chromatogram indicated 21% unreacted **17**. In addition, the ratio of the sum of the peak areas of **10**, **12** and **14** to that of **17** and **18** was 1.03:1. The molar ratio of **3** to **17** in the original reaction mixture was 1.02:1.

(d) **Relative Rates of Reaction of 3 and 17 in Ether Solution.**—A mixture of 0.192 g. (1.37 mmoles) of **3** and 0.192 g. (1.35 mmoles) of **17** was treated with 0.08 ml. of boron fluoride etherate in 10 ml. of dry ether for 1 hour at room temperature. The reaction mixture was worked up in the usual manner, and the dried ethereal solution analyzed at 112°, 8 p.s.i. Measurement of peak areas indicated 37% unreacted **17** and 26% unreacted **3**.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO, BOULDER, COLO.]

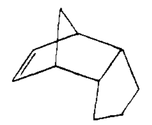
Bridged Polycyclic Compounds. XIX. Some Addition and Solvolysis Reactions in Norbornane Systems[1]

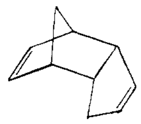
BY STANLEY J. CRISTOL, WOLFGANG K. SEIFERT, DONALD W. JOHNSON AND J. BYRNE JURALE

RECEIVED JUNE 14, 1962

Acid-catalyzed additions of acetic acid, formic acid and water to *endo*-dihydrodicyclopentadiene (I) lead to products in which almost complete ring isomerizations (to III, or its analogs) has occurred. On the other hand, addition of methanol (or of water in methanol solvent) to I or to dicyclopentadiene (II), followed by hydrogenation, gives a mixture containing about 1 part of *endo* skeleton unrearranged product (VI, Y = OMe, OH) to 6 parts of *exo* skeleton product III. Solvolysis of the toluenesulfonates of III and VI in methanol both give a large preponderance of *exo* product (*ca.* 30:1 = III:VI). Addition of methanol or of acetic acid to norbornadiene (X) gives substantially more dehydronorbornyl methyl ether (XI, Y = OMe) or dehydronorbornyl acetate (XI, Y = OAc) in the mixture with nortricyclyl products XII (Y = OCH_3, $OCOCH_3$) than solvolysis of the *p*-bromobenzenesulfonate of either XI or XII. Possible explanations of these results are discussed.

Ionic additions to *endo*-1,2-dihydrodicyclopentadiene (I) and to *endo*-dicyclopentadiene (II) have been reported to give products III (or the dehydro analogs) with *exo* configuration of addenda and also with rearranged, *i.e.*, *exo* ring skeletons.[2] *exo*-Dicyclopentadiene (IV) is reported,[2f] in contrast, to add HY reagents without rearrangement and thus to give products identical with those from II. In general, then, isomers with *endo* ring skeletons were not observed from addition to olefins with either *endo* or *exo* ring systems. In addition, it has been reported[3] that the *exo-exo* product III (Y = OAc) resulted from the acetolysis of the *p*-toluenesulfonate related to either *exo*-III or its epimer, or of the *p*-toluenesulfonate of *endo*-VI or its epimer. At the time most of the work listed in references 2 and 3 was done, techniques for analysis of very minor constituents were not available, so that products with *endo* ring systems might understandably be missed. We decided, therefore, to reinvestigate selected portions of this problem, and our initial results in this and analogous systems are reported herein.


I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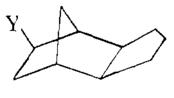
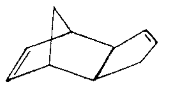
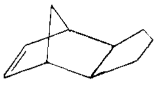
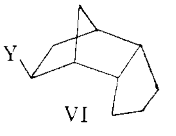


