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Bridged Polycyclic Compounds. XXXIX. Addition of Acetic Acid to Norbornadiene. Mechanisms of Addition Reactions[1]

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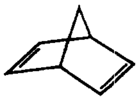
The addition of acetic acid to norbornadiene (I) has been studied under a large variety of conditions and the extents of both homoconjugate addition and Wagner–Meerwein rearrangements accompanying addition have been scrutinized in some detail. The work is described in this and in the following three papers. In this paper we have discussed our interpretation of the data; the second paper describes details of the acid-catalyzed additions; the third describes uncatalyzed additions; and the fourth describes details of mass spectral analysis. The data which are discussed herein include the nature of acid catalysis in acetic acid, salt effects, and medium effects on catalyzed and uncatalyzed reactions as noted by reaction rates and by amounts of rearrangement accompanying addition. The data require a multiplicity of mechanisms. *endo*-Protonated π complexes are not utilized, and *exo*-protonated π complexes are not product-determining intermediates. The data are accommodated by assuming competitions between cyclic (noncationic, but polar) processes and processes involving ion pairs, ion dipoles, and solvated ions as intermediates.

Some time ago it was reported from this laboratory[2] that acid-catalyzed addition of acetic acid (or of methanol) to norbornadiene (I) gave mixtures of *exo*-dehydronorbornyl acetate (II) and nortricyclyl acetate (III) (or the corresponding methyl ethers) significantly different from those mixtures produced by solvolysis in the same media. In particular, the mixtures produced in the addition reactions were considerably richer in the olefinic products than those produced in the solvolyses. This work made it clear that there had to be at least two mechanisms involved in the addition reactions. Of these, one or more appeared to lead to substantial amounts of homoconjugate addition and perhaps involved an intermediate (or intermediates) similar to that (those) involved in the solvolyses, and the other(s) appeared to lead to 1,2 addition.[2]



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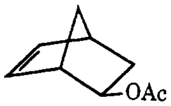

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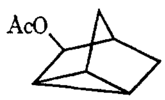

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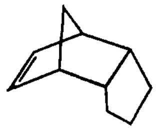

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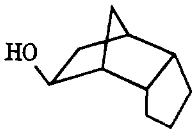
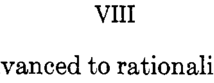


V

In the same paper, it was also reported that additions to *endo*-trimethylenenorbornene (IV) gave substantially more *endo*-trimethylene-*exo*-norborneol (V) derivatives in admixture with the *exo-exo* VI products than did additions to *exo*-trimethylenenorbornene (VII).[2,3] A number of intermediates and mechanisms were advanced to rationalize results observed in the norbornadiene–dehydronorbornyl–nortricyclyl systems and in the trimethylenenorbornene–trimethylenenorborneol



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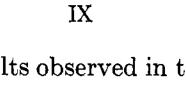

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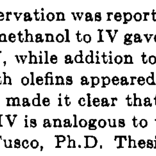
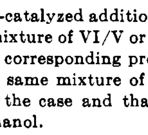


VIII



IX

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[1] Previous paper in series: S. J. Cristol and B. B. Jarvis, *J. Am. Chem. Soc.*, **88**, 3095 (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, W. K. Seifert, D. W. Johnson, and J. B. Jurale, *J. Am. Chem. Soc.*, **84**, 3918 (1962).

[3] The observation was reported that acid-catalyzed addition of methanol or of water in methanol to IV gave an 85/15 mixture of VI/V or of the methyl ethers of VI/V, while addition to VII gave a corresponding product ratio of 96.5/3.5. Both olefins appeared to give the same mixture of acetates, but further study[4] made it clear that this is not the case and that addition of acetic acid to IV is analogous to that of methanol.

[4] G. C. Fusco, Ph.D. Thesis, University of Colorado, Boulder, Colo., 1965.

system, but evidence was not at hand to exclude many of the possibilities.

Later,[5] it was shown that the alternative mechanism(s) leading to V from IV did not involve participation of an *endo*-protonated double bond (π complex)[6] species VIII, as the additions of deuterium oxide and of O-deuteriomethanol to give V were found to be largely, if not exclusively, *cis-exo* additions. At this stage, it appeared that one could explain the available results in additions to IV and to VII on the basis of a competition between a process involving a nonclassical cationic intermediate (or rapidly equilibrating classical cations) and a four-center cyclic process, or on the basis of competition between equilibration of classical cations and their capture by nucleophiles.

Rejection of an *endo*-protonated π complex IX in additions to norbornadiene did not appear to us to be required by our results with IV, particularly in view of the fact that a stable *endo*-iron carbonyl complex has been shown to have an analogous structure.[7]

In our early work,[2] we found that addition of acetic acid to norbornadiene *catalyzed by sulfuric acid* gave a product ratio of olefinic ester II to nortricyclyl ester III of 25/75. On the other hand, Vogelfanger[8,9] found that the same reaction *catalyzed by perchloric acid* gave a product ratio of 15/85, while the omission of the strong acid catalyst resulted in a product ratio of 72/28 (II predominating). These large differences in product ratios aroused our interest in the effects of reaction conditions upon this addition reaction.

