ratio was detected until the amount of olefin exceeded 10%. Above 10% small differences were noted and the values indicated that the *cis* alcohol (equatorial OH) was being dehydrated at a faster rate than the *trans* alcohol.

Control Experiment.—The isolated product obtained from the reaction of methylmagnesium bromide (0.1 *M*) with 4-*t*-butylcyclohexanone (Table I) was dissolved in 10 ml of ether and added to dimethylcadmium or dimethylzinc reagents under the conditions previously described for the reaction of *in situ* reagents with ketone. After hydrolysis and work-up, percentages obtained by glpc were unchanged within experimental error.

Registry No.—Methylcadmium, 506-82-1; methylzinc, 544-97-8; **1**, 98-53-3; methylmagnesium iodide, 917-64-6; methylmagnesium bromide, 75-16-1; methyllithium, 917-54-4.

Acknowledgment.—We thank the Central University Research Fund (University of New Hampshire) for partial support.

New Friedel–Crafts Chemistry. XIX. Cyclialkylations of Some Phenylalkanols[1]

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Tertiary 3- and 4-phenylalkanols underwent cyclialkylation readily at room temperature with sulfuric acid to yield the corresponding indans and tetralins. Primary and (ordinary) secondary 3-phenylalkanols did not undergo cyclialkylation even at high temperature with phosphoric acid; 1,3-diphenyl-1-propanol cyclized readily. 3-Methyl-3-phenyl-1-butanol was dehydrated (mainly) by phosphoric acid at 230°, but some cyclialkylation occurred. The requirement of a stable secondary or tertiary carbonium-ion intermediate is implied by these results; in the case of the last example, a 1,3-phenyl shift provides the required intermediate.

Some time ago Bogert and coworkers[2,3] investigated the cyclialkylations of some phenylalkanols and related alkenes. They identified their cyclization products by means of qualitative elemental analyses, comparison of physical constants, and characterization, of oxidation products. Since such identification methods are qualitative at best and probably liable to failure in detecting minor components, we decided to reinvestigate some of the reported results, applying modern instrumental methods of separation and identification. Some of the experiments are repetitions of cyclialkylations reported previously,[2,3] but others are new ones designed to provide more insight into the mechanisms of these reactions.

Results and Discussion

The conditions and results of our cyclization experiments are summarized in the accompanying Table I. 3-Phenyl-1-propanol (**1**) and 4-phenyl-1-butanol (**2**) were reported by Bogert and Davidson[2] to yield polymer and pure tetralin, respectively, upon treatment with phosphoric acid at high temperature. We obtained a product from the former that was shown to contain a trace of indan and a little *n*-propylbenzene, but the major constituents were the three isomeric phenylpropenes resulting from normal dehydration. Confirmatory evidence for the structure of the latter isomers was obtained by catalytic reduction which converted them to *n*-propylbenzene. The product from **2** was found to consist of tetralin (80%) and three lower boiling unidentified products (20%).

4-Phenyl-2-butanol (**3**) was reported by Bogert and Davidson[2] to yield polymer on treatment with sulfuric acid. When we treated this alcohol with phosphoric acid, we found the product to be a mixture of three isomeric phenylbutenes. This was confirmed by comparison with the alkene mixture obtained by the dehydration of 4-phenyl-2-butanol with 30% sulfuric acid at reflux temperature, as well as by catalytic reduction to *n*-butylbenzene.

Upon treatment with sulfuric acid at room temperature, the two tertiary alcohols, 2-methyl-4-phenyl-2-butanol (**4**) and 2-methyl-5-phenyl-2-pentanol (**5**), gave 1,1-dimethylindan and 1,1-dimethyltetralin, respectively. The secondary alcohol, 5-phenyl-3-pentanol (**6**), gave 1-methyltetralin. These were the products reported by Roblin, Davidson, and Bogert.[3] It should be noted that a hydrogen shift, converting one secondary carbonium ion to another, allows the formation of the tetralin in preference to the indan[4] in the last case.

It is clear from our present and previous work,[4] as well as from the work of Bogert and coworkers,[2,3] that ordinary primary and secondary phenylalkanols (or phenylalkyl chlorides) do not undergo ring closure to an indan derivative. However, 1,3-diphenyl-1-propanol (**7**) gave up to 34% cylization product, 1-phenylindan, as well as the main product, a higher boiling one which we believe to be the result of intermolecular condensation reactions.[5] The ability of this secondary phenylalkanol to undergo cyclialkylation confirms the idea that a stable carbonium ion intermediate, in this case stabilized by a phenyl group, is required.

