction mixture was stirred at 50 ± 2° for 9 hr, diluted with water, and extracted with petroleum ether. The extracts were washed with 10% sodium carbonate and water. The magnesium sulfate dried solution afforded 22.3 g of a red oil, which was refluxed for 4 hr with 4.8 g of lithium aluminum hydride in 300 ml of anhydrous ether. The reduction mixture gave 20 g of a red oil, which was distilled to give 6.5 g of material, bp 48–68° (0.5 mm). This was shown by glpc analysis *to contain approximately 83% of* **5** *relative to the isomeric alcohols present.* This 6.5 g of distillate was triturated with nitroethane to give 2 g of alcohol **5**, mp 50–53°. The mother liquors afforded 4.2 g of a colorless liquid which was chromatographed in benzene on 300 g of Fischer alumina. The column was washed with 7 pints of benzene, giving only trace amounts of eluted material, and was then eluted with 9:1 benzene ether. The course of the chromatography was followed by glpc. When the ratio of alcohol **5** to isomeric alcohols was shown to be 5:1; the column was washed with 9:1 ether–methanol to give 2.8 g of a colorless oil. This oil afforded 1 g of alcohol **5**, mp 51–53°, from nitroethane. This represents a yield of 7.4% based on ketone **6**.

An 80-mg sample was recrystallized from 100 mg of nitroethane and sublimed at 30–33° (0.1 mm) to give 55 mg of alcohol **5**, mp 54.2–55° (reversibly), λ_{max} (CCl_4) 2150 cm^{-1}.

Anal. Calcd for $C_{10}H_{15}OD$: D, 6.25 atom %. Found: D, 6.14 atom %.

B. A 30-g sample of 2-(3′-cyclopentenyl)-1-deuteriocyclopentyl *p*-nitrobenzenesulfonate was added to 750 ml of dry glacial acetic acid preheated to 50 ± 2°. *The solid containing reaction mixture* after 8 hr was worked up in the manner above. An 800-mg sample of alcohol **5**, mp 50–54°, was obtained.

Dehydration of 3a-Deuterio-5-hydroxytetrahydro-*exo*-dicyclopentadiene (5). The samples of alcohol **5** obtained in the formolysis and acetolysis reactions described in the preceding section were combined and recrystallized from nitroethane to give 3.1 g of a colorless solid, mp 52–55°. A 100-mg sample was recrystallized and sublimed at 35° (0.1 mm), mp 53–54°.

Anal. Calcd for $C_{10}H_{15}OD$: D, 6.25 atom %. Found: D, 6.17 atom %.

The remaining 3.0-g sample was dehydrated by passing it through a column of glass helices at 180° coated with 85% phorphoric acid, as described in the preparation of olefin **2**. The infrared spectrum of a sample of the 723 mg (27%) of preparative glpc purified deuterated olefin **2** showed C–D absorption at 2178 cm^{-1} with a shoulder at 2150 cm^{-1} (carbon tetrachloride). The neat nmr spectrum integrated to 13.19 protons with absorptions at δ 5.55 (2 H, reference), 3.3–1.8 (5.35 H), 1.8–1.35 (2.05 H), and 1.35–0.7 (3.8 H).

Anal. Calcd for $C_{10}H_{13}D$: D, 7.14 atom %. Found: D, 6.52 atom %.

5-*endo*-Deuteriodihydro-*exo*-dicyclopentadiene. To 0.336 g (0.008 mol) of lithium aluminum deuteride in 15 ml of dry tetrahydrofuran was added 1.58 g of crude 5-*exo*-dihydro-*exo*-dicyclopentadienyl *p*-toluenesulfonate in 10 ml of dry tetrahydrofuran. The reaction mixture was refluxed for 17 hr and worked up to give 836 mg of a colorless oil. This was chromatographed on 20 g of No. I Woelm alumina, affording 390 mg of petroleum ether eluted material. Further purification by glpc (15 ft × 0.25 in. SF-96, column temperature 90°, flow rate 52 cc/min) gave 250 mg of deuterio olefin, retention time 25 min. This 250-mg sample was distilled at 40° (21 mm) to give 200 mg of a colorless olefin, λ_{max} (CCl_4) 2184 cm^{-1} with a shoulder at 2160 cm^{-1} (reported[22] endo "C–D" stretch 2185 cm^{-1}, shoulder at 2160 cm^{-1}). The nmr showed absorptions at δ 5.6 (2 H), 3.0–1.84 (5.45 H), and 1.84–0.7 (4.78 H).

