A Reinvestigation of the Direction of Acid-Catalyzed Ring Opening of Substituted Spirocyclopropylcyclohexadienones[1]

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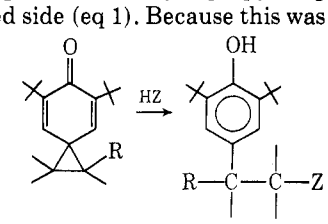
The reactions of 1-methyl-4,6-di-*tert*-butylspiro[2.5]octa-3,6-dien-5-one (**5b**) and 1,1-dimethyl-4,6-di-*tert*-butylspiro[2.5]octa-3,6-dien-5-one (**5c**) with various acidic reagents have been reinvestigated. In agreement with previous work, but in disagreement with that which would be concluded by using structural assignments from the literature, the cyclopropyl ring is shown to open from the more substituted side. The reason for the confusion is traced to the occurrence of aryl rearrangements, undetected by the previous investigators, during both the $LiAlH_4$ reduction of related 2-substituted 2-bromo-4′-hydroxy-3′,5′-di-*tert*-butylacetophenones (**1b** and **1c**) and the reaction of 2-(3′,5′-di-*tert*-butyl-4′-hydroxyphenyl)-1-propyl tosylate (**7b**) with LiBr in acetone.

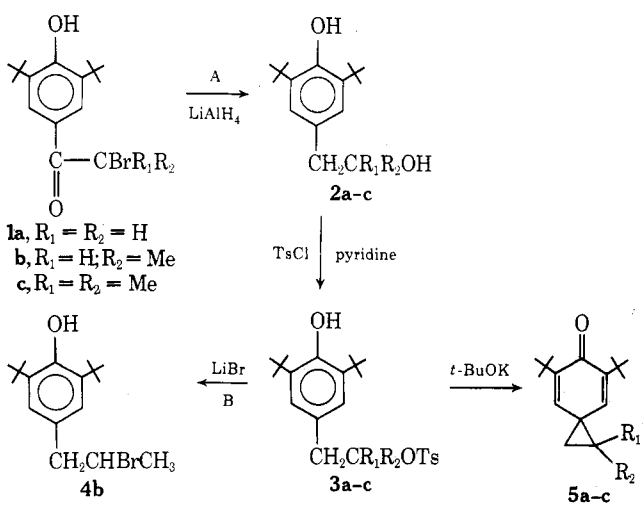
For several years, investigations have proceeded in our laboratory and that of Ershov on the reactions of 4-substituted hindered phenols. We have previously shown that some of the structural assignments made by the Russian workers were in error.[3] Using the corrected structures, a reinterpretation of the work done by Belostotskaya, Volod'kin, and Ershov[4] on the ring-opening reactions of various spirocyclopropylcyclohexadienones under acidic conditions suggests that the cyclopropyl ring opens from the less substituted side (eq 1). Because this was contrary to our



(1)

expectations, we decided to reinvestigate this work. The proposed reaction products, from both laboratories, are summarized in Charts I–IV.

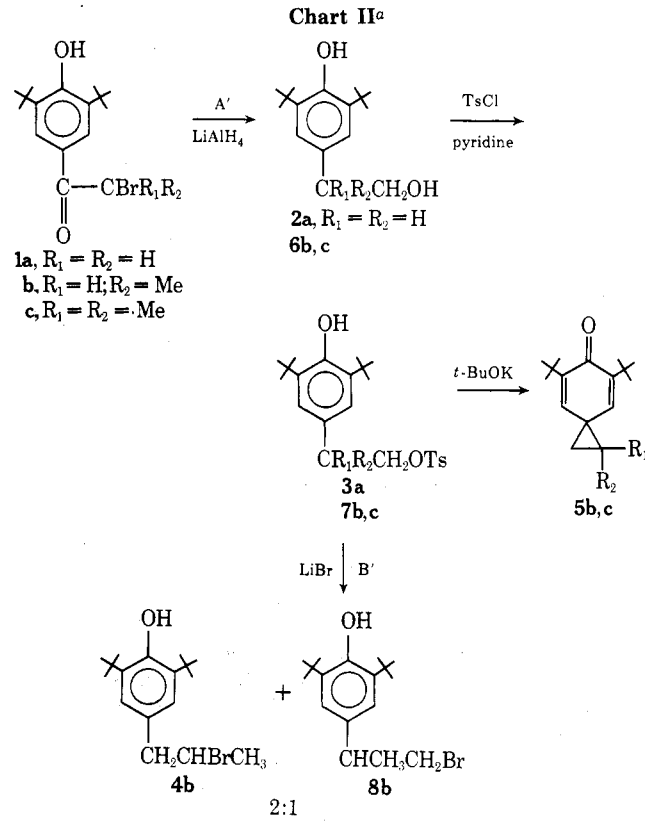
Chart I[a]