The reaction of 2-methyl-4-phenyl-1-butanol (**8**) with phosphoric acid presents a case of special interest, since it provides more insight into the cyclidehydration mechanism. The product of direct cyclization at the primary carbon atom, 2-methyltetralin, was obtained in smaller yield than the products involving rearrangement and cyclization at secondary and tertiary carbon atoms. These results may be rationalized in terms of the mechanism proposed for the formation of the same

(1) Generous support of this research, including a postdoctoral fellowship for A. A. Khalaf, by the Robert A. Welch Foundation is gratefully acknowledged.

(2) M. T. Bogert and D. Davidson, *J. Amer. Chem. Soc.*, **56**, 185 (1934).

(3) R. O. Roblin, Jr., D. Davidson, and M. T. Bogert, *ibid.*, **57**, 151 (1935).

(4) A. A. Khalaf and R. M. Roberts, *J. Org. Chem.*, **31**, 89 (1966).

(5) A. A. Khalaf and R. M. Roberts, *ibid.*, **31**, 926 (1966), and references there given.

products from treatment of 1-chloro-2-methyl-4-phenylbutane with aluminum chloride.[6] However, although this corresponding phenylalkyl chloride gave about the same yield of 2-methyltetralin, the yields of the rearranged cyclialkylation products were much lower, and the major product was isopentylbenzene, which was not produced from the phenylalkanol. Thus, apparently the tertiary carbonium ion that leads to 1,1-dimethylindan when produced from the phenylalkanol and phosphoric acid behaves differently when produced from the phenylalkyl chloride and aluminum chloride, as in the latter case it mainly abstracts a hydride ion to yield isopentylbenzene rather than cyclialkylating.

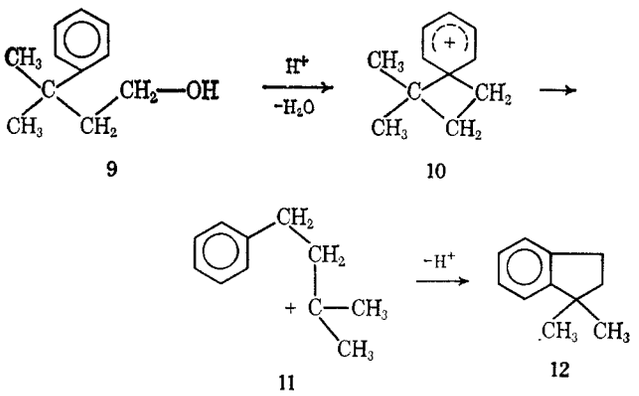
An even more interesting case is that of the primary alcohol **9**. Treatment of this alcohol with phosphoric acid was reported by Bogert and Davidson[2] to yield a mixture of hydrocarbons which on oxidation gave a mixture of benzoic acid and α,α-dimethylhomophthalic acid. They concluded from this result that the product was a mixture of the cyclidehydration product, 1,1-dimethylindan, and rearranged normal dehydration products, which they suggested to have either of the skeletal structures $C_6H_5C(CH_3)CCCH_3$ or $C_6H_5CCC(CH_3)_2$. We treated **9** with phosphoric acid according to their procedure[2] and found the result to be a mixture of 1,1-dimethylinan (18%) and 2-methyl-3-phenyl-2-butene (82%). The identity of the latter alkene was confirmed by catalytic reduction to 2-methyl-3-phenylbutane. The formation of 2-methyl-3-phenyl-2-butene can readily be accounted for in terms of current carbonium ion rearrangement theory.

The fact that **9** yielded 1,1-dimethylindan under cyclization conditions that did not produce indans from **1** deserves special consideration. Explanations of this were previously offered in terms of the general effect of the *gem*-dimethyl group in promoting ring closure, as well as in terms of 1,3-phenyl migration.[2]

Another possible explanation involves intermolecular alkylation followed by dealkylation at the tertiary carbon, leading to a tertiary cation capable of undergoing closure to an indan ring. However, this appears unlikely on the basis that no diphenylalkanes of the types p-t-$BuC_6H_4CH_2CH_2CH_2Ph$ or $PhCH_2CH_2CH_2Ph$, expected from such alkylation-dealkylation processes, could be obtained from a reaction of **1** with t-butylbenzene under similar conditions.

