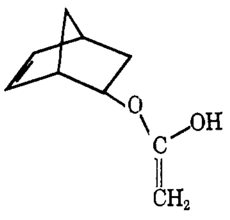
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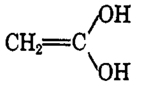
$CH_2{=}C(OH)_2$

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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Received April 26, 1966

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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[1] Paper XLII: S. J. Cristol, R. A. Sanchez, and T. C. Morrill, *J. Org. Chem.*, **31**, 2738 (1966).

[2] National Science Foundation Postdoctoral Fellow, 1964–1965.

[3] H. Kwart and J. L. Nyce, *J. Am. Chem. Soc.*, **86**, 2601 (1964).

[4] S. J. Cristol, W. K. Seifert, D. W. Johnson, and J. B. Jurale, *ibid.*, **84**, 3918 (1962).

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

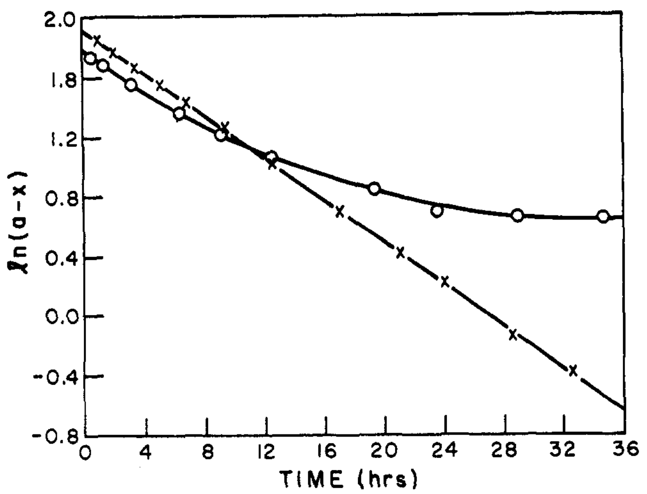
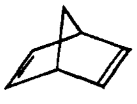


Figure 1.—Ethanolysis of IV. Straight plot with 1.5 equiv of NaOAc added, $k = 2.2 \times 10^{-5}$ sec^{-1}; curved plot in absence of added base.

wein rearrangement leading to *exo*-trimethylenenorborneol derivatives led to the inescapable conclusion that these reactions involved at least two alternative paths or product-determining intermediates.



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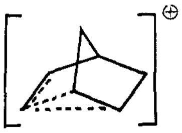

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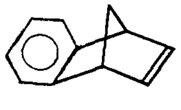
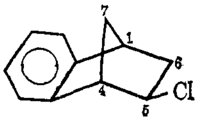
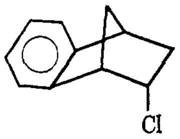


III



IV



V

Results on additions of acetic acid to norbornadiene (I)[4,6] under a variety of conditions, compared with solvolytic results on dehydronorbornyl *p*-bromobenzenesulfonate,[7] can be accommodated by (a) a series of slowly rearranging classical (or *nonsymmetrical* nonclassical) cations or (b) no fewer than three mechanisms, two of which involve either a single symmetrical nonclassical cation or a set of *rapidly* equilibrating nonsymmetrical cations, plus a concerted molecular addition process. The mechanisms proposed in this system had to explain results involving varying extents of homoconjugate addition, of 1,2-*cis-exo* addition and of addition accompanied by Wagner-Meerwein rearrangement. The two carbonium ion mechanisms[6a] could be considered as utilizing a single nonclassical ion (II) which gave different proportions of products depending upon whether it reacted with the gegen ion (acetate ion in the case of the uncatalyzed reaction) or gegen molecule (acetic acid in the case of catalysis with mineral acid) formed coincidentally with the cation from norbornadiene and acetic acid or protonated acetic acid, or whether it involved a free cation II, solvated with acetic acid. The latter process was assumed to give largely nortricyclyl acetate, and the former was assumed to give (when O-deuterioacetic acid was used) an equimolar amount of *exo*-3-deuterio- and *syn*-7-deuteriodehydro-2-norbornyl acetate. The molecular addition was assumed to embody only 1,2-*cis-exo* addition and thus to lead only (with deuterioacetic acid) to *exo*-3-deuteriodehydronorbornyl acetate.

We decided to extend our studies on electrophilic additions to other olefin substrates and to other electrophilic reagents. In this paper we wish to present and discuss data on polar additions of hydrogen chloride, deuterium chloride, acetic acid, and deuterioacetic acid to benzonorbornadiene (III). Benzonorbornadiene suffers, compared with norbornadiene, in that it is in effect a monoene rather than a homoconjugated diene, and one can only compare simple addition with addition coincident with Wagner-Meerwein rearrangement. However, these comparisons are not without interest, as they allow consideration of the factors that presumably promote utilization of paths involving cationic intermediates *vs.* concerted addition reaction paths.

Results. Addition of Hydrogen Chloride to Benzonorbornadiene.—When benzonorbornadiene was treated with concentrated aqueous hydrochloric acid, it was converted to a hydrochloride, which after distillation, was apparently one substance (IV or V), as measured by our inability to separate two substances by vapor phase chromatography. The configurational purity of the product, which is assigned structure IV (*exo*-5-chlorobenzonorbornene), was established by solvolysis results. The first-order rate plot (Figure 1) was linear (to over 90% reaction) when the rate at 103.5° was followed by titration for chloride ion in solvolysis in 80% aqueous ethanol in which a small excess of sodium acetate was present.[8] The value of the reaction-rate constant (2.2×10^{-5} sec^{-1}) may be considered good evidence[11] that the chlorine has the *exo* structure; this conclusion could be reached as well from the normal stereochemistry of additions to benzonorbornadienes.[11] The pmr spectrum confirms the fact that only one isomer is present in appreciable amounts. We have assigned the resonance at τ 6.18 to the proton in IV α to the chlorine atom at C_5, that at τ 6.52 to the bridgehead proton at C_4, and, that at τ 6.73 to that at C_1. The bridge protons absorb mainly in an envelope in the range τ 7.98–8.45, but one proton lies somewhat farther downfield at τ 7.87 ($J = 9.0$ cps). Its coupling constant[12,13] and its chemical shift[12,14] make it extremely likely that this is the proton at C_7 which is *syn* to the chlorine at C_5 and deshielded by it.