[a] The assignments shown are those of Ershov and coworkers.

Ershov, Volod'kin, and Portnykh first reported the $LiAlH_4$ reduction of 2-bromo-(3′,5′-di-*tert*-butyl-4′-hydroxy)acetophenone (**1a**) (Chart I).[5] Subsequently, the reduction products of 2-bromo-(3′,5′-di-*tert*-butyl-4′-hydroxy)propiophenone (**1b**) and 2-bromo-2-methyl-(3′,5′-di-*tert*-butyl-4′-hydroxy)propiophenone (**1c**) were described (Chart I).[6] Our first work reported the reduction of **1a** with $LiAlD_4$.[7] From the fact that this product had the structure $ArCH_2CD_2OH$, we concluded, in contrast to the earlier work,[5] that the reduction proceeds with aryl ring migration. We subsequently showed that the products from the $LiAlH_4$ reduction of **1b** and **1c** were **6b** and **6c**, respectively (Chart II),[3] rather than **2b** and **2c** (Chart I).[6]

Chart II[a]

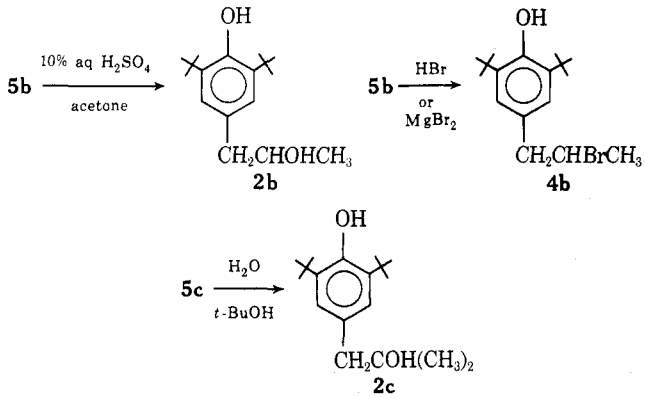


[a] Our results.

The Russian workers had used their structures, **2b** and **2c**, to assign structures to the products of the reactions shown in Chart III. Because the actual structures are **6b** and **6c**, respectively, a reinterpretation of these ring-opening reactions leads to the conclusion that the cyclopropyl ring opens from the less substituted side. This direction of ring opening is contrary to our expectations that the cleavage would be controlled by the stability of the incipient cationic center.[8]

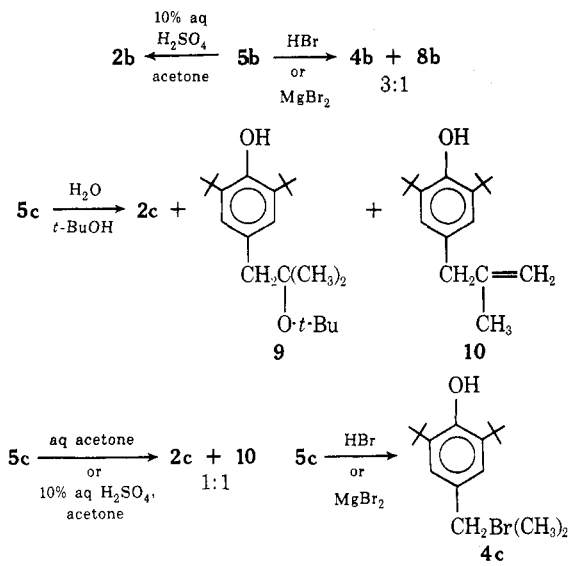
Chart IV summarizes our results. To our surprise we found that the products shown in the reactions of Chart III are in fact correct. As we had expected, the cyclopropyl ring does open mainly from the more substituted side,

Chart III[a]



[a] The assignments shown are those of Ershov and coworkers.