III


IV


V



VI

Addition of formic acid to *endo*-dihydrodicyclopentadiene (I) or to *endo*-dicyclopentadiene (II) and of acetic acid (catalyzed by 1.5% of sulfuric acid) to II led (after hydrogenation, where applicable) preponderantly, as suggested by earlier work,[2] to products with *exo* ring skeletons and *exo* substituents (III, Y = OCHO, $OCOCH_3$). The products were investigated by saponification or lithium aluminum hydride reduction to the alcohols; it was observed that the alcohol mixtures, which were largely III (Y = OH), were contaminated with small amounts of *endo* skeleton isomers VI (Y = OH). When we first began work on this problem, infrared analytical procedures were the best available to us, and our results indicated that the *endo* ring system was being converted to *exo* in substantially over 90% of the product. Work was not conducted with *exo*-olefin V, as it was felt that analytical methods were not precise enough to analyze mixtures using infrared techniques. Hydration of *endo*-olefin I with 22% sulfuric acid in water gave a product which was principally *exo* skeleton III (Y = OH), as reported earlier.[2a,d] This product was now analyzed by vapor-phase chromatography and contained about 2% *endo* skeleton; the reaction conversion was about 45%, and the remaining olefin was not isomerized. Again there appeared to be no reason to study the *exo*-olefin V, in view of the almost complete rearrangement observed with I.

The results described above appeared consistent with the idea that the products were derived largely, if not entirely, from a single *product-determining* intermediate, presumably a non-classical carbonium ion such as VII, for which the resonance structures VIII and IX can be written. This intermediate presumably could be the immediate precursor of both *endo* and *exo* products. Reaction

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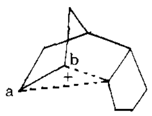
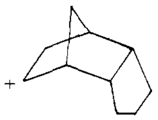
[1] Previous paper in series: S. J. Cristol, J. R. Douglass, W. C. Firth, Jr., and R. E. Krall, *J. Org. Chem.*, **27**, 2711 (1962).

[2] See, *inter alia:* (a) H. A. Bruson and T. W. Riener, *J. Am. Chem. Soc.*, **67**, 723 (1945); (b) **67**, 1178 (1945); (c) **68**, 8 (1946); (d) P. D. Bartlett and A. Schneider, *ibid.*, **68**, 6 (1946); (e) F. Bergmann and H. Japhe, *ibid.*, **69**, 1826 (1947); (f) P. D. Bartlett and I. S. Goldstein, *ibid.*, **69**, 2553 (1947); (g) M. Gates and P. S. Malchick, *ibid.*, **76**, 1378 (1954); (h) K. Alder, F. H. Flock and H. Wirtz, *Chem. Ber.*, **91**, 609 (1958); (i) P. Wilder, Jr., C. F. Culbertson and G. T. Youngblood, *J. Am. Chem. Soc.*, **81**, 655 (1959); (j) S. J. Cristol, W. K. Seifert and S. B. Soloway, *ibid.*, **82**, 2351 (1960).

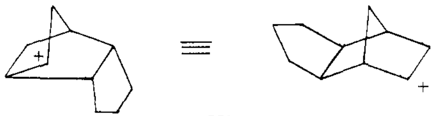
[3] (a) R. S. Barnes, Ph.D. thesis, Harvard University, 1951; (b) P. D. Bartlett, Abstracts of Papers, 12th National Organic Chemistry Symposium, June, 1951, p. 1.



VII



VIII



IX

of VII with solvent at position **a** would lead to *endo* products VI, while reaction at **b** would lead to *exo* products III. The *exo* stereochemistry of the nucleophilic portion Y of the addendum seemed strong evidence for the cation VII.[2g,3,4]

A relief from the monotonous complete or nearly complete rearrangement of *endo* to *exo* ring skeleton occurred on addition of methanol to I and to II. Treatment of I with methanol containing 22% of (96% aqueous) sulfuric acid for four hours at reflux gave a mixture of methyl ethers III and VI (Y = OCH_3) in a ratio of 85.5 to 14.5. Of particular interest was the fact that the water present in the solution led to a small yield of alcohols III and VI (Y = OH) in approximately the same ratio, rather than the 50:1 ratio observed in aqueous sulfuric acid. The product mixture was analyzed and separated by gas chromatography.