The availability of sensitive analytical procedures (vapor phase chromatography, nuclear magnetic resonance spectroscopy, and mass spectroscopy) coupled with the observation that dehydronorbornyl derivatives fragment in the mass spectrometer in a retrograde Diels–Alder pattern[10] offered us powerful tools with which to study addition of acetic acid to norbornadiene in considerable depth. We were thus able to scrutinize the effects of reaction conditions upon product ratios of II and III (apparent simple 1,2 addition *vs.* homoconjugate addition) and, with the use of O-deuterioacetic acid, upon the stereochemistry of the 1,2-addition reaction and upon the amount of Wagner–Meerwein rearrangement accompanying addition. We therefore began a serious effort to sort out and understand all of these reactions in terms of mechanistic details.

Acid Catalysis, Salt, and Medium Effects. 1,2 Addition *vs.* Homoconjugate Addition.—The simplest phenomenon to scrutinize in the addition of acetic acid to norbornadiene is the ratio of apparent 1,2-addition product II to homoconjugate addition product III, as this can be done readily by vapor phase chromatography.[2] We confirmed and extended the earlier observations that differing conditions[2,9] led to different ratios of II and III. Compare paper XL,[11] Tables I–IV and VII, and paper XLI,[12] Tables I–II and V. Thus, with low initial diene to carboxylic acid ratios (1/24), catalysis by 0.001–0.01 *M* perchloric acid gave a ratio of II/III of 12/88, while catalysis by 0.01 *M* sulfuric acid gave a varying ratio of II/III. The perchloric acid catalyzed addition appeared to be independent of per cent reaction, but that catalyzed by sulfuric acid gave more II as the reaction proceeded. This appears to be a solvent effect (see below). High temperatures favored III.

The reaction was catalyzed markedly by sodium perchlorate, but was unaffected by sodium acetate. Sodium perchlorate catalysis gave II/III ratios similar to that of sulfuric acid.

Reactions without added mineral acid, but with a large excess of acetic acid (initial ratio of acetic acid/diene of 35/1) gave a ratio of II/III of 75/25, similar to that reported by Vogelfanger.[9] We noted, however, that the product ratio was markedly influenced by the acetic acid/diene ratio. For example, the olefin ester II represented 98.5% of the product in an experiment run almost to completion with an initial acid/diene mole ratio of 0.55. Thus, in the *uncatalyzed* reaction, there appeared to be a strong solvent effect with the less polar solvent disfavoring the homoconjugate addition leading to nortricyclyl acetate III. This was confirmed (paper XLI, Tables II, III, and VI and Figure 1) by the addition of various solvents to the reaction medium. Hydrocarbon and ether solvents favored *exo*-dehydronorbornyl acetate (II) markedly, while admixture with water and methanol gave more III than did pure acetic acid. Experiments in which the mole percentage of cyclohexane or of heptane were increased from zero to about 80% caused a marked increase in the II/III ratio, giving as much as 98% unsaturated ester II. It would appear safe to assume that the reaction(s) leading to III has a more polar transition state than that (those) leading to II (or that the intermediate leading to II is trapped in the less polar solvent before it rearranges to that leading to III).

The effect of added solvents on the acid-catalyzed reaction is much less straightforward. In the *perchloric acid catalyzed* reaction, changing the acetic acid/diene ratio from 40/1 to 1.1/1 hardly affected the ratio of II/III. On the other hand, the *sulfuric acid catalyzed* reactions showed substantial solvent sensitivity. As noted above, the product composition varied with percentage reaction, formation of the unsaturated ester being favored with time (Table I, paper XL) or with extent of reaction, in general (Table II, paper XL).[13] That this was probably a solvent effect is supported by the data of Table VIII, paper XL, where it may be noted that addition of a few volume per cent of ethyl acetate changes the II/III ratio markedly, leading to substantial increases in II product.

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

[6] R. W. Taft, *J. Am. Chem. Soc.*, **74**, 5372 (1952).

[7] R. Pettit, *ibid.*, **81**, 1266 (1959).

[8] We were early apprised by Professor S. Winstein of related work in his laboratory in this area.[9] We are much indebted to him for drawing this to our attention and for useful discussions.

[9] E. Vogelfanger, Ph.D. Thesis, University of California at Los Angeles, Los Angeles, Calif., 1963.

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

[11] This reference is to the next paper in this series: S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *ibid.*, **31**, 2726 (1966).

[12] This reference is to the third paper in this immediate series: S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *ibid.*, **31**, 2733 (1966).

[13] That this was not the effect of an equilibration between II and III may be seen from the data of Table X, paper XL, where it is shown that the equilibrium composition ratio II/III (in pentane) is 4/96. In our opinion, this ratio should not be affected markedly by solvent, as II and III have little difference in polarity. Vogelfanger[9] has shown that additions of acetic acid to II and III are slow enough so that they can not be responsible for the changes noted. This was confirmed by us by showing that II and III do not disappear under our conditions.[11]

The effects of small amounts of a variety of solvents on the II/III ratio is given in Table IX, paper XL. Any relationship would appear to be complex.

Solvents affect both the strength of the catalyzing acid and the solvation of the reagents and transition state, and their effects on the II/III ratio must undoubtedly reflect these properties.