A mechanism that plausibly accounts for the role of the *gem*-dimethyl group in the formation of 1,1-dimethylindan from 3-methyl-3-phenyl-1-butanol (**9**) is outlined in Scheme I. The initial step in this mechanism involves anchimeric participation by the phenyl group to form a spiro phenonium-ion intermediate (**10**).[7]

SCHEME I



This can open, presumably irreversibly, to give the tertiary carbonium ion **11**. In going from **9** to **11**, the cleavage of the C–O bond is compensated by the formation of the C–Ph bond and also by the release of steric strain. The resulting tertiary carbonium ion **11** can then cyclize to an indan derivative (**12**).[8]

On the basis of the above mechanism, the failure of 3-phenyl-1-propanol (**1**) to undergo cyclization to indan can be rationalized, since a similar 1,3 shift of the phenyl group, if it occurred,[9] would produe a primary carbonium-ion intermediate which is incapable of cyclizing to an indan. Additional support for Scheme I may be found in the fact that an analogous mechanism (Scheme II) offers a more plausible rationale than others suggested for the reported cyclization of α-alkyl-β-hydroxypropiophenones (**13**) and related alkenes (**14**) to alkylindanones (**16**).[10] In this case, the stable acyl cation intermediates (**15**) can undergo ring closure to the corresponding indanone derivatives by intramolecular acylation.

Experimental Section[11]

The purity (in all cases 96% or higher) and identity of the starting materials, and of the final products, were determined by glpc and ir analysis and, in some cases, also by nmr and/or mass spectrometric analysis.

Synthesis of Phenylalkanols.—Of the required alcohols, only 3-phenyl-1-propanol (**1**) was commercially available. 4-Phenyl-1-butanol (**2**), 4-phenyl-2-butanol (**3**), 2-methyl-4-phenyl-2-butanol (**4**), 2-methyl-5-phenyl-2-pentanol (**5**), 5-phenyl-3-pentanol (**6**), and 2-methyl-4-phenyl-1-butanol (**8**) were prepared by the methods described previously.[4]

1,3-Diphenyl-1-propanol (**7**) was prepared by the reaction of β-phenylethylmagnesium bromide with benzaldehyde. The

(6) See Scheme I of ref 4.

(7) Support for this mechanism comes from the work of Winstein and his group on the role of aryl participation in various solvolytic reactions: Winstein, *et al.*, *J. Amer. Chem. Soc.*, **79**, 3105 (1957); *ibid.*, **79**, 3114 (1957); *Experientia*, **12**, 138 (1956). The results of their work show that more Ar$_2$-6 aryl participation is operating in compounds of the type $ArC(CH_3)_2(CH_2)_3OBs$ than in compounds of the type $Ar(CH_2)_4OBs$. Moreover, the same authors also mention unpublished data by P. Magee indicating that in molecules such as $(Ph)_3C(CH_2)_3OBs$, which are similar to **9** except for the replacement of the *gem* methyls by *gem* phenyls, Ar$_2$-5 aryl participation becomes important. We suggest that the type of participation taking place in compounds of these types is Ar$_1$-4 rather than Ar$_2$-5, since the role of the *gem* diaryl or dimethyl groups becomes more apparent in the Ar$_1$-4 mechanism. A distinction between these mechanisms can be made by determining the products from *meta*- or *para*-substituted derivatives of **9**. These studies are in progress and results will be reported in the near future.

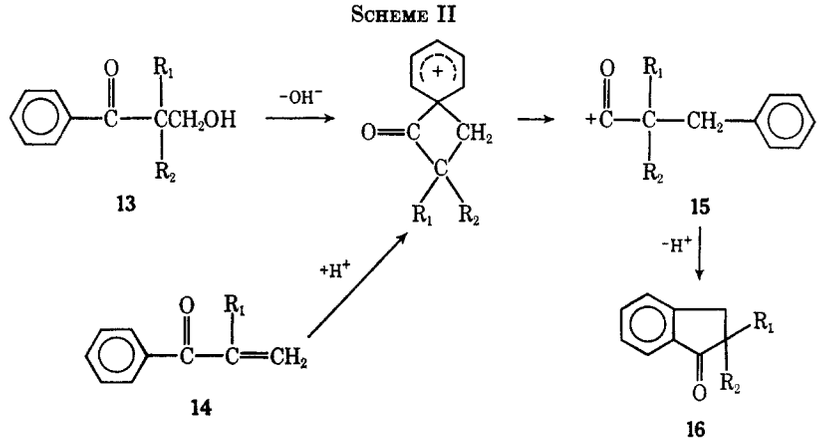
(8) With the assumption that phenyl-assisted ionization of **9** (Scheme I) leads only to the indan **12** and hydrogen-assisted ionization leads to the rearranged alkene, one can conclude from the experimental data that the latter mode of ionization is about four times as favored as the former mode.