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[6] (a) Paper XXXIX: S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *J. Org. Chem.*, **31**, 2719 (1966). (b) Paper XL: *ibid.*, 2726 (1966). (c) Paper XLI: *ibid.*, 2733 (1966).

[7] Paper XXXVI: S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *ibid.*, **88**, 3087 (1966).

[8] When no base was present, a nonlinear plot was obtained (Figure 1); the chloride ion production leveled off at about 65% reaction. Such results, which are commonly observed[9,10] when fairly slow solvolyses are studied in ethanol solutions at high temperatures, appear to be caused by the formation of ethyl chloride.[9]

[9] R. P. Arganbright, Ph.D. Thesis, University of Colorado, Boulder, Colo., 1956.

[10] J. W. Wilt and A. R. Zigman, Abstracts, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, p 24P.

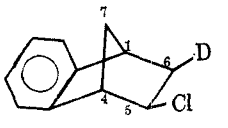
[11] P. D. Bartlett and W. P. Giddings, *J. Am. Chem. Soc.*, **82**, 1240 (1960).

[12] P. Laszlo and P. V. R. Schleyer, *ibid.*, **86**, 1171 (1964), and references cited therein.

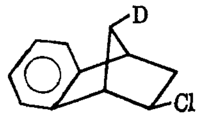
[13] K. Tori, R. Muneyuki, and H. Tanida, *Can. J. Chem.*, **41**, 3142 (1963).

[14] G. S. Reddy and J. H. Goldstein, *J. Chem. Phys.*, **38**, 2736 (1963).

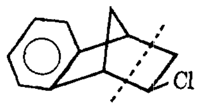
Addition of Deuterium Chloride to Benzonorbornadiene.—The addition of deuterium chloride to benzonorbornadiene (III) was carried out by bubbling deuterium chloride through a methylene chloride solution of III at −78° in the dark. Samples were obtained resulting from 23 to 100% reaction by varying the reaction times. For comparison purposes the addition was also carried out in deuterium oxide at room temperature. The deuteriochlorides, a mixture of compounds VI and VII, were separated from unreacted III by a fractional distillation. Only one peak could be detected by a vapor phase chromatographic (vpc) analysis.



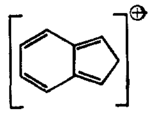
VI



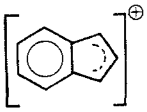
VII



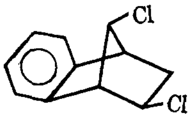
VIII



IX



X



XI

In the pmr spectrum of a 50:50 (see below) mixture of VI and VII the signal for the proton α to chlorine partially collapses owing to the loss of the *trans* coupling in VI, $J \cong 3$ cps, giving rise to a quartet which is interpretated as $J_{cis} = 7.8$ cps and $J_{5\text{-}anti\text{-}7} = 2.0$ cps.[5,12,15,16] Thus a *cis-exo* configuration of chlorine and deuterium exists in VI. This assignment is supported by the partial collapse of the narrow multiplet for the bridgehead proton at C_1 owing to the loss of the spin–spin coupling, $J \cong 4$ cps, between it and the *exo* hydrogen at C_6. This is the expected value for the coupling constant between a bridgehead proton and an *exo* proton,[12,16] whereas the coupling constant of the bridgehead proton and the *endo* proton is expected to be negligible.[12,16] The resonance signal for the other bridgehead proton which has no adjacent *exo* proton lacks any significant splitting. The coupling between the bridgehead protons and the methylene bridge protons is small.[13] The presence of VII is indicated by the integration of the resonance signal in the pmr spectrum for the methylene bridge proton *syn* to chlorine. While this signal integrates for one proton in IV, it has only about half the expected intensity in the mixture of VI and VII. This indicates approximately equal amounts of VI and VII are formed in the addition of deuterium chloride to benzonorbornadiene.

As previous workers in this laboratory had very good results using mass spectrometry to scrutinize deuterium distribution in dehydronorbornyl derivatives,[1] we anticipated that similar results might obtain with benzonorbornenyl derivatives. Thus one would predict that a principal fragment would be observed as a result of retro-Diels–Alder reaction[17] as shown in VIII. In fact, the most prominent peaks in the mass spectrum of *exo*-5-chlorobenzonorbornene (IV) correspond to the loss of C_2H_3Cl (*m/e* 116, 41.0% of Σ_{35}) and C_2H_4Cl (*m/e* 115, 12.9% of Σ_{35}). The peak at *m/e* 116 is interpretated as arising from a retro-Diels–Alder reaction[17] producing chloroethylene and the isoindene (or indene) cation IX. The formation of the *m/e* 115 peak is rationalized, at least in part, as a loss of a hydrogen from the *m/e* 116 fragment producing the indenyl cation X. Even in benzonorbornadiene (III) the most prominent peaks below the molecular ion (*m/e* 142, 21.7% of Σ_{35}) and the M − 1 peak (benzotropylium, *m/e* 141, 25.7% of Σ_{35}) are due to the loss of acetylene (*m/e* 116, 4.8% of Σ_{35}) and that formally resulting from the loss of hydrogen from the *m/e* 116 fragment (*m/e* 115, 10.1% of Σ_{35}).[18-20] The deuterium distribution for the VI–VII mixture was calculated assuming that the difference between the deuterium content of the molecular ion and the isoindene cation reflected the deuterium content of ethylene bridge which is lost in the retro-Diels–Alder fragmentation. Allowances were made (see Experimental Section) for the small uncertainty arising from the loss of hydrogen or deuterium in going from the isoindene cation to the indenyl cation. The results of the mass spectral analyses are given in Table I. It may be noted that, within the limits of experimental error, the deuterium is divided equally between C_6 (VI) and C_7 (VII). This confirms the rougher estimates made by pmr analysis.

It might here be noted that no exchange of aromatic protons by deuterium accompanying addition was observed. In the incomplete additions to benzonorbornadiene, no exchange of the vinylic or aromatic protons was detected in the unreacted olefin III. Furthermore no dideuterated species were detected in the mass spectrum of the mixture which contained VI and VII. Therefore, electrophilic attack by $H^{\oplus}$ (or $D^{\oplus}$) occurs selectively on the double bond, and every attack results in addition of a molecule of hydrogen chloride (deuterium chloride) or is reversible.