Rates of Reactions, Acid Catalysis, and Salt Effects.—Interpretation of kinetic and catalytic effects in reactions in acetic acid are made very difficult by the nature of the solvent. Liquid acetic acid may be presumed to be largely dimeric.[14] Its low basicity means that mineral acids may not be completely ionized in acetic acid solution, and its low dielectric constant (ϵ 6.2)[15] means that ionized substances will be only slightly dissociated, but will rather exist largely as ion pairs,[16] or in larger aggregates. It is possible, therefore, for the reaction path for addition to involve (besides diene) one or two (or more) molecules of acetic acid, a molecule of un-ionized mineral acid, ion pairs of solvated protons with gegenions from the mineral acid, and free solvated protons.

Since the pioneering work of Hall and Conant,[17] it has been clear that acids like perchloric and sulfuric acid are "stronger" in acetic acid than in water, although they are only slightly dissociated into free ions in acetic acid.[18] Unfortunately, there appears to be no way to determine whether differences in "strength" of acids (as measured by catalytic activities or by indicator color changes) are due to differences in the degree of ionization (eq 1) or to differences in proton-donating abilities of molecular species, or of ion pairs. However, in principle, a test of the catalysis by free ions is available by a study of the variance in rate with concentration of acid species.[19]

$$\mathrm{HX} + \mathrm{HOAc} \overset{K_i}{\rightleftharpoons} \mathrm{H_2OAc^{\oplus}X^{\ominus}} \qquad (1)$$

$$\mathrm{H_2OAc^{\oplus}X^{\ominus}} \overset{K_d}{\rightleftharpoons} \mathrm{H_2OAc^{\oplus}} + \mathrm{X^{\ominus}} \qquad (2)$$

Vogelfanger[9] observed that the rate of addition of acetic acid to norbornadiene was approximately linear with stoichiometric perchloric acid concentration over the range 0.0005–0.01 M, and also showed indirectly a first-order dependence on diene concentration. Our data with sulfuric acid as catalyst (Table II, paper XL) also indicate a significantly better fit when plotted *vs.* stoichiometric sulfuric acid concentration over the range 0.009–0.09 M than when plotted *vs.* its square root. These data suggest the importance of ion pairs $\mathrm{H_2OAc^{\oplus}X^{\ominus}}$ or molecular acid HX as the catalyzing species.

The data of Table III, paper XL, indicate that perchloric acid is approximately 350 times as effective a catalyst as sulfuric acid. Presumably this reflects the superior proton-donating power of $\mathrm{H_2OAc^{\oplus}ClO_4^{\ominus}}$ over $\mathrm{H_2OAc^{\oplus}HSO_4^{\ominus}}$. Were it not for the concentration dependence noted above, one would be tempted to correlate these rate differences with the relative extents of dissociation into free ions (eq 2) as K_d for perchloric acid is reported[18] to be 1.3×10^{-5} and for sulfuric acid is reported as 5.7×10^{-8}. A portion of the dilemma may be resolved by assuming that there may be different degrees of "tightness" of ion pairs, all of which are indistinguishable by conductivity measurements, *i.e.*, have zero conductivity, but which have significant differences in proton-donating abilities, the more tight or intimate ion pairs being less effective in this regard than those which are more completely solvated (solvent separated).[20]

In the uncatalyzed reaction (Table I, paper XLI), addition of sodium acetate did not affect the rate of addition. On the other hand, sodium perchlorate was an effective catalyst (Table III, paper XL) being almost one-tenth as effective as sulfuric acid. This would appear to be due to the reaction of eq 3, and

$$\mathrm{Na^{\oplus}ClO_4^{\ominus}} + 2\mathrm{HOAc} \rightleftharpoons \mathrm{H_2OAc^{\oplus}ClO_4^{\ominus}} + \mathrm{Na^{\oplus}OAC^{\ominus}} \qquad (3)$$

is in fact reversed by the addition of sodium acetate.[22,23] While sodium perchlorate has no effect on the rate of a perchloric acid catalyzed reaction, its effect on a sulfuric acid catalyzed reaction is dramatic (Table III, paper XL). Thus, for example, under conditions where 0.001 M sulfuric acid and 0.01 M sodium perchlorate separately give reaction extents of 0.1–0.2%, their combination induces 8.5% reaction. Under these conditions, 0.001 M perchloric acid induces 36% reaction. Similarly, under conditions where 0.005 M sulfuric acid induces 5.3% reaction and 0.05 M sodium perchlorate 4.4% reaction, the combination induces complete reaction. These results are accommodated by the reaction in eq 4, and assume that the "tightness" of the sodium bisulfate ion pair is great enough (compared with the others) to shift the equilibrium substantially toward the right side of eq 4. The

$$\mathrm{Na^{\oplus}ClO_4^{\ominus}} + \mathrm{H_2OAc^{\oplus}HSO_4^{\ominus}} \rightleftharpoons \mathrm{H_2OAc^{\oplus}ClO_4^{\ominus}} + \mathrm{Na^{\oplus}HSO_4^{\ominus}} \qquad (4)$$

ability of sodium perchlorate to enhance the apparent acidity (measured by catalytic efficiency) of "weak" acids in acetic acid has been noted before.[24] Here the acetylation of cellulose in mixtures of acetic acid and acetic anhydride was studied, and the efficacy of phosphoric acid and hydrogen chloride was found to be

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(14) C. R. Noller, "Chemistry of Organic Compounds," 2nd ed, W. B. Saunders, Co., Philadelphia, Pa. 1957, pp 148–149.