Small amounts of the pure III and VI (Y = OCH_3) were isolated and their infrared spectra and relative retention volumes were compared with similar properties of ethers synthesized by methylation of the known alcohols III and VI (Y = OH). Addition of methanol to II gave a mixture of ethers that, after hydrogenation, again gave analysis for 14.5% *endo* skeleton VI (Y = OCH_3). Analytical data were reproducible to about ±0.5% for the ethers and ±1.0% for the alcohols. When the *exo*-olefin V was treated similarly, the product mixture contained the ethers III and VI in the ratio of 96.5:3.5 and alcohol by-products in the same ratio. Products were not significantly isomerized or interconverted under reaction conditions, nor was *endo*-olefin converted to *exo*-olefin under these conditions. Mixtures of olefins I and V led to mixtures of III and VI compatible with those anticipated from the results above.

These results appeared exciting to us, as they indicated that methanol had succeeded in trapping an intermediate in the addition reaction to I and to II before that intermediate had a chance to rearrange completely to the intermediate or intermediates which lead to III and VI (or their dehydro analogs) in the high ratio observed with water or with acetic acid. One may assume, for example, that an intermediate such as VII is the one that partitions itself to give the high ratio of III to VI, but that a second *product-determining* cationic intermediate precedes (or accompanies) its formation from I and that coördination of the nucleophile with the first-formed intermediate competes with rearrangement of one to the other.

It has been noted a number of times[5] that cationic intermediates produced by deamination of aliphatic primary amines give different ratios of products (where rearrangements or partitions between various products are involved) from similarly formulated cationic intermediates produced by solvolysis reactions. This usually has been rationalized on the basis of either the formation of "hot" carbonium ions[5a] by the exergonic loss of nitrogen from the alkanediazonium ions, or by the compression of the relative heights of activation energy barriers in the various reactions[5b] possible to the alkanediazonium ion. In addition, Winstein and his collaborators[6] have noted a number of cases where different methods of preparing presumably identical cations by addition to olefins or by solvolysis gave differing mixtures of products and therefore must involve at least two *product-determining* intermediates. They have discussed the possible nature of such intermediates in some detail.

As we were now confronted with data where addition to isomeric olefins led to differing mixtures of the same addition products, it seemed worthwhile to extend our studies in various ways. It seemed possible to assume that intermediates which could best be represented by the classical ions VIII and IX were formed early in the addition reaction by protonation of I and V, respectively, and that in methanol (a relatively poor ionizing solvent compared with water[7]) and with either methanol or water as nucleophilic reagent (relatively strong nucleophiles compared with acetic acid and formic acid[7,8]), these early intermediates had been trapped before rearranging completely to the intermediate or mixture of intermediates, that under other circumstances appeared to be the common precursor (or precursors) of the final products. It seemed necessary, then, to study other reactions that might also lead to these intermediates. We therefore undertook a study of the products of solvolysis of the *p*-toluenesulfonates III and VI (Y = $OSO_2C_6H_4CH_3$-*p*) in methanol to see if they would lead to different mixtures of methyl ethers. Bartlett and Barnes[3] had already looked at these systems in acetic acid, absolute ethanol and 80% ethanol and had noted that good (and different) first-order rate constants were observed with each isomer, indicating that the isomers do not rearrange to each other in these solvents. Product studies in acetic acid indicated that III (Y = $OCOCH_3$) was the product of acetolysis of both tosylates.[3] These data suggested that solvolysis to an intermediate ion pair[9] led entirely to products (presumably through other ion intermediates) with

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(4) S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, **71**, 2193 (1949); **74**, 1154 (1953).

(5) (a) D. J. Cram and J. E. McCarty, *ibid.*, **79**, 2866 (1957); (b) A. Streitwieser, Jr., *J. Org. Chem.*, **22**, 861 (1957); (c) M. S. Silver, *J. Am. Chem. Soc.*, **83**, 3482 (1961); (d) B. M. Benjamin, P. Wilder, Jr., and C. J. Collins, *ibid.*, **83**, 3654 (1961).

(6) (a) S. Winstein and M. Simonetta, *ibid.*, **76**, 18 (1954); (b) S. Winstein and N. J. Holness, *ibid.*, **77**, 5562 (1955); (c) S. Winstein, *Experientia Suppl. II*, 137 (1955); (d) S. Winstein and E. S. Kosower, *J. Am. Chem. Soc.*, **81**, 4399 (1959).