Chart IV[a]



[a] Our results.

rather than from the less substituted side as the reinterpreted results of the Russian workers would indicate.

The preparation of 2-(3′,5′-di-*tert*-butyl-4′-hydroxyphenyl)-1-propanol (**6b**) has been described previously.[3] The preparation of its tosylate (**7b**) was accomplished in a manner similar to an earlier synthesis by Volod'kin, Belostotskaya, and Ershov.[9] The nmr spectrum was consistent with structure **7b**. Comparison to the nmr spectrum of alcohol **6b** is indicative, *viz.*, $CH_3CHArCH_2OH$, δ 1.28, 2.85, and 3.66, respectively, and $CH_3CHArCH_2OTs$, δ 1.25, 2.98, and 4.01, respectively. The structure $ArCH_2CHCH_3OTs$ (**3b**), proposed by the Russian workers, should exhibit methylene absorption near δ 2.76, as was found in $ArCH_2CD_2OH$.[6] However, the observed absorption at δ 4.01 is too far downfield to support this claim. We conclude that the Russian workers had tosylate **7b** rather than **3b**. If the reaction of this tosylate (**7b**) with LiBr proceeds by way of a simple displacement, as previously assumed,[4] then bromide **8b** would be formed. Since this bromide was claimed[4] to be the same as that formed from spiran **5b**, it would follow that the cyclopropyl ring opens from the less substituted side.

The critical reaction to investigate was now step B′ of Chart II. We repeated the previous procedure[4] with LiBr in acetone on tosylate **7b** and obtained a mixture whose nmr spectrum indicated the presence of approximately 67% 1-(3′,5′-di-*tert*-butyl-4′-hydroxyphenyl)-2-bromopropane (**4b**) and 33% 1-bromo-2-(3′,5′-di-*tert*-butyl-4′-hydroxyphenyl)propane (**8b**). The structure of **4b** follows on comparison with the nmr spectrum of 1-phenyl-2-bromopropane, *viz.*, $ArCH_2CHBrCH_3$, δ 3.07, 4.25, and 1.64, respectively, and $PhCH_2CHBrCH_3$, δ 3.11, 4.26, and 1.63, respectively. In order to confirm the structure of the minor product, **8b**, we attempted a direct bromination of alcohol **6b** with triphenylphosphine dibromide.[10] The bromination was successful and allowed us to identify the minor product as **8b**. However, efforts at removing small amounts of triphenylphosphine oxide during purification were unsuccessful and led to isomerization to **4b**. The product that the Russian group isolated in the LiBr–acetone reaction was apparently only the major product, **4b**. It is clear that the principal reaction of step B′ occurs with aryl ring migration. The sequence of reactions shown in Chart I therefore contains two aryl rearrangement steps (compare steps A and B with A′ and B′, respectively, of Chart II) that previously[4,6] went undetected.

The preparation of spiran **5b** was achieved by a minor variation of an earlier synthesis.[9] In our hands, reaction of **5b** with either HBr or $MgBr_2$ produced similar mixtures of products containing *ca.* 75% **4b** and 25% **8b**. Owing to the fortuitous cancellation of two errors in structural assignments, the Russian workers did in fact postulate the correct structure for the major product of the ring-opening reactions of **5b** with HBr and $MgBr_2$, and the ring does open predominantly from the more substituted side.

