Bridged Polycyclic Compounds. XLII. The Mass Spectral Analyses of Deuterated and Undeuterated Bridged Polycyclic Acetates[1]

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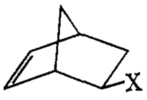
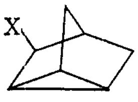
The mass spectral analyses of *exo*-dehydronorbornyl (Ia) and nortricyclyl (IIa) acetates are reported. In addition, the mass spectra are reported for *exo-cis*-3-deuteriodehydro-2-norbornyl acetate (IIIa) and for a sample containing equal amounts of C_3-deuterio- and C_7-deuterio-*exo*-dehydro-2-norbornyl acetate (IIIa and IVa). These spectra have been used to develop a technique to scrutinize those cations which determine the location of deuterium in dehydronorbornyl ring skeletons.

The limitations of proton magnetic resonance spectral analyses of deuterated *exo*-dehydronorbornyl acetate derivatives[1,2] make clear the necessity for a more precise method of measuring the extent and location of deuteration within such compounds. Accordingly studies of the mass spectral fragmentation patterns of *exo*-dehydronorbornyl acetate (Ia), of mixtures of the analogous deuterated species IIIa and IVa, and of nortricyclyl acetate (IIa) were carried out to develop more sensitive analytical procedures.



I



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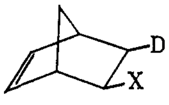

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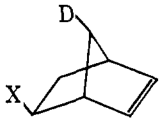
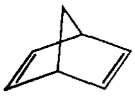


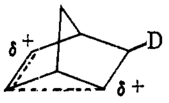
IV

a, X = OAc
b, X = OH
c, X = $OSO_2C_6H_4Br$-*p*
d, X = Cl
e, X = H

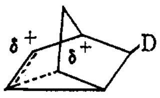
An intermediate cationic species is expected to be obtained either by deuteration (analogous to protonation) of norbornadiene (V), as an early step in an addition reaction) or by ionization of a sulfonate ester (Ic, IIc, or IIIc) in a solvolysis reaction. Such intermediates may be a combination (or just one) of a number of possibilities (VI–XI). The significance of homoallylic and nonclassical participation is discussed by us elsewhere.[1] Attack by a nucleophile to form olefinic ester may occur at either position 1 or 2 of the nonclassical ions VIII or IX (or at the corresponding positions of an equilibrating ion system VI and VII or X and XI) and would give esters IIIa and IVa, respectively. Thus, the determination of the relative amounts of IIIa and IVa may give an indication of the symmetry of the cationic system that determines such esters.



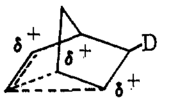
V



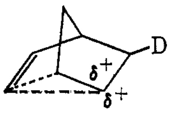
VI



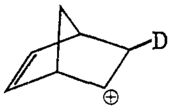
VII



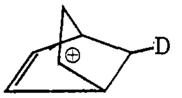
VIII



IX

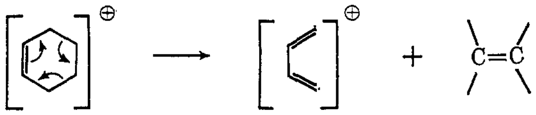


X



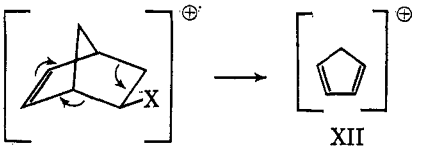
XI

Fragmentation of the molecular ion of cyclic olefins to give two rather stable unsaturated fragments (without rearrangement) *via* a "retro-Diels–Alder" reaction (eq 1) has been described by Bieman.[3] If



(1)

such a reaction would occur for ester Ia (and thus for IIIa and IVa), such as described in eq 2, then the rela-

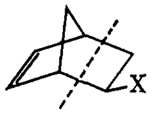


XII

$+\ CH_2{=}CHX$ (2)

XIII

tive deuterium contents of fragments XII and XIII would be a determination of the relative amounts of IIIa and IVa. This effectively partitions the molecule as indicated in XIV.