Addition of Acetic Acid-*O*-d_1, and -d_4 to Benzonorbornadiene.—Bartlett and Giddings[11] have shown that acetic acid adds to benzonorbornadiene in the presence of acid to give *exo*-benzonorbornenyl acetate (XII).

We utilized three sets of conditions in the addition of acetic acid-O-d_1 or -d_4 to benzonorbornadiene. The reaction is rapid and goes to completion within 24 hr at 60° when it is carried out in 0.18 *M* sulfuric acid-d_2 in acetic acid-O-d_1 or -d_4. In the absence of mineral acid catalysis the reaction is much slower, the addition

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(15) F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961).

(16) J. Meinwald, Y. C. Meinwald, and T. N. Baker, III, *J. Am. Chem. Soc.*, **85**, 2513, 2514 (1963), and references cited therein.

(17) K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 102.

(18) Pertinent to the present study, the mass spectrum of *exo*-5-*anti*-7-dichlorobenzonorbornene (XI) has its most intense peaks at *m/e* 149 and 151 corresponding to the chloroindenyl cation and has no peak at *m/e* 116.

(19) The fact that III gives a ratio for *m/e* 115/116 = 2.1, while the same ratio for IV is 0.31, makes it clear that there are a number of paths for formation of the indenyl cation (mass 115) peak. It has been shown[20] that the benzotropylium peak leads in large part to the mass 115 peak.

(20) After this work was completed, we were appraised by Dr. H. Tanida of work on mass spectroscopy which he and his co-workers had completed: T. Goto, A. Tatematsu, Y. Hata, K. Kitahonoki, R. Muneyuki, H. Tanida, and K. Tori, *Tetrahedron*, submitted for publication. Our results on norbornenes and on benzonorbornenes are very similar to theirs.

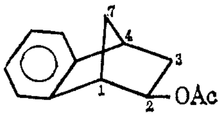
TABLE I

CONDITIONS AND RESULTS FOR THE ADDITION OF DEUTERIUM CHLORIDE TO BENZONORBORNADIENE

Expt	Reagent	Solvent	Temp, °C	Extent of reaction, %	% D in molecular ion	% D in isoindene ion	% D in ethylene[a] bridge
1	HCl	H_2O	27	100	0	0	0
2	DCl	D_2O	27	75	95.9	47.4	48.5
3	DCl	CH_2Cl_2	−78	100	93.3	46.9	46.6
4	DCl	CH_2Cl_2	−78	85	96.5	49.6	46.9
5	DCl	CH_2Cl_2	−78	23	94.9	48.1	46.8

[a] Calculated by difference.

proceeding to only 7% when a solution of 15 mole % of III in acetic acid-d_4 was heated at 111° for 7 days. If a hydrocarbon solvent is used the reaction is slowed down even further. When a solution of 19 mole % of III and 37 mole % cyclohexane in acetic acid-d_4 was heated at 136° for 14 days only 5% reaction occurred. For each case, only one peak[11] was detected by vpc analysis, and any *endo* isomer in excess of 5% could have been detected by pmr.



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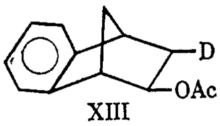
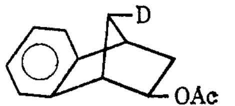
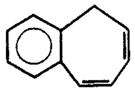


XIII



XIV



XV

For pmr and mass spectral comparisons the undeuterated acetate XII formed by the acid-catalyzed addition of acetic acid to III and XIII prepared by acetylation of *cis-exo*-3-deuterio-2-benzonorborneol, prepared by a deuteroboration–oxidation[21] scheme, were used.

In the pmr spectrum of XII the signal for the proton α to the acetoxy group occurs as a multiplet at τ 5.38. The bridgehead protons H_1 and H_4 occur at τ 6.72 and 6.81, respectively. No protons were distinguishable in the main methylene envelope, τ 8.09–8.42. The *cis-exo* configuration of the acetoxy group and deuterium in XIII is confirmed by the pmr spectrum. The multiplet for the proton α to the acetoxy group now occurs as a doublet, J_{cis} = 7.1 cps, with some finer splitting of less than 1 cps.[5,15,16] The narrow multiplet for H_4 collapses in going from XII to XIII, as the *exo* C_3 proton is exchanged for a deuterium atom,[12,15] whereas the signal for H_1 is unaffected. The pmr spectrum of a mixture of XIII and XIV resulting from the acid-catalyzed addition of acetic acid-O-d_1 indicated scrambling of the deuterium between C_3 and, presumably, C_7. Unfortunately, since the protons at C_3 and C_7 are not separated in the methylene envelope, a more quantitative estimation of the deuterium distribution by integration was not possible. Therefore mass spectral analysis was relied upon to give the deuterium distribution.

As in the case of *exo*-5-chlorobenzonorbornene (IV), *exo*-2-benzonorbornyl acetate (XII) undergoes a retro-Diels–Alder[17] process as the principal mode of electron impact induced fragmentation. In contrast to IV, however, the fragment at *m/e* 115 from XII is more intense relative to *m/e* 116, and a peak of *m/e* 117 of unknown origin is observed. The relative intensities of the peaks at *m/e* 115, 116, and 117 from XII are 31/51/18. As this introduces considerable uncertainty in determining the deuterium content of the isoindene ion (*m/e* 116), two approaches were made in an attempt to circumvent this difficulty.

The first was to pyrolyze the acetate and examine the deuterium content of the elimination product by mass spectroscopy. The pyrolysis was complete at 575° giving 1,2-benzocycloheptatriene (XV) and the isomeric methylnaphthalenes as the pyrolyzates. The thermal rearrangement of benzonorbornadiene, which gives rise to these products has been previously described.[22] This method assumes a *cis* elimination which would remove the *exo* deuterium at C_3.[23,24] Unfortunately in addition to an intense molecular ion peak at *m/e* 142 in the mass spectrum of the pyrolyzates, an equally intense M − 1 (*m/e* 141) peak (benzotropylium ion) was observed.[25] This introduces serious complications in the calculation of the deuterium content of the molecular ion. The pyrolysis procedure was nevertheless tried with *cis-exo*-3-deuterio-2-benzonorbornenyl acetate (XIII) and the deuterium content of the molecular ion was found to be 6 ± 1% indicating that *cis–exo* elimination had occurred to the extent of 94 ± 1%. A mixture of XIII and XIV formed by the acid-catalyzed addition of acetic acid-O-d_1 was also pyrolyzed. There was greater uncertainty in this determination but it indicates that about *ca.* 50% of the deuterium is at C_7 in the acid-catalyzed adduct.