(15) C. P. Smyth and H. E. Rogers, *J. Am. Chem. Soc.*, **52**, 1824 (1930).

(16) E. Grunwald, *Anal. Chem.*, **26**, 1696 (1954).

(17) (a) N. F. Hall and J. B. Conant, *J. Am. Chem. Soc.*, **49**, 3047, 3062 (1927). (b) N. F. Hall, *Chem. Rev.*, **8**, 191 (1931).

(18) I. M. Kolthoff and A. Willman, *J. Am. Chem. Soc.*, **56**, 1007 (1934). I. M. Kolthoff and S. Bruckenstein, *ibid.*, **78**, 1, 2975 (1956).

(19) An example of this test was described recently by R. B. Homer, R. B. Moodie, and H. N. Rydon [*J. Chem. Soc.*, 4399, 4403 (1965)] who showed that the rate of carbonium ion formation from N-benzyloxycarbonylglycine ether ester in acetic acid had first-order dependence upon sulfuric acid rather than the half-order dependence demanded (eq 2) if free ions rather than ion pairs were involved.

(20) That a variety of ion pairs exist in acetolysis reactions involving carbonium ions, that they differ in their degree of tightness or association (as reflected in their abilities to become solvent separated and free ions) with variation in the gegenions, and that perchlorate ion is one in which the degree of "tightness" is relatively low in acetic acid seem amply demonstrated from the classic work of Winstein and his collaborators.[21]

(21) S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck, and G. C. Robinson, *J. Am. Chem. Soc.*, **78**, 328, 2763, 2767, 2777, 2780, 2784 (1956), and references cited therein. We have used the concept of tightness rather differently from that of Winstein, but hope that the differences are self-evident.

(22) The efficacy of sodium perchlorate as a catalyst was demonstrated in this laboratory first by J. B. Jurale.

(23) That sodium perchlorate gives an acidic solution in acetic acid and that this solution is neutralized by small amounts of sodium acetate was noted by I. M. Kolthoff and A. Willman, *J. Am. Chem. Soc.*, **56**, 1014 (1934).

(24) D. Krüger and W. Roman, *Angew. Chem.*, **47**, 58 (1934).

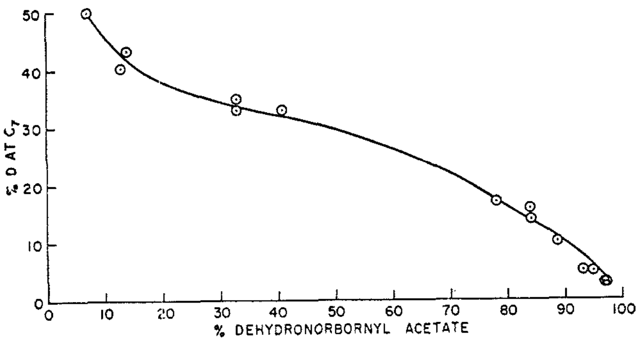


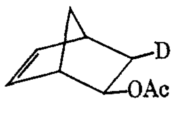
Figure 1.—The relationship between homoconjugate addition and Wagner–Meerwein rearrangement in the reaction of acetic acid and norbornadiene.

improved substantially by the addition of sodium perchlorate.[25]

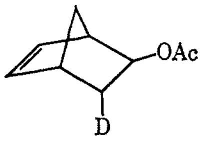
Rates of Reaction. Solvent Effects.—Solvent effects on reaction rate may be estimated (for the sulfuric acid catalyzed reaction) from the data of Table IX, paper XL, where the faster solvents are associated with higher ester yields. None of the solvents added gave much increase in rate, and, indeed, most solvents hardly affected the rates, and it would therefore appear that the transition state for the reaction has approximately the same charge distribution as the ground state of the reactants. However, the reaction was markedly inhibited by water, methanol, ethanol, and 1-butanol: The explanation that this is caused by transformation of the cationic portion of the acid to $ROH_2^{\oplus}$ (a weaker acid than $H_2OAc^{\oplus}$) seems reasonable, but, if this is the case, it is not clear why the same inhibition is not then also observed with dioxane, acetone, and acetonitrile. Clearly this is a very complicated situation.

Solvent effects on reactivity in the uncatalyzed reaction appear to be much more amenable to understanding. It may be noted (Table II, paper XLI) that ether, dioxane, and toluene all slow the rate when added to the diene–acetic acid solution, and that methanol and water increase the rate, water causing the larger increase. These data, plus the effects of adding cyclohexane as shown in Figure 1, paper XLI, and of adding *n*-heptane (shown in Table VI, paper XLI), may be taken as indication that the transition states involved in the rate-determining steps for both homoconjugate addition to give III and addition to give II have greater charge separation than do the ground-state reactants.