(9) The work of Winstein and his group on the solvolysis of the corresponding 3-aryl-1-propyl p-bromobenzenesulfonates, $Ar(CH_2)_3OBs$, shows no appreciable incursion of aryl participation in such cases.

(10) J. H. Burckhalter and R. C. Fuson, *J. Amer. Chem. Soc.*, **70**, 4184 (1948); *cf.* L. R. C. Barclay in "Friedel–Crafts and Related Reactions," Vol. II, Part 2, G. A. Olah, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p 826.

(11) The organic chemicals used were of reagent grade and were obtained from usual suppliers. Gas–liquid partition chromatographic (glpc) analyses were made on a Beckman GC-2A or a Varian Aerograph Hy-Fi, Model 600-D instrument. The columns used were (1) 12-ft, 30% silicone gum rubber SE-30 on 42–60 mesh firebrick; (2) 6-ft, 30% Carbowax 1000 on 60–80 mesh firebrick; (3) 12-ft, 5% Bentone-34 and 5% silicone SE-52 on 60–80 mesh Chromosorb W; (4) 6-ft, 15% QF-1 and 15% Carbowax 20M on 60–80 mesh Chromosorb W; (5) 6-ft, 30% cyano silicone on 60–80 mesh Chromosorb W. Infrared (ir) spectra were obtained with a Beckman IR-5A spectrophotometer. Proton magnetic resonance (nmr) spectra were measured on a Varian Associates A-60 spectrometer.

SCHEME II



$R_1 = CH_3$
$R_2 = CH_3, H$

TABLE I

ACTION OF SULFURIC ACID AND PHOSPHORIC ACID UPON SOME PHENYLALKANOLS

Phenylalkanol	Acid	Temperature, °C	Bp of products, °C	Yield, %[a]	Products[b] (%)
3-Phenyl-1-propanol (1)	85% phosphoric	230–240	130–140	46	Indan (trace), *n*-propylbenzene, (11), three isomeric phenylpropenes (89)
4-Phenyl-1-butanol (2)	85% phosphoric	230–240	200–208	61	Tetralin (80), three lower boiling unidentified (20)
4-Phenyl-2-butanol (3)	85% phosphoric	230–240	175–188	75	Mixture of three isomeric phenylbutenes (100)[c]
2-Methyl-4-phenyl-2-butanol (4)	85% sulfuric	10–25	189–191	57	1,1-Dimethylindan (100)
2-Methyl-5-phenyl-2-pentanol (5)	85% sulfuric	10–25	88 (8–10 mm)	83	1,1-Dimethyltetralin (100)
5-Phenyl-3-pentanol (6)	90% sulfuric	10–25	217–220	55	1-Methyltetralin (97), unidentified (3%)
1,3-Diphenyl-1-propanol[d] (7)	90% sulfuric	10–25			1-Phenylindan (34), 1-phenyl-1-indene (1), bimolecular condensation products (50), unidentified (14)
2-Methyl-4-phenyl-1-butanol (8)	85% phosphoric	230–240	189–222	84	1,1-Dimethylindan (40), 2-methyltetralin (32), 1-methyltetralin (14), unidentified (14)
3-Methyl-3-phenyl-1-butanol (9)	85% phosphoric	230–240	185–195	85	1,1-Dimethylindan (18), 2-methyl-3-phenyl-2-butene (82)[e]

[a] Mole per cent of distillable hydrocarbons based on original phenylalkanol. [b] The percentage composition of various products was calculated by integration of glpc recordings. [c] Reduction of this mixture by hydrogen and palladium on carbon in ethanol gave *n*-butylbenzene as the sole product. [d] The viscous oily product from this alcohol was not distilled. [e] These two products could be separated effectively only on the 6-ft mixed QF-1 and Carbowax 20M column using the Hy-Fi instrument at 140°. The identity of the latter product was also proved by reduction with hydrogen and palladium on carbon in ethanol to 2,3-dimethyl-2-phenylbutane.

carbinol, bp 155–156° (2 mm), $n^{25}D$ 1.5715 [lit.[12] bp 192–194° (12 mm)], was obtained in 40% yield.