A second approach to this problem was made by examining the alcohols, XVI, XVII, and mixtures of XVII and XVIII, derived from the corresponding acetates, in the hope that cleaner mass spectra would be found. Fortunately this was in fact the case. The principal mode of fragmentation was again the retro-Diels–Alder pathway but the ratio of *m/e* 115, 116, and 117 was 25.8/71.7/2.51. These relative intensities are certainly more acceptable, especially with respect to the *m/e* 117 peak. Allowances were made (see Experimental Section) for the 117 peak and calculations were made in the same manner as for the deuterium chloride adducts. The results are given in Table II and are felt to be accurate to within 4%. The pmr spectra of the alcohols XVI and XVII were as expected. The alcohols exhibited only one vpc peak. In order that all of the alcohols have similar

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[21] G. Zweifel, K. Nagase, and H. C. Brown, *J. Am. Chem. Soc.*, **84**, 183 (1962), and references cited therein.

[22] S. J. Cristol and R. Caple, *J. Org. Chem.*, **31**, 585 (1966).

[23] C. H. DePuy and R. W. King, *Chem. Rev.*, **60**, 431 (1960).

[24] P. S. Skell and W. L. Hall, *J. Am. Chem. Soc.*, **86**, 1557 (1964).

[25] Reference 17, p 84.

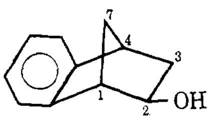
Table II

Conditions and Results for the Addition of Acetic Acid, O-Deuterioacetic Acid, and Tetradeuterioacetic Acid to Benzonorbornadiene

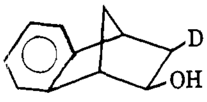
	Conditions for acetate formation							% D		
Expt	Substrates	Reagent	[Catalyst[a]], *M*	Mole %, III	Temp, °C	Time	% reaction	Molecular ion[b]	C_7[c]	C_3[d]
1	III	CH_3CO_2H	0.18	3	60	18 hr	100	0	0	0
2	XVII	Ac_2O	*e*	..	...	...	...	98.6	1.4	97.2
3	III	CD_3CO_2D	0.18	4	60	24 hr	100	87.9	41.1	46.8
4	III	CH_3CO_2D	0.18	11	60	27 hr.	100	85.2	36.3	48.9
5	III	CD_3CO_2D	0.00	15	111	7 days	7	91.4	24.5	66.9
6	III	CD_3CO_2D	*f*	19	136	14 days	5	91.8	7.8	84.0
7	XIII[g]	CD_3CO_2D	0.18	..	60	24 hr	...	98.7	12.5	86.5

[a] H_2SO_4 or D_2SO_4. [b] Percentage of deuterium labeled alcohol. [c] These results are not corrected for the small amount of scrambling which may be occurring in the analysis as indicated in expt 2. [d] Calculated by difference. [e] Pyridine was catalyst in this acetylation. [f] This reaction had 37 mole % of cyclohexane present. [g] This contained 5 mole % of XIII and no III.

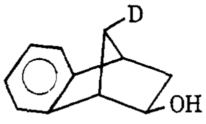
histories, the sample of XVI was prepared by saponification of XII, the sample of XVII was prepared by pyridine-catalyzed acetylation of XVII to give XIII, which was then saponified to XVII, and the mixtures of XVII and XVIII were obtained by saponification of mixtures of XIII and XIV.



XVI



XVIII



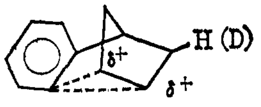
XVIII

A sample of *cis-exo*-3-deuterio-2-benzonorbornenyl acetate (XIII) was subjected to the acid-catalyzed addition conditions. The resulting deuterium distribution, determined from the corresponding alcohol, is shown in expt 7 in Table II. Although some scrambling of deuterium did occur, it was not sufficient to account for the deuterium distribution in the direct acid-catalyzed additions of acetic acid-O-d_1 or -d_4 to benzonorbornadiene.

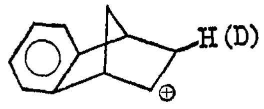
When O-deuterioacetic acid was used in the additions, exchange was observed between the methyl hydrogens (of acetic acid or the ester product) and the active deuterium. The extent of this exchange could be determined by comparing the molecular ion and acylium ion peaks in the spectra of the acetates. This phenomenon, which has been observed before,[1] became more serious as the reaction time and temperature were increased. Thus, although it was not very serious for the acid-catalyzed additions, it became critical for the uncatalyzed additions where both a higher temperature and longer reaction time were necessary. The use of acetic acid-d_4 eliminated this problem, and the later experiments which we carried out were with the completely deuterated acid.

Discussion of Results.—The results given above force the conclusion that there are at least two pathways utilized in these electrophilic additions to benzonorbornadiene. Thus, the results are similar in general to those with norbornadiene, where multiple (at least three) pathways were required to accommodate them.[6] Our results show that the kinetically controlled distribution of deuterium in the polar addition of deuterium chloride to benzonorbornadiene in methylene chloride at −78° or in deuterium oxide at room temperature is divided equally between the ethylene VI and methylene VII bridges. The pmr spectrum indicates that the deuterium on the ethylene bridge is at C_3 and *exo*, and that the deuterium on the methylene bridge at C_7 is *syn* to the *exo* C_2 chlorine. The stereochemical data are incompatible with the formulation of an *endo* protonated π complex (true for acetic acid addition as well), and are thus identical with additions to trimethylenenorbornene[5] and norbornadiene.[6]