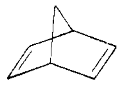
(7) E. Grunwald and S. Winstein, *ibid.*, **70**, 846 (1948); S. Winstein and A. H. Fainberg, *ibid.*, **79**, 5937 (1957).

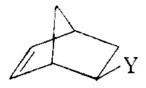
(8) C. G. Swain, *ibid.*, **70**, 1119 (1948); C. G. Swain, R. B. Mosely and D. E. Bown, *ibid.*, **77**, 3727, 3731 (1955).

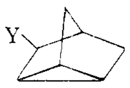
(9) S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck and G. C. Robinson, *ibid.*, **78**, 328 (1958), and references cited therein.

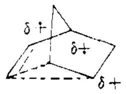
no internal return to rearranged toluenesulfonates, so that there might be a possibility, if ions such as VIII and IX were formed, of capturing them before rearrangement. In fact, however, we found that solvolysis of the *endo*-tosylate VI in methanol (either with or without added sodium acetate) led to a mixture of methyl ethers III and VI containing 3.3 ± 0.3% of VI, while *exo*-tosylate III gave a mixture containing 2.9 ± 0.4% of *endo*-ether VI. These results are comparable with those reported for addition of methanol to *exo*-olefin V (which gives 3.5 ± 0.6% of ether VI), but markedly different from those obtained with *endo*-olefin I (14.5% of ether VI). It seems clear then that the solvolysis reaction, which has been shown to involve generally a series of ion pairs and/or relatively free ions,[9] either gives an ion immediately with a structure (possibly like VII) similar to that of the immediate precursor of the final products, or allows sufficient life-time in the cationic states to allow any possibly different original cations from III and VI tosylates to lose their original identities, either by transformation to a mesomeric ion such as VII or by equilibrium between the original ions.

Comparison of addition *vs.* solvolysis in another system may now also be made. Treatment of norbornadiene (X) with methanol containing 10% sulfuric acid for one week at room temperature gave a mixture of dehydronorbornyl methyl ether (XI, Y = OCH_3) and nortricyclyl methyl ether (XII, Y = OCH_3) in a ratio of 33:67, while treatment of X with acetic acid containing 1% sulfuric acid for 1.5 hr. at room temperature gave the corresponding acetates XI and XII (Y = $OCOCH_3$) in the ratio 25:75.[10] In both cases the reaction was run only part way and no 2:1 addition product was formed. On the other hand, solvolysis (at room temperature) of the *p*-bromobenzenesulfonate XI (Y = $OSO_2C_6H_4Br$-*p*) in methanol (with or without pyridine present) gave a mixture of methyl ethers XI and XII containing 7.9 ± 0.3% of ether XI, while solvolysis of the brosylate XII gave a mixture containing 6.7 ± 0.3% of ether XI. Solvolysis of the brosylate XI in acetic acid (with or without sodium acetate) at room temperature gave an acetate mixture containing 8.0 ± 0.3% of acetate XI and 92.0 ± 0.3% of acetate XII, while that of brosylate XII gave a mixture containing only 4.7 ± 0.4% of acetate XI.[11,12] Less than 1% of *endo* product was found in any case.


X


XI


XII

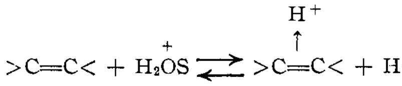

XIII

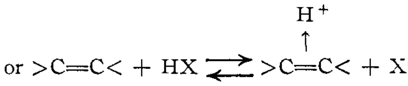

XIV

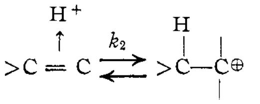
Experiments to show that the various products are substantially unisomerized under reaction conditions have been conducted.

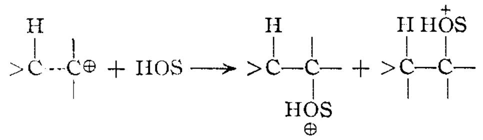
Recently Dauben and Cargill[13] have shown that addition of acetic acid to quadricycloheptane (XIV) also leads to a mixture of acetates XI and XII, but in this case to about equal amounts of each isomer.