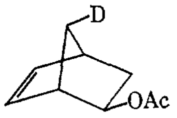
Addition of Deuterium Acetate. Stereochemistry of and Wagner–Meerwein Rearrangements Accompanying Addition.—In the sections described above, we have not considered the stereochemistry of the formation of dehydronorbornyl acetate (II), nor have we discussed the question of whether it arises solely by 1,2 addition. The facts that additions to *endo*-trimethylenenorbornene (IV) were accompanied by substantial amounts of Wagner–Meerwein rearrangement to give derivatives of *exo*-trimethylene-*exo*-norborneol (VI),[2] that addition of bromine to I gives much Wagner–Meerwein addition with the formation of 5,7-dibromonorbornene,[26] and that acetolysis of *exo*-*cis*-3-deuteriodehydro-2-norbornyl *p*-bromobenzenesulfonate gives complete mixing of C_3 and C_7 in the product acetate *via* Wagner–Meerwein scrambling[27] suggest that similar phenomena might accompany addition to I. We decided to inquire into these questions by the use of O-deuterioacetic acid, and to look at the deuteriodehydronorbornyl acetates, produced under various conditions, with the aid of proton magnetic resonance and mass spectra. As mentioned in the introduction to this paper, these tools offer the possibility of distinguishing[5,10,27] the isomeric materials X, XI, and XII and thus limiting the number of the possible paths leading to II.



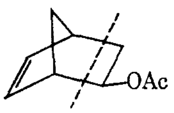
X



XI



XII



XIII

Mass spectroscopy may be used to test for the extent of Wagner–Meerwein rearrangement, as retrograde Diels–Alder fragmentation of II occurs in the mass spectrometer[10] between C_1 and C_2 and between C_3 and C_4 as in XIII. Compound II has its principal peak in the mass spectrum at *m/e* 66, equivalent to $C_5H_6^{\oplus}$ and containing atoms C_1 and C_4–C_7 *and the hydrogens attached to them.* Deuterium at C_7 gives a peak at mass 67; the ratio of peak heights at 67 and at 66 (appropriately corrected)[10] gives the proportion of XII–X and XI. Details are described in papers XL–XLII.

Proton magnetic resonance spectra (Figures 1 and 3, paper XL, and Figures 2, 3, and 5, paper XLI) indicate that all vicinal deuteration is apparently *cis* to the acetoxy group, as in X, and there appears to be no evidence requiring consideration of XI as an important constituent of either acid-catalyzed or uncatalyzed additions.

The data from the mass spectral measurements are also clear. Wagner–Meerwein scrambling to give XII accompanies addition, but is never complete; that is, all additions lead to greater amounts of X than of XII. This may be contrasted with the acetolysis of the *p*-bromobenzenesulfonate related to X, which yields equivalent quantities of X and XII.[27] The acid-catalyzed reactions (Tables IV and V, paper XL) had substantially greater Wagner–Meerwein rearrangement (36–44% deuterium at C_7) than did the uncatalyzed reactions (3–18% deuterium at C_7, Tables IV–VII, paper XLI).[10-12]

It is clear that those factors that promote homoconjugate addition to give III (acid catalysis, polar

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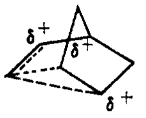
(25) One notes here the interesting phenomenon that the salt of a strong acid and a weak acid combine to give the salt of the weak acid and "liberate" the strong acid, a result uncomfortable to those of us accustomed to thinking about highly aqueous solutions. However, the concept of variability of tightness of association among ion pairs in solvents like acetic acid discussed above nicely explains the observed phenomena.

(26) S. Winstein and M. Shatavsky, *Chem. Ind.* (London), 56 (1956).

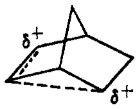
(27) Paper XXXVI: S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *J. Am. Chem. Soc.*, **88**, 3087 (1966).

solvents in uncatalyzed reaction) also promote Wagner–Meerwein rearrangement to give XII. Figure 1 shows this relationship graphically and includes all data except those of Table V, paper XLI, where reactions were run under extremely severe conditions and kinetic control is not assured. For the uncatalyzed reaction, the effect of solvent polarity changes caused by adding *n*-heptane on both homoconjugate and Wagner–Meerwein addition are displayed in Table VI and Figure 4, paper XLI. Both types of rearrangement are decreased substantially by heptane addition, and clean 1,2 *cis* addition may be anticipated in a purely nonpolar system.

Plausible and Impossible Mechanisms.—In the initial publication[2] from this laboratory on additions to and solvolyses of norbornadiene, norbornene, and norbornane derivatives, we pointed out that there were sufficient data to require the participation of a multiplicity of *product-determining* intermediates or processes in such reactions. The present work confirms this. Among the carbonium ion intermediates (the gegenions and/or associated dipolar molecules were not indicated) proposed were the symmetrical nonclassical homoallylic cation XIV (below), the unsymmetrical homoallylic cation XV and its Wagner–Meerwein isomer XVI, a variety of "classical" cations XVII, XVIII, and XIX, and several π-complex cations XX, XXI, and IX. In addition, the idea of a four-center transition state was considered. The data which have been summarized above now make it possible to exclude certain of these intermediates and to discuss certain plausible mechanisms in more detail.