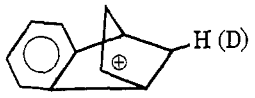
Dewar and Fahey[26] noted that hydrogen chloride and hydrogen bromide added to acenaphthylene and to indene predominantly by *cis* addition and concluded that the reaction involved first the formation of a carbonium ion–$[X(HX)_n]^\ominus$ ion pair. They argued that the *cis* addition occurred when the cation coordinated with an X anion from its gegen ion rapidly (before inversion of the cation with respect to the anion by any of a variety of processes), and argued against a concerted *cis* addition. Our results with benzonorbornadiene confirm their hypothesis of the involvement of ionic intermediates rather than the involvement of a cyclic *cis* addition process. The data permit us to assume that there is only one cationic intermediate, formulated as a nonclassical species XIX, or that there is a set of classical ions, XX and XXI, which equilibrate so rapidly compared with their rate of coordination with chloride ion that they simulate XIX. The nonclassical cation XIX has been proposed[27] to accommodate the complete loss of activity associated with the acetolysis of optically active *exo*-benzonorbornenyl *p*-bromobenzenesulfonate, although the preliminary report of their work did not show that loss of activity in the *p*-bromobenzenesulfonate by internal return[7] could be neglected.



XIX



XX



XXI

Although the apparent stereochemistry of addition of acetic acid to benzonorbornadiene is identical with that of hydrogen chloride (only *exo* acetate is formed), the deuterium distributions resulting from the additions of deuterium acetate are quite different from the

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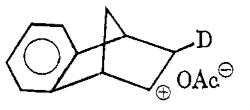
(26) M. J. S. Dewar and R. C. Fahey, *J. Am. Chem. Soc.*, **85**, 2245, 2248 (1963).

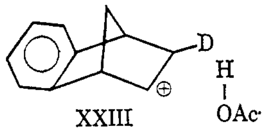
(27) W. P. Giddings and J. Dirlam, *ibid.*, **85**, 3900 (1963).

equal distribution at the ethylene and methylene bridges observed with deuterium chloride. Thus (Table II, expt 3 and 4), even with sulfuric acid catalysis, the amount of deuterium at C_7 was only 46.7 and 42.5%, respectively, with the lesser amount of deuterium at C_7 occurring when the original mixture had a lower acetic acid/olefin ratio. These results are not consistent with the concept that the single intermediate XIX is the progenitor of all of the product, as this should give 50% of deuterium at C_3 (XIII) and 50% at C_7 (XIV). In the absence of mineral acid, the amount of Wagner-Meerwein rearrangement accompanying addition was reduced further, with only 27% deuterium at C_7 when the starting mixture contained 15 mole % of benzonorbornadiene and 85 mole % of acetic acid (Table II, expt 5) and only 8% at C_7 when the starting mixture had 19 mole % of benzonorbornadiene, 37 mole % of cyclohexane, and 44 mole % of acetic acid (Table II, expt 6).

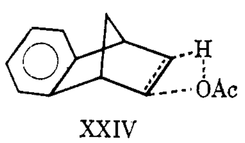
These observations are analogous to those[6] with norbornadiene and can be rationalized in two ways.[28] One may assume that unsymmetrical cations such as the classical ions XX and XXI are involved, with XIX being formed first by proton (deuteron) transfer. In the uncatalyzed system the ion pair XXII would be formed and in the acid-catalyzed system the ion-dipolar molecule XXIII would be formed. These species could then either collapse to XIII (or its conjugate acid) or isomerize by a Wagner-Meerwein shift to the corresponding ion pair or ion dipole in which XXI is the cation. If the rates of coordination of XX and XXI with acetate and acetic acid are competitive with that of isomerization, the mechanisms are acceptable. The facts that with acid catalysis the Wagner-Meerwein equilibration process represents over 85% of the reaction (twice the percentage of deuterium at C_7) and in the uncatalyzed reaction (Table II, expt 5) only 54% are in accord with this interpretation, as one may assume that coordination of XX with acetic acid (from XXIII) would be slower than that with acetate ion (from XXII). Similarly, with addition of cyclohexane, the life time of the ion pair XXII toward collapse to XIII should be cut down considerably by the nonpolarity of the solvent, consistent with the observation that only 17% of the product results from a Wagner-Meerwein process.



XXII



XXIII



XXIV

An equally acceptable hypothesis assumes that two quite different routes are utilized in the acetic acid additions. One, leading to complete mixing of C_3 and C_7, involves a nonclassical ion XIX (or a set of *rapidly* equilibrating cations, such as XX and XXI, which simulates XIX) involved in an ion pair with acetate ion or in an ion dipole with acetic acid. These systems then lead to equal amounts of XIII and XIV, and their importance may be measured by twice the deuterium content at C_7.[29] The alternate route, leading to the excess *cis-exo* addition over that involved in the Wagner-Meerwein equilibration, could be a single-step process not involving a carbonium ion intermediate, but rather a four-center transition state. The model for the uncatalyzed reaction is shown as transition state XXIV; that for the catalyzed reaction would have an additional proton present.[30] The solvent effects which we have observed in these additions are readily rationalized by these mechanisms. Compared with the uncatalyzed reactions, acid catalysis should favor proton transfer without coincident acetic acid coordination. Furthermore, the concerted addition process should be favored in the uncatalyzed case by reduced polarity of solvent,[6] as the alternative process involves the formation of ions from neutral molecules.

Experimental Section

Reagents.—Benzonorbornadiene (III), 98% by vpc, was prepared by the method of Wittig.[31] Deuterium oxide, 99.7%, was obtained from General Dynamics Corp. and reagent acetyl chloride from J. T. Baker Chemical Co. Acetic acid-O-d_1, acetic acid-d_4 and sulfuric acid-d_2 were obtained from Merck Sharp and Dohme of Canada Ltd. The lithium aluminum deuteride, 98%, was obtained from Metal Hydrides, Inc.

Preparation of Deuterium Chloride.—Deuterium chloride was prepared by the addition of acetyl chloride to deuterium oxide.[26] The gas was collected in a trap cooled with liquid nitrogen and then distilled directly into the reaction vessel. Contamination by addition of hydrogen chloride to benzonorbornadiene (III) averaged about 5% as seen by the mass spectral data for the adducts (Table I).