5-*exo*-Deuteriodihydro-*exo*-dicyclopentadiene. A solution of 1.83 g of 5-*endo*-dihydro-*exo*-dicyclopentadienyl *p*-toluenesulfonate in 50 ml of dry tetrahydrofuran was refluxed with 0.390 g of lithium aluminum deuteride for 48 hr. The isolated 937 mg of yellow oil was chromatographed on 25 g of No. I Woelm alumina to give 150 mg of petroleum ether eluted olefin. Glpc analysis (15 ft × 0.25 in. SF-96, *column temperature* 100°, *flow rate* 50 *cc/min*) indicated that 72% of the mixture was olefin, retention time 12 min. Without further purification the crude olefin ws submitted to an infrared analysis. The spectrum (carbon tetrachloride) showed C–D stretch at 2174 cm^{-1} (reported[13] exo C–D stretch 2170 cm^{-1} for *endo*-deuterionorbornane).

Oxidation of Deuterated Olefin 2 Prepared from Alcohol 5. A 560-mg (4.17 mmol) sample of deuterated 5,6-dihydro-*exo*-dicyclopentadiene (**2**) prepared from alcohol **5** in 15 ml of A.R. Acetone was stirred with 1.85 g (11.7 mmol) of potassium permanganate and 0.100 g (5.57 mmol) of water for 18 hr. After recrystallization from water, 400 mg of deuterated 1,3-diacid **9** was isolated, mp 163–163.5° (reported[2] mp 165°).

Anal. Calcd for $C_{10}H_{13}O_4D$: D, 7.14 atom %. Found: D, 6.20 atom % with 1% residue.

Esterification of Deuterated Diacid 9. An 80-mg (0.4 mmol) sample of deuterated diacid **9** in 10 ml of anhydrous ether was treated with enough ethereal diazomethane, generated from Diazald, to give a permanent (15 min) yellow solution. This solution was *concentrated in vacuo to give 91 mg of a colorless liquid* which was chromatographed on 10 g of Fischer alumina. A 71-mg (78%) sample of a colorless benzene-eluted liquid was isolated, homogeneous to glpc analysis (15 ft × 0.25 in. 20% UCON Polar at 190°, flow rate 100 cc/min, retention time 57 min). A 52.7-mg sample in 0.265 ml of carbon tetrachloride showed C–D absorption at 2188–2184 cm^{-1} with an apparent molecular extinction coefficient of 7.3.

A 71-mg sample of this deuterated dimethyl ester was refluxed with 100 mg of lithium aluminum hydride in 20 ml of anhydrous ether for 12 hr to give 75 mg of an extremely viscous oil, which was chromatographed on 1 g of Fischer alumina. The 40 mg of purified viscous diol showed C–D absorption at 2174 cm^{-1} with an apparent molecular extinction coefficient of 8.

Anal. Calcd for $C_{12}H_{17}O_4D$: D, 5.55 atom %. Found: D, 4.85 atom %.

Deuterated Lactone 12. A 300-mg sample of deuterated diacid **9** was converted into 126 mg of crude deuterated lactone **12** according to the procedure described for the formation of lactone **12**. *This* 126 *mg of yellow liquid was chromatographed on* 2.5 g of Fischer alumina to give 66.2 mg of deuterated lactone **12** containing silicone grease.

A sample of this mixture containing 46.6 mg of the lactone and a 73.1-mg sample of naphthalene was dissolved in carbon tetrachloride. The nmr spectrum showed absorptions for the lactone at δ 4.32–3.82 (0.95 H), 3.82–1.7 (4.57 H), and 1.70–0.6 (5.80 H). The presence of silicone grease was evident from its characteristic absorption at δ 0.1. This mixture was chromatographed to give a sample of lactone, which showed C–D absorption at 2187 cm^{-1}.

Anal. Calcd for $C_9H_{11}O_2D$: D, 8.33 atom %. Found: D, 6.90 atom %.

Infrared spectra were recorded on a Perkin-Elmer 421 spectrophotometer. Aerograph Models A-700, 600, and A-90-P were used for glpc analyses. All nmr spectra were recorded on a Varian A-60 nuclear magnetic resonance spectrometer. Boiling and melting points are uncorrected.