3-Methyl-3-phenyl-1-butanol (9).—β-Phenylisovaleric acid was prepared from neophylmagnesium chloride and Dry Ice as described by Whitmore, Weisgerber, and Shabica.[13] The acid was reduced by lithium aluminum hydride to the alcohol, bp 135–136° (14.5 mm), $n^{25}D$ 1.5200 [lit.[2] bp 137–138° (16 mm)]. The over-all yield which was based on neophyl chloride was 60%.

Synthesis of Authentic Hydrocarbons.—1-Methylindan, 1-ethylindan, 1,1-dimethylindan, 1-methyltetralin, 2-methyltetralin, and 2-methyl-3-phenylbutane were obtained as previously described.[4]

1-Phenylindan.—1-Indanone was treated with phenylmagnesium bromide, yielding 1-phenyl-1-indanol. Reduction by hydrogen and palladium on carbon in glacial acetic acid containing perchloric acid gave 1-phenylindan, bp 146–148° (10 mm) [lit.[14] bp 148–150° (13 mm)].

1-Phenyl-1-indene.—1-Phenyl-1-indanol was refluxed with 20% sulfuric acid for 1 hr to give the title compound, bp 152–153° (14 mm) [lit.[14] bp 153–154° (14 mm)].

1,3-Diphenyl-1-propene.—1,3-Diphenyl-1-propanol (7) was refluxed with 20% sulfuric acid for 1 hr to give the title compound, bp 178–180° (15 mm) [lit.[12] bp 178–179° (15 mm)].

1,3-Diphenylpropane.—1,3-Diphenyl-1-propene was reduced by hydrogen and palladium on carbon in ethanol containing a little sulfuric acid to give the title compound, bp 113–115° (0.1 mm) [lit. bp 177–178° (10 mm)].

Reaction of Phenylalkanols with Sulfuric Acid or Phosphoric Acid.—The procedures described by Bogert and coworkers[2,3] were essentially followed. The only modification was in the manner in which the products were obtained. The distillate and residue from each experiment were combined, diluted with water, and extracted with ether. The ether layer was separated, washed with 10% sodium carbonate solution followed by water, dried over anhydrous sodium sulfate, and finally distilled. The results obtained are summarized in Table I.

Reaction of 3-Phenyl-1-propanol (1) **and *t*-Butylbenzene with Phosphoric Acid.**—A mixture of 3-phenyl-1-butanol (0.05 mol) and *t*-butylbenzene (0.07 mol) was treated with phosphoric acid according to the normal procedure. Besides *t*-butylbenzene,

(12) W. Dieckmann and H. Kammerer, *Ber.*, **39**, 3046 (1906).
(13) F. C. Whitmore, C. A. Weisgerber, and A. C. Shabica, Jr., *J. Amer. Chem. Soc.*, **65**, 1469 (1943).
(14) F. Mayer, A. Sieglitz, and W. Ludwig, *Ber.*, **54**, 1397 (1921).

products similar to those obtained from the reaction of 1 with phosphoric acid were also obtained. Neither the possible alkylation product, 1-phenyl-3-(*p*-*t*-butylphenyl)propane, nor its dealkylated form, 1,3-diphenylpropane, were produced.

Registry No.—**1**, 12-29-74; **2**, 336-04-16; **3**, 234-47-09; **4**, 10-30-59; **5**, 297-97-06; **6**, 1992-50-3; **7**, 14097-24-6; **8**, 3023-61-8; **9**, 21438-74-4.