The reaction of spiran **5b** with 10% H_2SO_4 in acetone yielded the reported[4] secondary alcohol **2b** as the major product. Therefore, the ring opens from the more substituted side. The confusion here is that this secondary alcohol was previously[4] incorrectly identified as being the same alcohol as obtained from step A of Chart I. If this is correct, and since it is now known that the correct structure of the product from step A is **6b** (see step A′ of Chart II), one would conclude that the ring opens from the less substituted side. To confirm the structure of the alcohol product, **2b**, from **5b**, we repeated the synthesis of **2b**[11] and compared the nmr spectrum to that of 1-phenyl-2-propanol. Apparently, the previous conclusion of the identity of the alcohols from **5b** and step A was based solely on similarity of melting points.[12a,b] To investigate the possibility that **6b** forms first and subsequently rearranges to **2b**, we subjected **6b** to the reaction conditions. A quantitative recovery of **6b** was obtained.

The preparation of spiran **5c** was achieved in a manner similar to that used by the Russian workers.[9] Reaction of **5c** with aqueous *tert*-butyl alcohol was previously reported to yield only the tertiary alcohol **2c**.[4] In our hands this reaction was not reproducible and yielded a mixture containing alcohol **2c**, olefin **10**, and possibly ether **9**, in varying amounts. The structure of alcohol **2c** was confirmed by an independent synthesis, and its nmr spectrum, $ArCH_2COH(CH_3)_2$, δ 2.68 and 1.21, respectively, is quite different from that of isomer **6c**, $ArC(CH_3)_2CH_2OH$, δ 1.32 and 3.57, respectively. The product from the ring opening of **5c**, alcohol **2c**, was previously incorrectly identified[4] as being the same alcohol as obtained from step A of Chart I (compare step A′, Chart II).[4] This conclusion was apparently based on similarity of melting points.[12b,c] The presence of olefin **10** in the reaction mixture was indicated by comparison of the nmr spectrum, $ArCH_2CCH_3{=}CH_2$, δ 3.23, 1.70, and 4.71, respectively, to that of $PhCH_2CCH_3{=}CH_2$, δ 3.25, 1.62, and 4.75, respectively. The presence of ether **9** was indicated by a singlet at δ 2.63 (CH_2), additional absorption at δ 1.23 [$OC(CH_3)_3$], and additional absorption in the aromatic region. Further efforts to confirm its structure were not undertaken.

We also studied the ring-opening reactions of **5c** with aqueous acetone and 10% H_2SO_4 in acetone. In each case, the product consisted of a mixture containing approximately equal amounts of **2c** and **10**. In all three cases of ring opening in aqueous solvents, control experiments were performed which established the stability of alcohol **6c** under the reaction conditions.

The Russian workers did not indicate whether they studied the reactions of spiran **5c** with HBr or $MgBr_2$. We performed these experiments and in both cases found the product mixture to consist almost entirely of the tertiary bromide **4c**. The structure of the reaction product was established by comparison of its nmr spectrum with that of an independently synthesized sample.

It is clear from these results that spirodienone **5c** also undergoes cyclopropyl ring opening at the more substituted carbon atom.

Experimental Section[13]

2-(3′,5′-Di-*tert*-butyl-4′-hydroxyphenyl)-1-propyl Tosylate (7b). Compound **7b** was prepared according to the previous procedure:[9] mp 98.5–100.0° (lit.[8] mp 84–86°); nmr δ 7.79, 7.65, 7.34, 7.20 (4 H, AA′BB′, ArH of tosyl group), 6.90 (2 H, s, ArH), 5.00 (1 H, s, ArOH), 4.01 (2 H, AB portion of ABX, CH_2O), 2.98 (1 H, sextet, J = 7 Hz, CH), 2.39 (3 H, s, $ArCH_3$), 1.39 (18 H, s, *t*-Bu), 1.25 (3 H, d, J = 6.5 Hz, CH_3).

1-Methyl-4,6-di-*tert*-butylspiro[2.5]octa-3,6-dien-5-one (5b). To a solution of **7b** (8.4 g, 0.020 mol) in 30 ml of THF was added KO-*t*-Bu (2.70 g, 0.024 mol) followed by an additional 20 ml of THF. The solution was stirred for 2 hr, added to ether, washed with water, and dried, and the solvent was removed under vacuum. The crude product was recrystallized from hexane to yield 2.9 g (59%) of white solid: mp 79.5–81.5° (lit.[9] mp 75–77°); nmr δ 6.39 (1 H, d, J = 2.5 Hz, vinyl H), 6.03 (1 H, d, J = 2.5 Hz, vinyl H), 1.2–1.8 (6 H, m, cyclopropyl and CH_3), 1.25 (18 H, s, *t*-Bu).