XIV

Figure 1 displays the mass spectra of some pertinent esters. The spectrum in Figure 1a has by far the most intense peak at *m/e* 66, which we attribute to the cyclopentadiene (XII) cation. Thus, the "retro-Diels–Alder" fragmentation pattern described by Bieman[3] appears to be applicable. Next in intensity (in Figure 1a) is the *m/e* 43 peak, attributed to the acylium $(CH_3CO)^+$ cation.[4] The importance of the acylium cation will be discussed. On the other hand, in the spectrum of nortricyclyl acetate (Figure 1b), the *m/e* 66 peak is not the most intense peak in the spectrum. Reasons for this have been discussed by Dudek and his co-workers.[5] Instead, the most intense

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(1) (a) Paper XXXIX: S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *J. Org. Chem.*, **31**, 2719 (1966). (b) Paper XL: S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *ibid.*, **31**, 2726 (1966). (c) Paper XLI: S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *ibid*, **31**, 2733 (1966). (d) S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *J. Am. Chem. Soc.*, **88**, 3087 (1966). This work was presented in part in papers presented at the First International Symposium on Organic Reaction Mechanisms in Cork, Ireland, July 1964, and at the Symposium on Electrophilic Addition Reactions of the Division of Organic Chemistry at the 148th National Meeting of the American Chemical Society in Chicago, Ill., Sept 1964.

(2) S. J. Cristol, L. K. Gaston, and D. W. Johnson, *Tetrahedron Letters*, 185 (1963).

(3) K. Bieman, "Mass Spectrometry, Organic Chemical Applications," McGraw-Hill Book Co., Inc, New York, N. Y., 1962, p 102.

(4) Reference 3, p 101.

(5) W. C. Steele, B. H. Jennings, G. L. Botyos, and G. O. Dudek, *J. Org. Chem.*, **30**, 2886 (1965).

peak is the acylium (m/e 43) ion peak. The assumption that the mass 66 peak represents largely the result of the reaction of eq 2 is consistent with previous investigations as well.[5,6]

Mass spectral analysis of a sample which is believed to be pure (or almost pure) *exo-cis*-3-deuteriodehydro-2-norbornyl acetate (IIIa) results in the spectrum of Figure 1c. This sample was prepared by oxidative deuteroboration to give *exo-cis*-3-deuteriodehydro-2-norborneol, which was then acetylated.[1b] Figures 1a and c are quite similar. This similarity in the mass 66–67 regions is indicative of the lack of deuterium of the portion of ester IIIa ($C_{1,4-7}$) which gives rise to the cyclopentadiene cation. A more exact determination of the degree of Wagner–Meerwein scrambling (partitioning of deuterium between the $C_{1,4-7}$ and C_{2-4} portions of the ester ring skeleton) is made by considering the relative intensities in the m/e 66–67 (cyclopentadiene cation) and m/e 152–154 (molecular ion, not completely visible in Figure 1) regions (see Table I). A measure of the extent of total molecular deuteration is obtained from the molecular ion region, and the amount of Wagner–Meerwein rearrangement is measured by comparing the extent of deuteration of the cyclopentadiene ion to the total molecular deuteration.