***exo*-2-Chlorobenzonorbornene (IV).**—Benzonorbornadiene (III, 5.0 g, 35 mmoles) was shaken with 25 ml of concentrated hydrochloric acid in a sealed tube at room temperature for 15 hr. The reaction mixture was extracted with ethyl ether, and the ethereal solution was washed with water and dried over anhydrous magnesium sulfate. Removal of the ether under vacuum left a dark oil, the pmr of which indicated no starting olefin III. The oil was distilled twice, bp 55° (0.2 mm), yielding 5.1 g (81%) of the hydrochloride of IV, $n^{25}\text{D}$ 1.5664.

Anal. Calcd. for $C_{11}H_{11}Cl$: C, 73.94; H, 6.21; Cl, 19.85. Found: C, 74.02; H, 6.36; Cl, 19.71.

Kinetics of Solvolysis of IV.—*exo*-5-Chlorobenzonorbornene (IV), 1.423 g (7.96 mequiv), and 0.964 g (11.8 mequiv) of sodium acetate were dissolved in 80 vol % aqueous ethanol and made up to 100 ml of solution. Aliquots (5 ml) were placed in Pyrex tubes, sealed, and immersed in a constant-temperature bath at 103.5 ± 0.2°. The chloride ion formed was determined by a Volhard titration.[32] The chloride ion determination was substracted from that for the infinity titer and the natural logarithm of this value was plotted *vs.* time. The infinity titer agreed within 2% of the initial amount of IV. Duplicate runs were made.

Addition of Deuterium Chloride to Benzonorbornadiene (III) in Methylene Chloride.—Deuterium chloride, about 0.5 mole,

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[28] In previous papers[6] we have discussed the nature of the acid catalysis and the question of the number of acetic acid molecules involved in the transition states for the addition reaction. The work we are reporting in this paper gives us no further information about these questions, and for simplicity we shall display mechanisms involving only one acetic acid molecule, and assume that, in acid catalysis, the catalyzing species is the conjugate acid of acetic acid, ignoring its gegen ion.

[29] In the norbornadiene case,[6] one could estimate how much of the product came from coordination of the cation with the gegen ion or gegen molecule formed coincidentally with the cation, and how much formed from solvent separated ion pairs or ions. This is not possible with benzonorbornadiene.

[30] We have represented these as four-membered ring transition states, as it appears that certain additions of water and methanol utilize similar mechanisms.[5] However there is no evidence that equivalent[6] six-membered ring transition states are not in fact involved; these would be the reverse of mechanisms generally accepted for pyrolytic eliminations.[23]

[31] G. Wittig and E. Knauss, *Chem. Ber.*, **91**, 895 (1958).

[32] D. S. McKittrick and C. L. A. Schmidt, *Arch. Biochem.*, **6**, 273 (1945).

was passed through 100 ml of reagent methylene chloride containing 4.40 g (31.0 mmoles) of benzonorbornadiene (III) at −78°. The reaction vessel was kept at this temperature for 48 hr. Solvent and excess deuterium chloride was removed under vacuum. No unreacted benzonorbornadiene (III) could be detected in the pmr spectrum. The adduct was purified by a distillation.

When the reaction time was shortened to 4 hr the addition proceeded to 85% of completion. At 4-hr reaction time with about 0.25 mole of deuterium chloride, the per cent reaction was 23. The deuterium chloride adducts were separated (vpc pure) by a fractional distillation.

Addition of Deuterium Chloride to Benzonorbornadiene (III) in Deuterium Oxide.—Deuterium oxide, 23 ml, was saturated with deuterium chloride at room temperature and added to 4.50 g (31.7 mmoles) of benzonorbornadiene (III) in a tube and sealed. The sealed tube was shaken vigorously at room temperature for 11 hr. The reaction mixture was extracted with diethyl ether, dried over anhydrous magnesium sulfate, and the ether was removed under vacuum. The pmr spectrum of the crude reaction product indicated addition had proceeded to 75% of completion. The deuterium chloride adduct was removed from unreacted benzonorbornadiene by a fractional distillation, the adduct fraction being redistilled and a center cut taken for the mass and pmr spectra.

***exo*-5-*anti*-7-Dichlorobenzonorbornene (XI).**—Benzonorbornadiene (III), 8.74 g (61.5 mmoles) was dissolved in 600 ml of reagent carbon tetrachloride, and anhydrous chlorine was passed through the solution until the color of chlorine persisted (about 12 min). Excess chlorine and solvent were removed under vacuum yielding 13.1 g (quantitative) of the crude dichloride. The product was characterized as the 5,7-dichloride XI by comparison of the pmr spectrum with the one for 5,7-dibromobenzonorbornene of established configuration.[33] A second isomer was observed in the vpc of crude dichloride, *ca.* 4%, which was identified[33] as the 5,6-*trans* adduct. The 5,7-dichloride XI was purified by a distillation, bp 86° (0.2 mm), followed by a recrystallization from petroleum ether (bp 60–70°), mp 50–51°.

Anal. Calcd for $C_{11}H_{10}Cl_2$: C, 61.99; H, 4.73; Cl, 33.28. Found: C, 62.09; H, 4.61; Cl, 33.03.

Deuterium Distribution in Mixtures of VI and VII. Mass Spectral Analysis.—The isotope corrected[34] relative peak intensities for samples 1–5 in Table I are given in Table III. Two sets of calculations were made to reflect the maximum and minimum possible values for the deuterium content at C_7, *i.e.*, the isoindene (indene) fragment. This was necessitated by the uncertainty arising from the formation of the indenyl cation. The maximum value for the deuterium content at C_7 was determined by assuming that the deuterated isoindene ion (*m/e* 117) lost only hydrogen in forming the indenyl fragment. Statistical considerations and isotope effects[35,36] make this a reasonable assumption. Since the peak at *m/e* 116 is then corrected for the maximum value of indenyl-D (*m/e* also 116), its comparison with isoindene-D (*m/e* 117) gives the maximum value for deuterium in the isoindene fragment. A minimum value for the deuterium content at C_7 was calculated by assuming that there was an equal chance of losing a hydrogen or deuterium from the isoindene-D (*m/e* 117) peak. Both sets of calculations were determined by a series of approximations, an example of which is given below for the determination of the maximum value for the deuterium content at C_7 in run no. 2 in Table I.