Bridged Polycyclic Compounds. LIX. Stereochemistry of Rearrangements in Dibenzobicyclo[2.2.2]octadienyl and Dibenzobicyclo[3.2.1]octadienyl Systems and of Additions to Dibenzobicyclo[2.2.2]octatriene[1]

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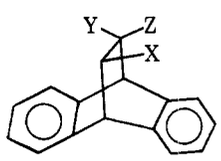
cis-3-Deuteriodibenzo-2-bicyclo[2.2.2]octadienyl *p*-toluenesulfonate (**6**) is converted stereospecifically upon acetolysis into *syn*-8-deuteriodibenzo-*exo*-2-bicyclo[3.2.1]octadienyl acetate (**7**). In perchloric acid–acetic acid this *exo* acetate is rapidly transformed to an equilibrium mixture with its *endo* epimer and is then stereospecifically rearranged to *cis*-3-deuteriodibenzo-2-bicyclo[2.2.2]octadienyl acetate (**8**). The results are discussed in terms of a single classical cationic intermediate (**12**). Addition of acetic acid to dibenzobicyclo[2.2.2]octatriene (**3**) gives dibenzo-2-bicyclo[2.2.2]octadienyl acetate (**11**). This reaction is substantially slower than the rearrangement of either *endo*- or *exo*-dibenzo-2-bicyclo[3.2.1]octadienyl acetates (**9** and **10**) to dibenzo-2-bicyclo[2.2.2]-octadienyl acetate (**11**), so that their intermediacy cannot be ascertained. Addition of deuterioacetic acid leads to both *cis*- and *trans*-3-deuteriodibenzobicyclo[2.2.2]octadienyl acetates (**8** and **15**), but most (and perhaps all) of the *trans* product arises from acid-catalyzed isomerization of the *cis*-addition product **8**. Similar results obtain with trifluoroacetic acid and deuteriotrifluoroacetic acid.

In previous work, largely in this laboratory, it has been shown that dibenzobicyclo[2.2.2]octadiene derivatives (**1**) undergo Wagner–Meerwein rearrangements to dibenzobicyclo[3.2.1]octadiene derivatives (**2**), and *vice versa*. The reactions which occurred were generally stereospecific, at least with respect to the carbon skeletal migration.[2,3] In all of the cases heretofore



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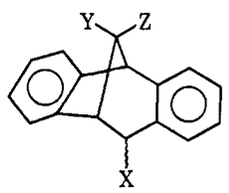

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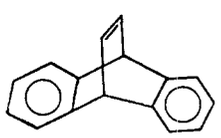

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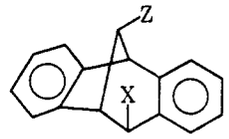

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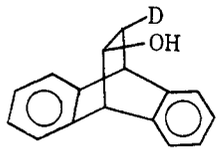
reported, substituents were present as Y or Z in **1** or **2** and we were therefore interested in extending our knowledge about stereochemistry with Y or Z labeled only with deuterium. In these experiments, we were aided by our previous work on pmr spectra of dibenzobicyclooctadienes,[4,5] where large differences in couplings were observed for diastereoisomers, so that we had available simple means for studying the steric course of rearrangements.

In conjunction with this work, we began a study of the course of addition of protic species to dibenzobicyclo[2.2.2]octatriene (**3**). Earlier work[2,6] had shown that the electrophilic additions of halogens or of halogen-like species (bromine in acetic acid, Prévost reagent) to **3** gave *syn,exo* products **4**. Study of addition of protic and deuterated species to this bicyclooctatriene system seemed an interesting extension of our previous work on similar additions to bicycloheptadiene and bicycloheptene systems.[7-11]

The desired deuterium-labeled compounds were prepared from **3** by treatment with deuteriodiborane followed by oxidation. Comparison of the pmr spectrum of the product (**5**) with the analyzed[4] spectrum of the undeuterated analog showed that the product had the anticipated[12] *cis* stereochemistry. Acetolysis of the



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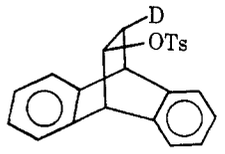

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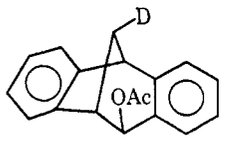

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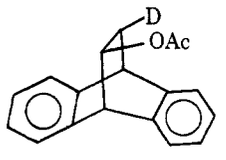

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(3) S. J. Cristol, F. P. Parungo, D. E. Plorde, and K. Schwarzenbach, *ibid.*, **87**, 2879 (1965).

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(5) S. J. Cristol, J. R. Mohrig, and D. E. Plorde, *ibid.*, **30**, 1956 (1965).

(6) S. J. Cristol, R. P. Arganbright, and D. D. Tanner, *ibid.*, **28**, 1374 (1963).

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(8) S. J. Cristol and R. Caple, *ibid.*, **31**, 2741 (1966).

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