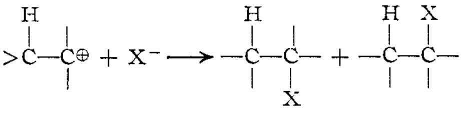
The data we have obtained seem to require several cationic intermediates in these additions and/or solvolysis reactions. Much recent evidence and discussion are pertinent to these data.[6,14] In particular, acid-catalyzed addition reactions of protonic species are believed to proceed through alternate routes as shown in eq. 1 to 4 or 1a to 4a. In the first extended discussions of acid-catalyzed hydration, Taft[14b] assumed that the initial π-complex formed by protonation of the olefin (eq. 1) is isomerized to an open carbonium ion (eq. 2) before reaction with water (eq. 3). Later results[6b,14e,15] suggest that under certain conditions the π-complex (or equivalent hydrogen bridged cation[6b]) reacts directly with solvent or with anion (eq. 4 and 4a) resulting in *trans* addition, while in other systems the non-stereospecific paths represented by eq. 1, 2 and 3 or 1a, 2 and 3a were followed. The relative values of k_2 compared with k_4 (or k_{4a}) in any given set of conditions then controls the stereochemical result.


$$>C{=}C< + \overset{+}{H_2OS} \rightleftarrows \overset{\overset{H^+}{\uparrow}}{>C{=}C<} + HOS \qquad (1)$$


$$\text{or } >C{=}C< + HX \rightleftarrows \overset{\overset{H^+}{\uparrow}}{>C{=}C<} + X^{\ominus} \qquad (1a)$$


$$\overset{\overset{H^+}{\uparrow}}{>C=C} \overset{k_2}{\rightleftarrows} >\overset{H}{\overset{|}{C}}—\underset{|}{\overset{|}{C}}{}^{\oplus} \qquad (2)$$


$$>\overset{H}{\overset{|}{C}}\cdots\underset{|}{\overset{|}{C}}{}^{\oplus} + HOS \longrightarrow >\overset{H}{\overset{|}{C}}—\underset{\underset{\underset{\oplus}{HOS}}{|}}{\overset{|}{C}}— + >\underset{|}{\overset{\overset{H}{|}}{C}}—\underset{|}{\overset{\overset{\overset{+}{HOS}}{|}}{C}}— \qquad (3)$$


$$\text{or } >\overset{H}{\overset{|}{C}}—\underset{|}{\overset{|}{C}}{}^{\oplus} + X^- \longrightarrow —\underset{|}{\overset{\overset{H}{|}}{C}}—\underset{\underset{X}{|}}{\overset{|}{C}}— + —\underset{|}{\overset{\overset{H}{|}}{C}}—\underset{|}{\overset{\overset{X}{|}}{C}}— \qquad (3a)$$

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(10) The fact that norbornadiene gives mixtures of dehydronorbornyl and nortricyclyl ethers and esters upon addition of alcohols and carboxylic acids has already been reported. *Cf.* H. Bluestone, S. B. Soloway, J. Hyman and R. E. Lidov, U. S. Patent 2,730,548 (January 10, 1956); U. S. Patent 2,738,356 (March 13, 1956); U. S. Patent 2,782,238 (February 19, 1957); and L. Schmerling, J. P. Levisi and R. W. Welch, *J. Am. Chem. Soc.*, **78**, 2819 (1956); H. Krieger, *Suomen Kemistilehti*, **33B**, 183 (1960). These experiments were run under conditions leading to some 2:1 addition products, and are therefore not necessarily comparable to ours.

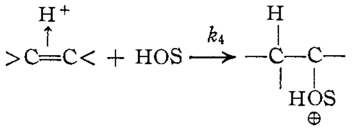
(11) J. D. Roberts, C. C. Lee and W. H. Saunders, *J. Am. Chem. Soc.*, **77**, 3034 (1955), report that brosylate XI gives 11% of acetate XI and 89% of acetate XII on acetolysis at 45°.