XIV



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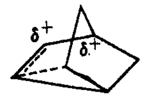

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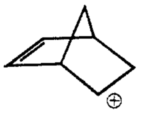

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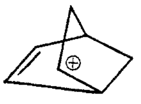

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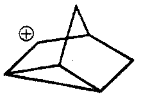

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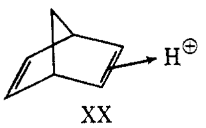
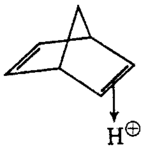
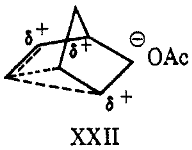


XX



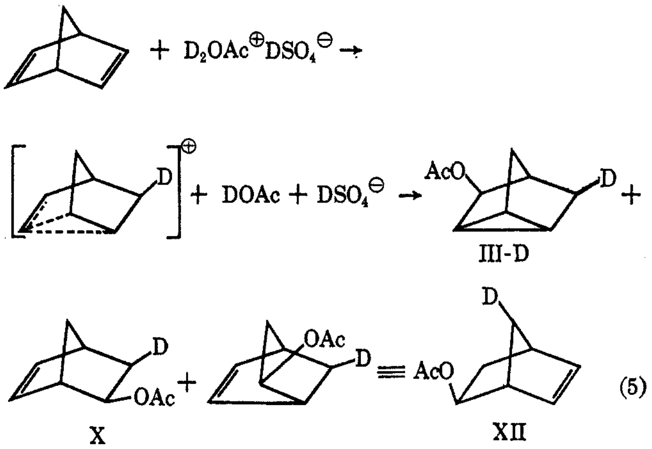
XXI



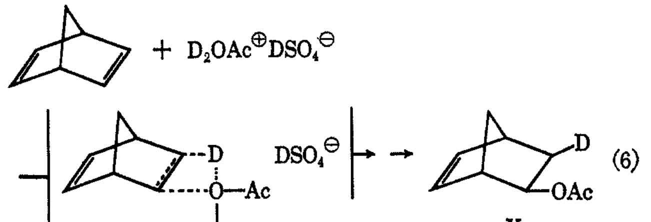
XXII

As indicated in the earlier paper,[2] the *exo*-protonated π-complex cation XX is excluded as a *product-determining* intermediate, as it should lead to *endo* acetate, which is not observed.[2] No information regarding its participation as a species which could return to diene I or which could isomerize to another cation or cations can be derived from our data. The present work excludes both of the *endo* π complexes (IX or XXI) as being mechanistically important. The observation that the vicinal deuteration in the dehydronorbornyl acetate is *cis* and *exo* as in X rather than in XI definitely excludes these intermediates. As we can exclude *endo*-protonated π complexes, and as we have no information on *exo* species as antecedents to product-determining intermediates, we will ignore them during the remainder of this discussion.

The relationship shown in Figure 1 between the extent of homoconjugate addition and the extent of Wagner–Meerwein rearrangement suggests that these two processes occur through intermediates such as XIV, *rapidly equilibrating* XV and XVI, or *rapidly equilibrating* XVII, XVIII, and XIX. (The *rapidly equilibrating* sets of cations would of course simulate the nonclassical ion.)[28] Then one may assume that the *cis* addition not accompanied by Wagner–Meerwein rearrangement (measured by the excess of deuterium at C$_3$ over that at C$_7$) is the result of a four-center cyclic process not involving a carbonium ion.[29] These assumptions can be tested, if one makes the further assumption that the cation XIV or its simulating cationic systems react identically with the same species produced in the solvolysis of dehydronorbornyl *p*-bromobenzenesulfonate. If these assumptions are correct, the mechanisms for the acid-catalyzed reactions would be given by eq 5 and 6 or 6a.[31] The



(5)



(6)

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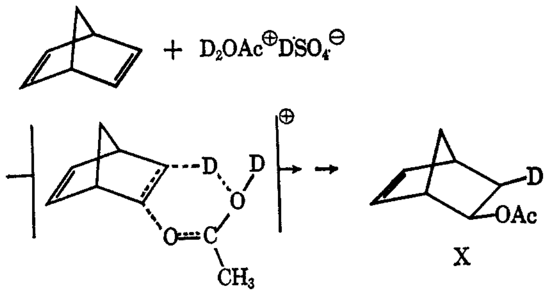
[28] For a discussion of the concept that a rapidly equilibrating set of cations may simulate a nonclassical cation in stereochemistry and in rearrangements, see H. C. Brown, K. J. Morgan, and F. J. Chloupek, *J. Am. Chem. Soc.*, **87**, 2137 (1965).

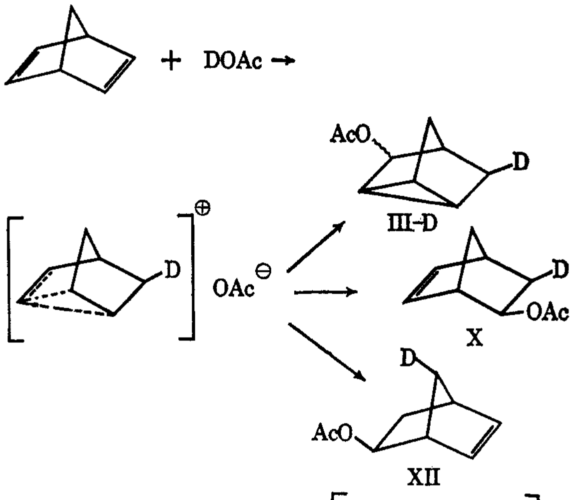
[29] The data discussed above on solvent effects in the uncatalyzed reactions make it clear that the homoconjugate addition and addition accompanied by Wagner–Meerwein rearrangement utilize substantially more polar transition states than does the process not accompanied by rearrangement. However, the rate of the latter process also is markedly sensitive to solvent changes, and its transition state cannot be considered as nondipolar. If a four-center transition state is involved, one would arrive at a highly polar transition state by assuming that proton transfer to one of the olefinic carbon atoms leads coordination of the acetoxy group to the second carbon atom. Thus, the transition state would have cationic character on one of the carbon atoms and anionic character on the acetate oxygens.[30]

[30] For a recent discussion of the effect of solvent polarity on reactions between molecules, see K. B. Wiberg, "Physical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1964, pp 376–388.