Table III

	Relative intensities			Max	Min	% D in
Expt	*m/e* 115	*m/e* 116	*m/e* 117	% D at C_7	% D at C_7	molecular ion
1	116	364	0	0	0	0
2	68	251	185	50.4	44.4	95.9
3	146	546	395	49.4	43.9	93.3
4	908	3331	2618	53.2	46.1	96.5
5	744	2689	2018	51.4	44.9	94.9

The maximum and the minimum values so determined are given in Table III, the range for each set being about 6%. For the lack of anything better, averages were taken and are the values reported in Table I.

The D content at C_7 in run no. 2, Table I.

First approximation: neglect contribution of indenyl-D to *m/e* 116.

$$\%\ \mathrm{D\ at\ C_7} = \frac{m/e\ 117 \times 100}{m/e\ 117 + m/e\ 116} = 42.4$$

Second approximation: peak at *m/e* 115 (indenyl-H) constitutes only 57.6% of total indenyl cation.

$$\frac{m/e\ 115}{0.576} = \text{total indenyl cation} = 118$$

$$\text{hence, indenyl-D} = m/e\ 115\text{–}118 = 50$$

$$\%\ \mathrm{D\ at\ C_7} = \frac{m/e\ 117 \times 100}{m/e\ 117 + (m/e\ 116 - 50)} = 47.9\%$$

Third approximation: repeat of second approximation, peak at *m/e* 115 constituting only 52.1% of total indenyl cation.

$$\%\ \mathrm{D\ at\ C_7} = 49.9\%$$

Fourth approximation: repeat.

$$\%\ \mathrm{D\ at\ C_7} = 50.3\%$$

Fifth approximation: repeat.

$$\%\ \mathrm{D\ at\ C_7} = 50.4\%$$

***exo*-3-Benzonorbornenyl Acetate (XII).**—Benzonorbornadiene (III), 4.31 g (30.4 mmoles), was heated at 60 ± 2° in 50 ml of 0.18 *M* sulfuric acid in acetic acid for 18 hr. The reaction was initially a light purple but became colorless upon work-up. Work-up was accomplished by adding 75 ml of water and extracting with diethyl ether. The ether extracts were washed consecutively with water, a 10% sodium carbonate solution, and more water. The ether extracts were dried over anhydrous magnesium sulfate and the ether removed under vacuum. The pmr spectrum of the crude product indicated no unreacted olefin III. The acetate was purified by a distillation yielding 5.60 g (91%) of vpc pure product, bp 84° (0.2 mm), $n^{25}\mathrm{D}$ 1.5342.

Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.32; H, 7.14.

A sample of the acetate XII was converted to the alcohol XVI by basic hydrolysis,[11] mp 75–76°, lit.[11] 74.1–75.4° and lit.[37] 74.5–75.5°. The spin-spin multiplet for the proton α to the hydroxyl group in the pmr spectrum of XVI occurs at τ 6.17. As with the corresponding acetate this multiplet collapses to a doublet, $J_{cis} = 7.1$ cps, with finer splitting being less than 1 cps[5,15,16] in the *cis*-*exo*-deuterated alcohol XVII.

***cis*-*exo*-3-Deuterio-2-benzonorbornenol (XVII).**—Benzonorbornadiene (III), 7.77 g (54.7 mmoles), and 1.95 g (46.5 mmoles) of lithium aluminum deuteride were placed in a 500-ml, 3-necked, round-bottom flask and 200 ml of dry ethyl ether was added.[21] A continuous stream of dry nitrogen was passed through the apparatus which included a dropping funnel and a condenser with a drying tube. The reaction flask was cooled in an ice bath; the contents were stirred while 8.80 g (61.9 mmoles) of freshly distilled boron trifluoride etherate (Eastman Kodak) was added dropwise over a period of *ca.* 15 min. The mixture was stirred for 18 hr more at room temperature. The reaction flask was cooled and 2 ml of water was added dropwise followed by 7.5 ml of a 10% sodium hydroxide solution and then 5.8 ml of 30% hydrogen peroxide. The mixture was stirred at room temperature for 1 hr. The ether layer was removed by decantation and the residues were washed again with 100 ml of ether. The combined ether extracts were washed with water and dried over anhydrous magnesium sulfate, and the ether was removed under vacuum. Only one peak could be detected by vpc. The crude alcohol was recrystallized from petroleum ether (bp 60–70°) yielding 7.88 g (89%) of the deuterated alcohol XVII. The melting point, 75–76°, agrees with previously reported values for *exo*-2-benzonorbornenol, 74.1–75.4°[11] and 74.5–75.5°.[37]

Addition of Acetic Acid-O-d_1 or -d_4 to Benzonorbornadiene (III). A. Acid Catalyzed.—Benzonorbornadiene (III), 2.81 g (20.0 mmoles), was dissolved in 10.0 g (156 mmoles) of acetic acid-O-d_1 and 100 μl of sulfuric acid-d_2 was added. The contents were sealed off and placed in an oil bath at 60 ± 2° for 27 hr. The solution was then poured into 75 ml of ether. The resulting ethereal solution was washed successively with a 10% sodium

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[33] G. W. Nachtigall of this laboratory, unpublished results.

[34] J. H. Beynon, "Mass Spectrometry and Its Applications to Organic Chemistry," Elsevier Publishing Co., Amsterdam, 1960, Appendix I.

[35] J. H. Beynon, *ibid.*, p 453.

[36] Reference 17, Chapter 5.

[37] P. Bruck, *Tetrahedron Letters*, **No. 10**, 449 (1962).

acetate solution, a 10% sodium carbonate solution, and finally water. The ether extracts were dried and the ether was removed under vacuum. No starting olefin III could be detected by vpc. The crude product was purified by a vacuum distillation. A second run was made using 0.843 g (5.9 mmole) of benzonorbornadiene, 9.0 g (0.14 mmoles) of acetic acid-d_4, and 90 μl of sulfuric acid-d_2. The reaction was run at 60 ± 2° for 24 hr. After work-up the acetate was recovered by preparative vpc.