Reaction of Tosylate 7b with LiBr. The previous procedure[4] was followed. Reaction periods of 3 hr produced mixtures estimated by nmr to contain 11–17% starting material, 61–62% **4b**, and 21–27% **8b**. After 21 hr no starting material remained, and the reaction product consisted of a mixture of *ca.* 67% **4b** and 33% **8b**.

1-Bromo-2-(3′,5′-di-*tert*-butyl-4′-hydroxyphenyl)propane (8b). Br_2 (3.8 g, 0.024 mol) in 10 ml of benzene was added to a solution of Ph_3P (4.7 g, 0.018 mol) in 20 ml of benzene in an ice–water bath, followed by dropwise addition of **6b**[3] (2.6 g, 0.010 mol) in 1.5 ml of pyridine and 10 ml of benzene at 25°. The solution was stirred for 1 hr and added to water, and the organic material was extracted into ether. The ether solution was washed with 5% $NaHCO_3$ and water, dried, and evaporated to a yellow oil which contained an appreciable quantity of Ph_3PO. Most of the Ph_3PO was removed by repeated solution in hexane to yield 2.9 g of oil: nmr δ 7.5 (Ph_3PO, <5%), 7.0 (2 H, s, ArH), 5.17 (1 H, s, ArOH), 2.7–3.9 (3 H, m, CH and CH_2), 1.42 (21 H, singlet and shoulder, *t*-Bu and CH_3); mass spectrum m/e (rel intensity) 328 (33), 326 (33), 313 (71), 311 (71), 233 (100).

Efforts at further purification of **8b** for microanalysis were unsuccessful; *e.g.*, chromatography on silica gel removed the Ph_3PO but also caused complete rearrangement of **8b** to **4b**.

Reactions of 5b. A. With HBr. HBr was slowly bubbled through a solution of **5b** (0.223 g, 0.90 mmol) in 25 ml of anhydrous ether for 20 min under N_2 at 0°. The solution was diluted with ether, washed with 5% $NaHCO_3$ and water, and dried, and the solvent was evaporated under vacuum to yield 0.231 g (78%) of oil. The product distribution by nmr was *ca.* 75% **4b** and 25% **8b**: nmr of **4b** δ 6.99 (s, ArH), 5.10 (s, ArOH), 4.25 (sextet, J = 6.5 Hz, CHBr), 3.07 (AB portion of ABX, CH_2), 1.64 (d, J = 6.5 Hz, CH_3), 1.42 (s, *t*-Bu); nmr of **8b**, the same as that reported in the preceding experiment. Spin-decoupling experiments using a Bruker HFX spectrometer were consistent with the above assignments.

B. With $MgBr_2$. Anhydrous $MgBr_2$ (0.267 g, 1.45 mmol) was added to a solution of **5b** (0.220 g, 0.89 mmol) in 10 ml of anhydrous ether, and the mixture was stirred for 3.75 hr at 25°. The ether solution was washed with water and dried, and the solvent was evaporated under vacuum to yield 0.21 g of light yellow oil. The nmr spectrum showed 27% starting material and bromides **4b** and **8b** in the ratio 75:25, respectively.

C. With 10% H_2SO_4. A solution of **5b** (0.589 g, 2.4 mmol) and 1.5 ml of 10% aqueous H_2SO_4 in 7.5 ml of acetone was stirred for 2.5 hr at 25° and diluted with 50 ml of ether and 25 ml of water. The ether layer was dried and evaporated under vacuum to yield 0.55 g of viscous oil. Nmr analysis indicated the presence of *ca.* 93% **2b**. See the following experiment for the nmr spectrum.