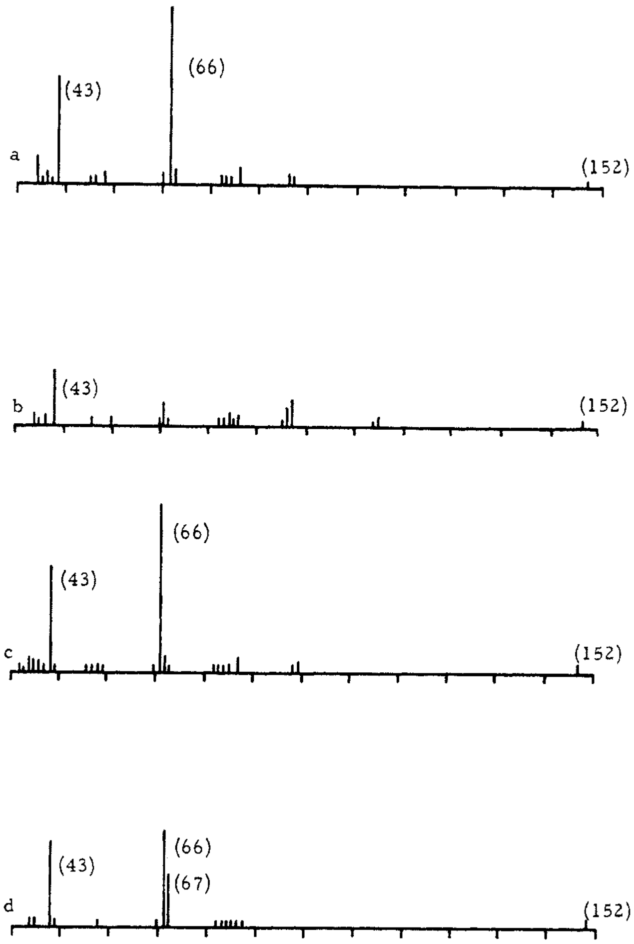

Figure 1.—Mass spectra: (a) *exo*-dehydronorbornyl acetate (Ia), (b) nortricyclyl acetate (IIa), (c) *exo-cis*-3-deuteriodehydro-2-norbornyl acetate (IIIa), and (d) a mixture of 73% deuterated *exo*-dehydronorbornyl acetate (44% IIIa and 56% IVa) and 27% undeuterated *exo*-dehydronorbornyl acetate.

TABLE I

DATA FROM THE MASS SPECTRAL ANALYSES OF *exo*-DEHYDRO-2-NORBORNYL ACETATE (Ia) AND *exo-cis*-3-DEUTERIODEHYDRO-2-NORBORNYL ACETATE (IIIa)

	Rel peak intensities[a]		% of ions undeuterated and deuterated[b]	
	m/e			
Molecular ion	152	153	d_0	d_1
From Ia	100	10.0	100	. . .
From IIIa	2.66	100	2.6	97.3
	m/e			
Cyclopentadiene ion	66	67	d_0	d_1
From Ia	100	7.6	100	. . .
From IIIa	100	9.45	98.2	1.9

[a] These data are relative peak intensities in each mass region (152–153 region calculated separately from 66–67 region). The results for the undeuterated ester correspond very well to isotopic abundances (for the empirical formula of the respective ion structures) as reported in Beynon.[7] [b] The method of calculation for these data involves correction for isotopic abundances and is described in the text of this paper.

A sample calculation is as follows (data on IIIa sample of Table I). For a peak height of 100 the isotopic abundance correction[7] for $C_5H_6^+$ is 7.6. Thus, corrected for isotopic abundance, the peak height at mass 67 (for IIIa) attributable to $C_5H_5D^+$ is 9.5 − 7.6 = 1.9. In the molecular ion ($C_9H_{12}O_2$, mass 152) the isotope correction for $(M + 1)^+$ (mass 153) is 10%.[7] Thus, the value of 100 at mass 153 (for $C_9H_{11}O_2D$ = IIIa) must be reduced by 10% of the intensity of the peak at mass 152 (10% of 2.7) and the value attributed to $C_9H_{11}O_2D$ is then 100 − 0.3 = 99.7. Thus, the percentage of monodeuteration of the cyclopentadiene ion fragment is 1.9/(100 + 1.9) = 1.9% and the fraction of monodeuteration in the molecular ion is 99.7/(99.7 + 2.7) = 97.3%. Use of these figures yields 1.9/97.3 or 1.9% D at $C_{1,4-7}$ and 98.1% D distributed at C_2 and C_3. As one may assume[1] that scrambling of deuterium is limited to C_3 and C_7, one may surmise that 3.8% of the reaction, at most,[8] proceeded through an intermediate or process that equated positions C_1 and C_2.

Such a procedure is usually general and may be used to calculate the amount of Wagner–Meerwein scrambling associated with products of addition reactions and solvolyses.[1] Cases in which this procedure is not general are discussed later in this paper. As the assumption is made that the deuterium in the $C_{1,4-7}$ portion of the molecule arrived *via* the type of cationic intermediate(s) described above and is located upon C_7, such data are given[1] as per cent of D on C_7. Complete scrambling would result in 50% of the deuterium being found at C_7 (as was found in this laboratory for acetolysis of IIIc).[1d]

The mass spectrum of the olefinic acetate resulting from the deuterium perchlorate catalyzed addition of acetic acid-d_1 to norbornadiene[1a] is given in Figure 1d. One should note that the size of the m/e 67 peak is

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(6) S. Meyerson, J. D. McCollum, and P. N. Rylander, *J. Am. Chem. Soc.*, **83**, 1401 (1961).