B. Uncatalyzed.—Benzonorbornadiene (III), 3.06 g (21.5 mmoles), was dissolved in 7.58 g (118 mmoles) of acetic acid-d_4 and sealed. The sealed tube was heated at 111 ± 2° in an oil bath for 7 days. Most of the acetic acid-d_4 was recovered by a distillation before the normal work-up. The acetate, which was formed only to the extent of 7%, was recovered by preparative vpc.

C. In Cyclohexane.—Benzonorbornadiene (III), 6.90 g (48.6 mmoles) was dissolved in 7.21 g (113 mmoles) of acetic acid-d_4 and 7.8 g (93 mmoles) of cyclohexane (sulfuric acid washed and redistilled) was added. The solution was sealed and heated at 136 ± 2° in an oil bath for 14 days. The usual work-up was carried out and the acetate, formed to the extent of 5%, was separated from unreacted benzonorbornadiene by preparative vpc.

Treatment of *cis-exo*-3-Deuterio-2-benzonorbornenyl Acetate (XIII) under the Acid-Catalyzed Addition Conditions.—Acetate XIII, 250 mg (1.76 mmoles) was dissolved in 2.0 g (31 mmoles) of acetic acid-d_4 and 20 μl of sulfuric acid-d_2 was added. The solution was heated in a sealed tube at 60 ± 2° for 24 hr. Work-up was in the usual procedure and the acetate was recovered by preparative vpc.

***cis-exo*-3-Deuterio-2-benzonorbornenyl Acetate (XIII).**—*cis-exo*-3-Deuterio-2-benzonorborneol (XVII), 7.60 g (47.2 mmoles), was dissolved in 15 ml of reagent acetic anhydride and 15 ml of pyridine and heated at 100° with stirring for 3 hr. The reddish solution was then poured into 100 ml of water and extracted with diethyl ether. The ether extracts were washed successively with 10% hydrochloric acid, water, a 10% sodium carbonate solution, and finally water. The ether extracts were dried and the ether was removed under vacuum. The crude acetate was carefully distilled, bp 80° (0.1 mm), yielding 5.98 g (63%) of the deuterated acetate XIII. The vpc retention time was identical with that of *exo*-3-benzonorbornenyl acetate (XII) obtained by the addition of acetic acid to III.

Pyrolysis of *exo*-2-Benzonorbornenyl Acetate (XII).—The pyrolysis of the acetate XII was accomplished by adding, dropwise, at a rate of about 5 ml/hr, a 10% benzene solution of XII onto a 0.25 × 12 in. column filled with glass helices and heated to 575°. The pyrolysates were collected in a Dry Ice trap at the bottom of the column. The excess benzene was removed under vacuum yielding an essentially quantitative yield of 1,2-benzocycloheptatriene (XV) and the isomeric methylnaphthalenes.[22] The pyrolyses of the deuterated acetates were carried out in a similar manner. The mass spectral data in relative intensities are given in Table IV. By comparison with the spectrum from XII a fairly reliable value of 6% can be calculated for the deuterium content of the pyrolysates from XIII. For larger deuterium contents in the pyrolysates, as from a mixture of the deuterated acetates XIII and XIV, this comparison introduces large uncertainties in the calculations, and this approach was discarded.

TABLE IV

Acetate	D content of acetete, %	Pyrolysates m/e 141	m/e 142	m/e 143
XII	0	1310	1546	. . .
XIII	97.5	2677	3474	203
Mixture of XIII and XIV[a]	88	1896	3456	1506

[a] From acid-catalyzed addition of CD_3CO_2D to III.

Saponification of the Acetates.—The acetates were converted to the alcohols for mass spectral analysis by refluxing for 48 hr in a mixture of 10 ml of ethanol and 10 ml of a 50% potassium hydroxide solution. Work-up was accomplished by an ether extraction from the basic solution. The alcohol in every case was recovered in essentially quantitative yield.

Deuterium Distribution in Mixtures of XVII and XVIII. Mass Spectral Analysis.—The isotope corrected[34] relative peak intensities of samples 1–7 in Table II are given in Table V.

TABLE V

No.	Relative intensities m/e 115	m/e 116	m/e 117	Max % D at C_7	Min % D at C_7	% D in molecular ion
1[a]	990	2753	0	0	0	0
2	832	2534	35	1.37	1.36	98.6
3	1878	5878	3178	43.5	38.6	87.9
4	1384	4494	2222	38.0	34.6	85.2
5	651	1309	373	25.6	23.4	91.4
6	1043	3097	255	7.8	7.7	91.8
7	869	2662	368	12.7	12.4	98.7

[a] This sample was always run in parallel with runs 2–7 for correction purposes.

Numbers 2–7 have been further corrected for the small but significant m/e 117 peak. Since no significant change occurred in the very small m/e 118 peak in the deuterated samples 2–7 as opposed to sample 1, a correction of the m/e 117 peak was made assuming the same ratio of m/e 117 to the molecular ion in the deuterated and undeuterated samples. Justification for this approximation comes in the result for the deuterium distribution in *cis-exo*-3-deuterio-2-benzonorborneol (XVII) which indicates that 1.4% of the deuterium is at C_7. Analogous results with *cis-exo*-3-deuterio-2-norborneol[6] indicated that the cyclopentadiene ion fragment (m/e 66) contained about 3% of the available deuterium. The presence of deuterium in these fragments possibly arises from a process inside the ionization chamber.[38] The calculations were made in exactly the same manner as for the deuterium chloride adducts and maximum and minimum values for deuterium content in the isoindene ion (C_7) are given in Table V.

Analytical.—The gas chromatographic analyses were formed on a 2 m × 0.25 in. silicon 710 column (30%) on Chromosorb, 35–80 mesh, at a column temperature of 164° and a helium flow rate of about 110 cc/min. The retention times of III, IV, XII, and XVI were 7, 15, 36, and 34 min, respectively. Nuclear magnetic resonance spectra were obtained in carbon tetrachloride using a Varian Associates Model A-60 spectrometer with tetramethylsilane (τ 10.0) as the internal standard. Mass spectra were obtained on a Consolidated Electrodynamics Corp. Model 21-103C spectrometer. All spectra were determined with an ionizing current of 50 μa and an ionizing energy of 70 ev. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Melting points are uncorrected.

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(38) Reference 34, p 275.