1-(3′,5′-Di-*tert*-butyl-4′-hydroxyphenyl)-2-propanol (2b). The previous procedure[11] was followed: mp 58–61.5° (lit.[11] mp 56–58°); nmr δ 7.00 (2 H, s, ArH), 5.10 (1 H, s, ArOH), 3.90 (1 H, sextet, J = 6 Hz, CH), 2.65 (2 H, AB portion of ABX, CH_2), 1.70 (1 H, br s, OH), 1.42 (18 H, s, *t*-Bu), 1.20 (3 H, d, J = 6 Hz, CH_3); mass spectrum m/e (rel intensity) 264 (17.4), 249 (14.9), 219 (100).

Anal. Calcd for $C_{17}H_{28}O_2$: C, 77.22; H, 10.67. Found: C, 77.31; H, 10.80.

For comparison, the nmr spectrum of 1-phenyl-2-propanol shows δ 7.2 (5 H, s, ArH), 3.96 (1 H, sextet, J = 6 Hz, CH), 2.66 (2 H, AB portion of ABX, CH_2), 2.28 (1 H, br s, OH), 1.16 (3 H, d, J = 6 Hz, CH_3).

2-Methyl-2-(3′,5′-di-*tert*-butyl-4′-hydroxphenyl)-1-propyl Tosylate (7c). Compound **7c** was prepared according to the previous procedure:[9] mp 82.0– 83.0° (lit.[9] mp 100–102°); nmr δ 7.77, 7.63, 7.34, 7.20 (4 H, AA′BB′, ArH of tosyl group), 7.08 (2 H, s, ArH), 5.10 (1 H, s, ArOH), 3.92 (2 H, s, CH_2O), 2.40 (3 H, s, $ArCH_3$), 1.39 (18 H, s, *t*-Bu), 1.30 (6 H, s, CH_3).

1,1-Dimethyl-4,6-di-*tert*-butylspiro[2.5]octa-3,6-dien-5-one (5c). The same procedure as that used for **5b** was followed: mp 92.8–96.0 (lit.[9] mp 92–94°); nmr δ 6.48 (2 H, s, vinyl H), 1.65 (2 H, s, CH_2), 1.39 (6 H, s, CH_3), 1.26 (18 H, s, *t*-Bu).

Methyl 3,5-Di-*tert*-butyl-4-hydroxyphenylacetate (11). A solution of 3,5-di-*tert*-butyl-4-hydroxyphenylacetic acid[14] (23.2 g, 0.088 mol) and 6 ml of concentrated H_2SO_4 in 580 ml of CH_3OH was heated under reflux for 4 hr and diluted with 3 l. of H_2O, and the organic material was extracted into $CHCl_3$. The solution was dried and evaporated under vacuum. Recrystallization from hexane yielded a pale yellow solid (50%): mp 83.6–84.5°; nmr δ 7.10 (2 H, s, ArH), 5.15 (1 H, s, ArOH), 3.69 (3 H, s, CH_3), 3.52 (2 H, s, CH_2), 1.42 (18 H, s, *t*-Bu); mass spectrum m/e (rel intensity) 278 (32.4), 263 (100), 219 (16.2).

Anal. Calcd for $C_{17}H_{26}O_3$: C, 73.35; H, 9.41. Found: C, 73.56; H, 9.55.

1-(3′,5′-Di-*tert*-butyl-4′-hydroxyphenyl)-2-methyl-2-propanol (2c). A solution of **11** (16.3 g, 0.058 mol) in 250 ml of ether was added to 0.77 mol of CH_3MgBr in 750 ml of ether over a period of 30 min without external heating. The solution was stirred at 25° for 2 hr, cooled to 0°, and quenched with water followed by 3.7% HCl. The ether layer was washed with water, dried, and evaporated, and the residue was recrystallized from hexane: mp 95.4–96.0° (lit.[4] mp 150–152°); nmr δ 7.01 (2 H, s, ArH), 5.11 (1 H, s, ArOH), 2.68 (2 H, s, CH_2), 1.50 (1 H, br s, ROH), 1.42 (18 H, s, *t*-Bu), 1.21 (6 H, s, CH_3); mass spectrum m/e (rel intensity) 278 (12), 263 (4.1), 219 (49), 205 (100).