(7) J. H. Beynon, "Mass Spectrometry," Elsevier Publishing Co., New York, N. Y., 1960, Appendix I.

(8) The error in the determination of per cent of D at C_7 is estimated to be about 2–3%, based on duplicate runs,[1d] extraneous peaks in each spectrum, an $(M - 1)^+$ (mass 151) peak (for Ia) which has an intensity 1% that of M^+, and results of per cent of D on C_7 = 2–3% for esters resulting from oxidative deuteroboration and acetylation.[1] It is not known whether these latter results are a result of mass spectroscopically induced rerrangements or the actual location of deuterium at C_7 in such esters. A more detailed analysis of *exo*-dehydronorbornyl derivatives will be reported later by R. A. Sanchez and D. C. Sheesley.

TABLE II

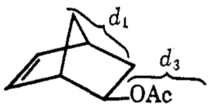
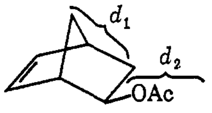
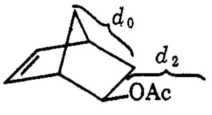
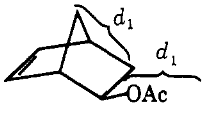
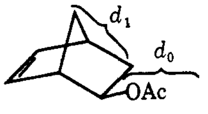
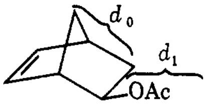
MASS SPECTRAL ANALYSES OF *exo*-DEHYDRO-2-NORBORNYL (Ia) AND POLYDEUTERATED *exo*-DEHYDRO-2-NORBORNYL (IIIa, IVa, AND OTHERS)[a] ACETATES

Molecular ion	Relative peak intensities					% of ions deuterated and polydeuterated[b]				
	m/e									
	152	153	154	155	156	d_0	d_1	d_2	d_3	d_4
From Ia	100.0	10.0	1.0	...	..	100	...	...	...	...
From polydeuterated ester	86.6	100.0	41.5	11.1	11.5	38.2	40.2	13.9	3.1	4.6
		m/e								
Cyclopentadiene ion		66	67	68		d_0	d_1	d_2		
From Ia		100.0	7.6	0.4		100	...	...		
From polydeuterated ester		100.0	8.73	0.7		98.6	1.4	...		
	m/e									
Acylium ion	43	44	45	46		d_0	d_1	d_2	d_3	
From Ia	100.0	2.9	0.9	...		100	...	...	...	
From polydeuterated ester	100.0	67.2	15.4	10.4		53.3	34.7	6.8	4.7	

[a] Presumed to be a mixture of IIIa, IVa, and similar species deuterated in the acetoxy methyl group arising from the uncatalyzed addition of acetic acid-O-d_1 to norbornadiene at *ca.* 200° (see Experimental Section). [b] Calculated in the same manner as described for the data of Table I.

TABLE III

PARTITIONING OF THE DEUTERIUM DISTIBUTIONS OF TABLE II BETWEEN THE RING SKELETON AND THE ACETOXY METHYL GROUP[a]

Molecular ion deuteration, %					
d_4 = 4.6	d_3 = 3.1	d_2 = 13.9		d_1 = 40.2[b]	
		3.7	10.2	15.7	24.5
					
XV	XVI	XVII	XVIII	XX	XIX

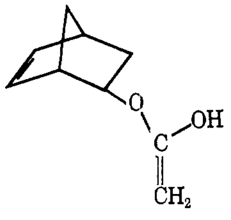
[a] All polydeuteration is assumed to take place in the acetoxy methyl group and the details of the calculations which determine this partitioning are described in the text. That polydeuteration does in fact take place in the acetoxy methyl group was confirmed as follows. Saponification of the polydeuterated ester, followed by acetylation of the resulting alcohol (see Experimental Section), gave an acetate sample that had the same ring skeleton deuterium distributions as the original acetate and total molecular deuteration equal to that calculated for the ring skeleton only of the original acetate. [b] The difference of 100 − (d_4 + d_3 + d_2 + d_1) = 100 − 61.8 = 38.2 is the number of molecular species with no deuteration (d_0).

more of the order of the *m/e* 66 peak, relative to the same comparison in Figures 1a and c. If one carries out the previously described calculations, the per cent of D on C_7 is found to be 44%, which indicates 88% scrambling due to Wagner-Meerwein rearrangement. Such a calculation upon the acetate resulting from arenesulfonate IIIc acetolysis,[1d] as mentioned above, indicated complete (100%) scrambling (50% D on C_7).