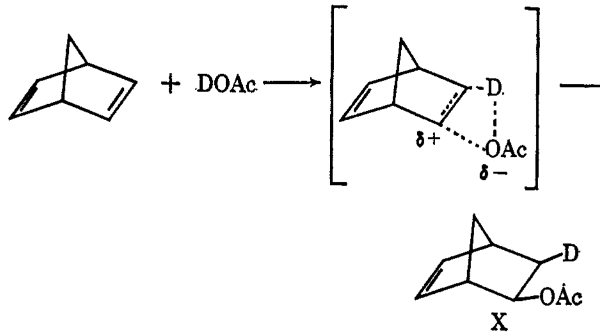
[31] We have assumed, with complete lack of knowledge, that only one molecule of acetic acid is involved in the transition states for carbonium ion and cyclic addition. Should more than one molecular be involved, the changes that would be involved would not affect this discussion. Also, no information is at hand to choose between eq 6 and 6a or 8 and 8a.



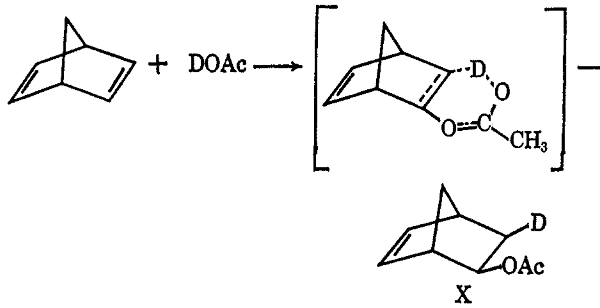
(6a)



(7)



(8)



(8a)

corresponding mechanisms[31] for the uncatalyzed reactions would be given by eq 7 and 8.

These assumptions may be readily shown to be *incorrect* for both the acid catalyzed and the uncatalyzed reaction. For the acid-catalyzed reaction, we may consider the data of expt 1, Table V, paper XL. Here the product contained 67% of deuterated III-D and 33% of II-D isomers of which 22% was X and 11% was XII. Put another way, 67% of the product was the result of homoconjugate addition, 22% (all of XII and an equivalent amount of X) can be assigned to a symmetrical Wagner-Meerwein process and the remainder of X (11%) may be assigned to a cyclic process. We know, however, that the cation XIV (or its simulators) produced in acetolysis gives 92% of III-D and 8% of II-D, and also that the II-D produced has its deuterium distributed evenly between C_3 and C_7,[27] *i.e.*, gives equal quantities of X and XII. An experiment in which all of the XII arose from a XIV cation produced as in solvolysis and giving 67% of III-D would give 67 × 8/92 = 6% of an equimolar mixture of X and XII or 3% of XII. The 3% of XII would be mixed with 30% of X and the deuterated dehydronorbornyl acetate would therefore be expected to have 9% of its deuterium at C_7 rather than the 33% actually observed. Put another way, this mechanism would predict, based upon the 67% homoconjugate addition, 6% of a symmetrical Wagner-Meerwein process and 27% of a cyclic process. The observed Wagner-Meerwein addition is in fact much greater than that predicted.

Similar considerations obtain with the noncatalyzed addition. An example is (data of Table IV, paper XLI) a result in which 16% of III-D and 84% of a mixture containing 71% of X and 13% of XII were formed. Consideration of the assumptions made above would suggest that, for 16% of homoconjugate addition, 16 × 8/92 = 1.4% of Wagner-Meerwein addition should result. In fact, however, 26% (twice the yield of XII) of a Wagner-Meerwein symmetrical process did occur. One notes the interesting comparison that, while considerably fewer of the II-D isomers in the uncatalyzed case have the structure described in XII than in the catalyzed case, the fraction of the total reaction occurring by a Wagner-Meerwein rearrangement happens to be greater in this case than in the catalyzed case. Thus, the results make it certain that the assumptions made above are incorrect. One may therefore abandon these assumptions and instead assume that there are several cationic species which are *not* rapidly equilibrating, but whose rates of equilibration are competitive with rates of capture by acetic acid, and thus one may rationalize these data. Our own bias[2] toward an explanation of this sort was greatly diminished when it was discovered[4] that acetic acid is not unlike methanol in additions to trimethylenenorbornene, although such an explanation may still be required for solvolysis results.[2,4,32]

An alternative explanation, and one particularly attractive to those[33] who hold that the dehydronorbornyl cation is the nonclassical symmetrical ion XIV or a series of rapidly equilibrating simulators, is the abandonment of the assumption that the XIV ion produced should behave as it does when produced by the acetolysis of dehydronorbornyl *p*-bromobenzenesulfonate. Indeed, it seems most reasonable to assume that it should not be the same because of its neighboring substances. Let us first consider the noncatalyzed reaction. We may assume then that eq 7 may be modified as shown in eq 9. Here we assume that the tight ion pair XXII comprising ion XIV and an acetate gegenion is formed first. It has equal probability of giving X or XII, or it may lose its acetate ion into the bulk solvent (where it becomes mixed with the bulk acetic acid present). When the latter occurs, the XIV cation is then presumably like the species formed in solvolysis reactions. The fact[27] that internal return during the acetolysis of *exo*-3-deuterio-*exo*-2-norbornyl *p*-bromobenzenesulfonate leads only to the Wagner–