Registry No. 1, 10271-44-0; **2,** 3129-29-1; **2a,** 42913-47-3; **2b,** 42913-48-4; **4,** 42913-49-5; **5,** 42913-50-8; **6,** 42908-41-8; **6** semicarbazone, 42908-42-9; *cis*-**7a,** 43027-55-0; *trans*-**7a,** 43000-59-5; **9,** 43000-60-8; **9**-*d*, 42912-45-8; **10**-*d*, 42912-46-9; **12,** 33045-15-7; **12a,** 42913-35-9; **12b,** 42913-36-0; ethyl bromide, 74-96-4; cyclohexylimine cyclopentanone, 42908-34-9; 2-(3′-cyclopentyl)cyclopentyl *p*-nitrobenzenesulfonate, 42908-35-0; 5-formyloxydihydro-*exo*-dicyclopentadiene, 42913-37-1; 5-*endo*-hydroxydihydro-*exo*-dicyclopentadiene, 42913-38-2; 5-ketodihydro-*exo*-dicyclopentadiene, 42913-39-3; 5-*endo*-hydroxydihydro-*exo*-dicyclopentadiene phenylurethane, 42913-40-6; 5-*exo*-dihydro-*exo*-dicyclopentadiene *p*-toluenesulfonate, 42913-41-7; 5-*exo*-deuteriodihydro-*exo*-dicyclopentadiene, 42913-42-8; 5-*endo*-dihydro-*exo*-dicyclopentadienyl *p*-toluenesulfonate, 42913-43-9; *trans*-2-(3′-cyclopentenyl)-1-deuteriocyclopentyl 3,5-dinitrobenzoate, 42913-44-0.

References and Notes

(1) Hooker, Fellow, 1964–1965; Union Carbide Fellow, 1963–1964.

(2) P. v. R. Schleyer and M. M. Donaldson, *J. Amer. Chem. Soc.*, **78**, 5702 (1956).

(3) P. Wilder, Jr., and G. T. Youngblood, *J. Amer. Chem. Soc.*, **78**, 5706 (1956).

(4) For convenience, we name this and related substances as derivatives of dicyclopentadiene but use the *Chemical Abstracts* numbering.

(5) H. A. Bruson and T. W. Riener, *J. Amer. Chem. Soc.*, **70**, 2809 (1948).

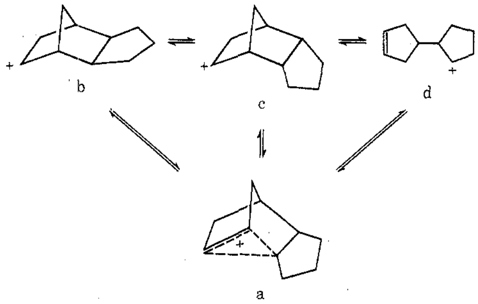
(6) (a) W. S. Johnson, D. M. Bailey, R. Owyang, R. A. Bell, B. Jaques, and J. K. Crandall, *J. Amer. Chem. Soc.*, **86**, 1959 (1964); (b) P. D. Bartlett, S. Bank, R. J. Crawford, and G. H. Schmid, *ibid.*, **87**, 1288 (1965); (c) R. G. Lawton, *ibid.*, **83**, 3399 (1961); (d) G. LeNy, *C. R. Acad. Sci.*, **251**, 1526 (1960); (e) H. L. Goering and M. F. Sloan, *J. Amer. Chem. Soc.*, **83**, 1397, 1992 (1961); (f) S. Winstein and P. Carter, *ibid.*, **83**, 4485 (1961).

(7) G. Stork and S. R. David, *J. Amer. Chem. Soc.*, **85**, 2178 (1963).

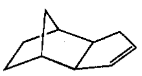
(8) W. Hückel and H. Kindler, *Ber.*, **80**, 202 (1947), have shown that hydrogenation of 2-methylcyclopentanone over platinum gives predominantly *cis*-2-methylcyclopentanol, and it was by analogy to this finding that we have assigned configuration to our reduction products. Similar reduction of our epimeric mixture of unsaturated alcohols (see Experimental Section) allowed glpc comparisons of the mixtures of saturated epimeric alcohols prepared in these two ways.