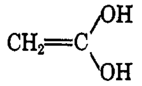
An additional form of scrambling occurs in the case of uncatalyzed and catalyzed additions of acetic acid-O-d_1 at elevated temperatures.[1b,c] In such experiments deuterium exchanges with the hydrogen on the acetoxy methyl group during the course of the addition reaction. Calculations for distributions in such additions are carried out as has been described, except that, in addition, the same type of calculations are applied to the acylium ion (see Table II). The application of such distributions to the determination of the degree of Wagner-Meerwein scrambling involves the assumption that the observed polydeuteration is the result of deuteration in the acetoxy methyl group. (This was confirmed as described below.)

Application of such an assumption to the data of Table II is shown in Table III. In this table, we have shown the distribution of deuterium in the product of an uncatalyzed addition of acetic acid-O-d_1 to norbornadiene. In this experiment (labeled in Table II as "from polydeuterated ester") 38.2% of the *exo*-dehydronorbornyl acetate had no deuterium, 40.2% had one deuterium atom, and 13.9, 3.1, and 4.6% were d_2, d_3, and d_4 molecular species, respectively. The observation that $Ac^+(d_3)$ (Ac^+ = acylium ion) is 4.7% agrees quite well with the $M^+(d_4)$ = 4.6% (M^+ = molecular ion) and the tetradeuterated species are assigned the distribution in structure XV (Table III). The 3.1% of species containing $M^+(d_3)$ are assumed to all have the distribution in structure XVI, since, within our experimental error, there are essentially no remaining $Ac^+(d_3)$ species. Since there are 6.8 − 3.1 = 3.7% of $Ac^+(d_2)$ species remaining, an equivalent 3.7% of $M^+(d_2)$ is assigned the distribution in structure XVII. This leaves 13.9 − 3.7 = 10.2% of species which must have the distribution in structure XVIII. We have thus assigned 10.2% of the species with $Ac^+(d_1)$ and, therefore, 34.7 − 10.2 = 24.5% of species with $M^+(d_1)$ have the deuterium distribution of structure XIX, leaving 40.2 − 24.5 = 15.7% of the $M^+(d_1)$ species as XX. The total number of ring skeletons (from Table II) containing one deuterium atom is then 4.7 + 3.1 + 10.2 + 15.7 = 33.7. Scrambling due to Wagner-Meerwein rearrangement is 1.4/33.7 = 4% D on C_7 or represents 8% of the total processes.

Deuterium scrambling into the acetoxy methyl group presumably occurs through the enol form of the ester (XXI, by reaction with the acetic acid-O-d_1), although it is also possible that a part of the deuterium is incorporated into the acetic acid prior to the addition to the substrate (*via* XXII). Whichever process it is, the activation energy of this process apparently



XXI



$CH_2{=}C(OH)_2$

XXII

is higher than that of addition, since deuterium incorporation only accompanies addition at relatively high temperatures.[1c] It also has been noted that such deuterium incorporation is not induced by acid catalyses at room temperature.[1b]

Experimental Section

Mass spectra were measured in a CEC 21-103c mass spectrometer, operating at a voltage of 70 ev and an ionizing current of 10 or 50 μa. The source temperature was 250° and the inlet temperature was 100–200°.

Addition of Acetic Acid-d_1 to Norbornadiene at 200°.—A 4-ft, heavy-walled glass tube was charged with 21.0 g (0.342 mole) of acetic acid-d_1 (Merck of Canada) and 120 ml (1.18 moles) of freshly distilled norbornadiene. The tube contents were frozen (Dry Ice) and the tube was sealed and heated for 161 hr at 200° (±20°). The tubes were refrozen and opened. The contents were worked up as described in the addition of acetic acid-d_4 to norbornadiene.[1d] Gas chromatographic analysis (DEGA, 5 m, $^3/_8$ in., 170°, 200 cc/min) indicated a ratio of polydeuterated *exo*-dehydronorbornyl acetate/polydeuterated nortricyclyl acetate of 99.5/0.5 (identification by identity of retention times with corresponding undeuterated esters). No absolute yield was measured at this point. A sample of *exo*-dehydronorbornyl acetate collected from the gas chromatograph was submitted for mass spectral analysis.