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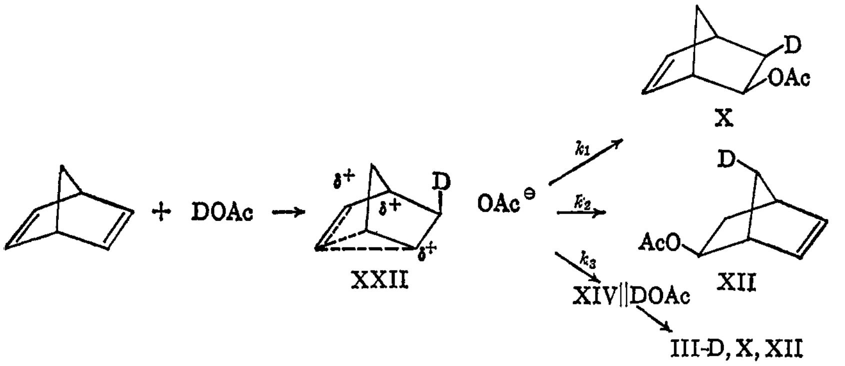
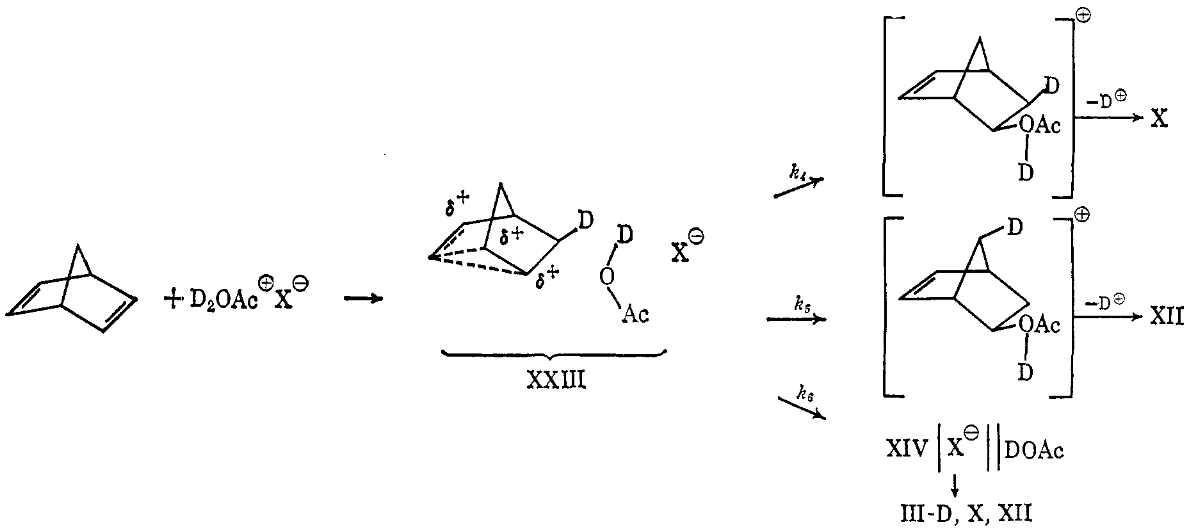
[32] K. Takeuchi, T. Oshika, and Y. Koga, *Bull. Chem. Soc. Japan*, **38**, 1318 (1965).

[33] See ref 27 for a discussion of this point.



(9)



(10)

Meerwein isomer and not to the nortricyclyl sulfonate is also consistent with the paths formulated in eq 9, and with the fact that Wagner–Meerwein rearrangement during addition becomes more important than homoconjugate addition. We then propose that a combination of the reactions of eq 9 plus that represented by eq 8 and 8a are reasonable ones for the noncatalyzed additions.

The catalyzed additions may be formulated similarly (eq 10), except that the intermediate XXIII contains acetic acid and a presumably nonnucleophilic anion rather than acetate ion. The collapse of XXIII to the conjugate acids of X and XII by the paths governed by k_4 and k_5 compared with the loss of acetic acid into the medium (governed by k_6) may be anticipated to be considerably less favored than in the uncatalyzed case ($k_1 + k_2$ compared with k_3), as one involves an ion-dipole interaction *vs.* an ion-pair interaction in the other.[34] Thus, a combination of the paths outlined in eq 10 with the cyclic process of eq 6 or 6a nicely fits the catalyzed reaction.

The fact that the ratio of products in the acid-catalyzed reactions is dependent upon the catalyzing acid also appears to be consistent with this formulation as the reaction governed by k_6 is essentially a reaction in which a molecule of acetic acid in an ion-dipole complex is displaced by an anion to give an ion pair.

Acknowledgments.—The authors are indebted to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation, for support of this work. We are also indebted to Professor Edward L. King for a number of very useful discussions.

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[34] A. F. Diaz and S. Winstein, *J. Am. Chem. Soc.*, **86**, 4484 (1964).