(9) P. D. Bartlett, S. Bank, R. J. Crawford, and G. H. Schmid, *J. Amer. Chem. Soc.*, **87**, 2188 (1965), found a ratio of cyclized to uncyclized products of 2.6:1 in the acetolysis of 1-(3′-cyclopentyl)-2-propyl *p*-nitrobenzenesulfonate and further found that, in going from the primary 2-(3′-cyclopentenyl)ethyl *p*-nitrobenzenesulfonate to the secondary 1-(3′-cyclopentenyl)-2-propyl *p*-nitrobenzenesulfonate, the unassisted solvolysis to give uncyclized products is enhanced considerably, whereas assisted solvolysis to give cyclized material is little changed.

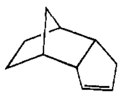
(10) The bridged ion a formed in this solvolysis is in equilibrium with the three classical ions b, c, and d, and Schleyer [P. v. R. Schleyer and M. M. Donaldson, *J. Amer. Chem. Soc.*, **82**, 4645 (1960)] has shown that the products formed from this system in the presence of sulfuric acid are derived almost exclusively from structure b.



(11) We anticipated the predominant formation of the exo isomer **1** in solvolysis in formic acid, since Schleyer (ref 10) has shown that in this solvent equilibrium between e and f appears to be reached and this equilibrium favors the exo isomer e 99:1.



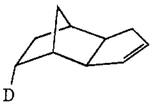
e



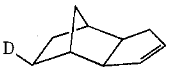
f

(12) All deuterium analyses were carried out by Mr. Joseph Nemeth by the falling-drop method.

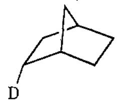
(13) Compounds g and h, prepared by $LiAlD_4$ reduction (with inversion of the corresponding exo and endo tosylates, respectively (see Experimental Section), show C–D stretching absorption at 2184 cm^{-1} with a shoulder at 2160 and 2174 cm^{-1}, respectively. These data agree well with the values reported by Nickon and Hammons [*J. Amer. Chem. Soc.*, **86**, 3322 (1964)] for i and j, *i.e.*, 2185 cm^{-1}, shoulder at 2160 and 2170 cm^{-1}, respectively.



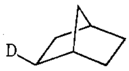
g



h



i



j

(14) In this or subsequent compounds derived from it, the lower deuterium content is considered to be a reflection of contamination of the samples by silicone grease, shown to be present by its characteristic absorption at δ 0.1 in the nmr. On the scale of these experiments, processing to remove this contaminant seemed impractical.

(15) Calculated according to N. Jones and C. Sandorfy, "Technique of Organic Chemistry," Vol. IX, A. Weissberger, Ed., Interscience, New York, N. Y., 1956, p 271.

(16) A. Nickon and J. H. Hammons, *J. Amer. Chem. Soc.*, **86**, 3322 (1964).

(17) R. N. Jones and B. Nolin, *Can. J. Chem.*, **34**, 1382 (1956).

(18) (a) L. Melander, "Isotope Effects on Reaction Rates," Ronald Press, New York, N. Y., 1960, p 22. (b) After this work was completed, Lee's study of the acetolysis and formolysis of 2-(Δ^3-cyclopentenyl)-2-^{14}C-ethyl *p*-nitrobenzenesulfonate appeared [*J. Amer. Chem. Soc.*, **88**, 2834 (1966)]. His results suggest that some equilibration between **13a** and **13b** (as much as 12% in the analogous norbornyl case studied by Lee) may take place during the formation of **5** by the π route solvolysis of **4**. Any such equilibration would lead to a further apparent reduction in isotope effect but would not affect our main conclusions.

(19) K. Jewers and J. McKenna, *J. Chem. Soc.*, 2209 (1958).

(20) S. Winstein, E. L. Allred, and J. Sonnenberg, *J. Amer. Chem. Soc.*, **81**, 5833 (1959).

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(22) H. A. Bruson and T. W. Riener, *J. Amer. Chem. Soc.*, **67**, 727 (1945).

(23) S. J. Cristol, W. F. Seifert, and S. B. Soloway, *J. Amer. Chem. Soc.*, **82**, 2351 (1960).

(24) P. D. Bartlett and A. Schneider, *J. Amer. Chem. Soc.*, **68**, 6 (1946).

(25) This analysis was carried out for us through the courtesy of Drs. David Stewart and T. Reagan, Eastman Kodak Laboratories, Rochester, N. Y.