Saponification of Polydeuterated *exo*-Dehydro-2-norbornyl Acetate.—Two-thirds of the sample of the preceding experiment (0.23 mole, theoretically maximum amount) was treated with 22 g (0.39 mole) of potassium hydroxide in 250 ml of methanol for 23 hr at ice-bath temperature. The reaction product was worked up as described for the saponification product of the adduct of norbornadiene and acetic acid-d_4.[1d] Gas chromatographic analysis (Carbowax 20M, $^3/_8$ in., 5 m, 140°, 150 cc/min) indicated >99% conversion of ester to alcohol.

Esterification of Partially Deuterated *exo*-Dehydro-2-norborneol.—One-tenth of the solution resulting from the preceding experiment (0.023 mole theoretically maximum amount) was treated with 4.0 ml (4.3 g, 0.042 mole) of acetic anhydride in *ca.* 50 ml of pyridine. The reaction was carried out for 19.5 hr at room temperature and the resulting mixture was worked up as described for the adduct of acetic acid-d_4 and norbornadiene.[1d] A sample of ester was collected from the gas chromatograph (conditions as described in the previous experiment) and submitted to mass spectral analysis. Gas chromatographic analysis indicated >95% conversion of alcohol to ester. The crude yield was 0.59 g (17% of theoretical based on acetic acid-d_1 used for initial step). The mass spectral analysis of this ester indicated 33.8% total molecular deuteration and 3.8% D on C_7.

Acknowledgments.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for support of this work.

Bridged Polycyclic Compounds. XLIII. Polar Addition of Deuterium Chloride and Acetic Acid-O-d_1 and -d_4 to Benzonorbornadiene[1]

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The stereochemistry and skeletal deuterium distribution resulting from the polar addition of deuterium chloride and acetic acid-O-d_1 and -d_4 to benzonorbornadiene have been studied. Under kinetic control the deuteriochloride derived from benzonorbornadiene had the chlorine solely *exo* at C_5, while the deuterium was equally distributed between C_6 (*exo*) and C_7 (*syn* to chlorine). The results are consistent with those expected from a symmetrical carbonium ion intermediate, or from a rapidly equilibrating set of ions which simulate such an intermediate. In contrast, the uncatalyzed addition of acetic acid-d_4 to benzonorbornadiene produced primarily *cis-exo* addition. The fraction of deuterium appearing at C_7 was increased by mineral acid catalysis and was decreased by carrying out the addition in a hydrocarbon solvent. The data may be rationalized by assuming that nonsymmetrical cations are involved, which rearrange at rates competitive to coordination with acetate ion or acetic acid, or that the Wagner–Meerwein addition accompanying rearrangement involves a symmetrical cationic system, while the excess *cis-exo* addition observed is the result of a concerted one-step addition pathway in which a carbonium ion intermediate is not involved.

The polar addition of deuterium bromide in deuterium oxide to norbornene has been shown by Kwart and Nyce[3] to produce *exo*-2-bromonorbornane with the deuterium essentially equally distributed between C_3 and, presumably, C_7. The deuterium distribution, which was determined by a degradative scheme, and the stereochemistry were interpreted as evidence for the intervention of a single nonclassical norbornyl cation (or a set of rapidly equilibrating classical ions simulating that cation) as the intermediate.

Polar addition of O-deuteriomethanol and deuterium oxide to *endo*-trimethylenenorbornene catalyzed by deuteriosulfuric acid gives mixtures of *endo*-trimethylene-*exo*-2-norborneol derivatives with *exo*-trimethylene-*exo*-norborneol derivatives.[4] The unrearranged ring skeleton isomers have been shown to arise *via* a *cis–exo* addition pathway,[5] so that an *endo*-protonated π complex cannot be an intermediate in the reaction. The combination of *cis-exo* addition leading to *endo*-trimethylenenorborneol derivatives and Wagner–Meer-

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