Anal. Calcd for $C_{18}H_{30}O_2$: C, 77.81; H, 10.98. Found: C, 77.65; H, 10.86.

1-(3′,5′-Di-*tert*-butyl-4′-hydroxyphenyl)-2-bromo-2-methylpropane (4c). A mixture of **2c** (1.4 g, 5.0 mmol) in 25 ml of $CHCl_3$ and concentrated HBr (48%, 40 g) was heated under reflux for 8 hr and then diluted with water. The organic layer was washed with water, dried, and evaporated under vacuum to yield 1.6 g (93%) of brown oil which appeared to be pure by its nmr spectrum: nmr δ 7.08 (2 H, s, ArH), 5.13 (1 H, s, ArOH), 3.12 (2 H, s, CH_2), 1.72 (6 H, s, CH_3), 1.42 (18 H, s, *t*-Bu).

Efforts at further purification of **4c** for microanalysis were unsuccessful.

Reactions of 5c. A. With HBr. Procedures similar to those used for **5b** were followed. The crude product appeared to be pure by its nmr spectrum, which was virtually identical with that of **4c** prepared above. This bromide is not stable and appreciably decomposed on storage at 4° for 3 days.

B. With $MgBr_2$. The crude product exhibited an nmr spectrum virtually identical with that of **4c**.

C. With 10% H_2SO_4. Analysis of the crude product by nmr spectroscopy revealed the presence of *ca.* 50% **2c** and 50% of olefin **10**: nmr of **10** δ 6.99 (2 H, s, ArH), 5.02 (1 H, s, ArOH), 4.6–4.9 (2 H, m, vinyl H), 3.23 (2 H, br s, CH_2), 1.70 (3 H, br s, CH_3), 1.42 (18 H, s, *t*-Bu).

D. With Aqueous Acetone. A solution of **5c** (0.268 g, 1.0 mmol) in 5 ml of acetone and 1 ml of H_2O was stirred at room temperature for 3 hr, diluted with water, and extracted with ether. The

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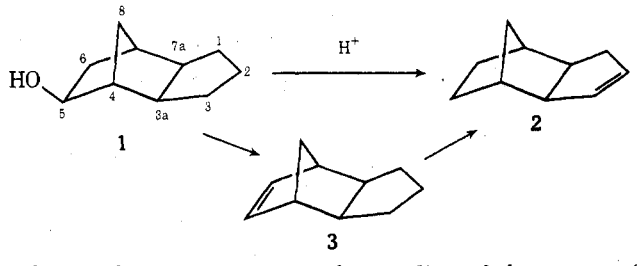
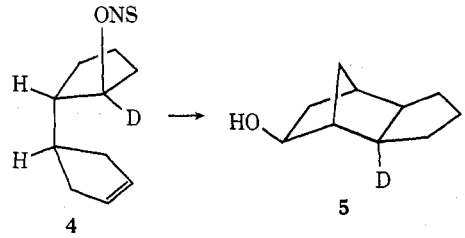
A study of the dehydration of 3a-deuterio-5-hydroxytetrahydro-*exo*-dicyclopentadiene with acid suggests that the formation of 5,6-dihydro-*exo*-dicyclopentadiene proceeds through 2,3-dihydro-*exo*-dicyclopentadiene or the equilibrating ions formed from the latter by protonation followed by a 1,3-hydride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



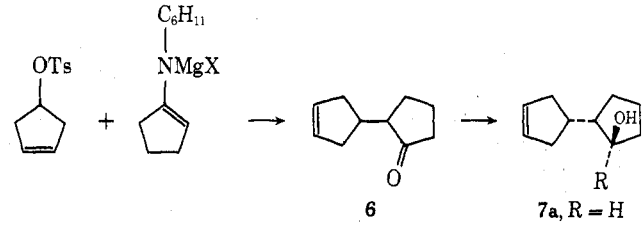
1 **2** **3**

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.



4 **5**

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.



6 **7a**, R = H; **b**, R = D

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