(12) S. Winstein and H. J. Schmid (unpublished work) have also noted a different ratio of acetate products XI and XII from brosylates XI and XII; see footnote 23 in ref. 6d. In addition, solvolysis of brosylate XI is accompanied by rearrangement to brosylate XII (S. Winstein, private communication).

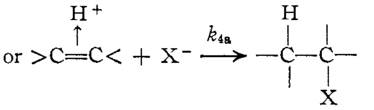
(13) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **15**, 197 (1961).

(14) (a) M. J. S. Dewar, "Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, p. 144; (b) R. W. Taft, Jr., *J. Am. Chem. Soc.*, **74**, 5372 (1952); (c) E. L. Purlee and R. W. Taft, Jr., *ibid.*, **78**, 5807 (1956); (d) P. Riesz, R. W. Taft, Jr., and R. N. Boyd, *ibid.*, **79**, 3724 (1957); (e) C. H. Collins and G. S. Hammond, *J. Org. Chem.*, **25**, 911 (1960).

(15) G. S. Hammond and T. D. Nevitt, *J. Am. Chem. Soc.*, **76**, 4121 (1954).

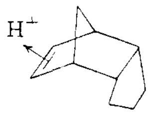


$$\overset{\overset{\mathrm{H}^+}{\uparrow}}{>\mathrm{C}}=\mathrm{C}< + \mathrm{HOS} \xrightarrow{k_4} -\underset{|}{\overset{\overset{\mathrm{H}}{|}}{\mathrm{C}}}-\underset{\underset{\underset{\oplus}{\mathrm{HOS}}}{|}}{\mathrm{C}}- \qquad (4)$$

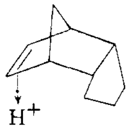


$$\text{or } \overset{\overset{\mathrm{H}^+}{\uparrow}}{>\mathrm{C}}=\mathrm{C}< + \mathrm{X}^- \xrightarrow{k_{4a}} -\underset{|}{\overset{\overset{\mathrm{H}}{|}}{\mathrm{C}}}-\underset{\underset{\mathrm{X}}{|}}{\overset{|}{\mathrm{C}}}- \qquad (4a)$$

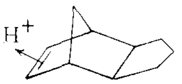
It would appear possible to explain our data on additions to I and to V (or to their dehydro analogs) using similar models for intermediates. The carbon–carbon double bond in the *endo*-olefin I could be protonated from the *exo* side to give the π-complex XV or from the *endo* side to give the alternate π-complex XVI. Correspondingly, the *exo*-olefin V would give XVII and XVIII. The π-complexes with *exo* protons obviously can not lead directly to *exo*-Y products, as *trans* ring opening of such π-complexes would lead to ethers or alcohols related to XIX or XX with the Y groups having *endo* configurations. These were not found in the reaction mixture, although we would easily have been able to detect as little as 1% of these materials. These π-complexes, then, if formed, must either lose protons to return to unisomerized olefin[14] or isomerize to carbonium ions. It might be anticipated that XV would isomerize either to the carbon-bridged mesomeric cation VII or to the classical *endo* ion VIII, while XVII might correspondingly isomerize to VII or to IX. These, as discussed above, could be the immediate precursors of the products III and VI. Thus, if XV and XVII are the sole π-complexes formed, it is necessary to assume that the classical carbonium ions VIII and XI, or one of these with VII, are involved in the addition reaction.



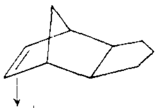
XV



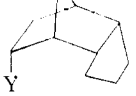
XVI



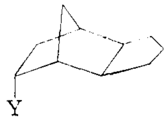
XVII



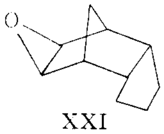
XVIII



XIX



XX



XXI

On the other hand, it may be assumed that the *endo*-protonated π-complexes XVI and XVIII are involved. The formation of these π-complexes should be less favored than that of XV and XVII, as *exo* addition is usually observed to norbornenes.[16] However, if the formation of π-complexes is reversible (eq. 1) and if the *trans* "ring-opening" reaction (eq. 4) of say, XVI, is significantly faster than that of XV,[17] then the compositions of the product mixtures can be accommodated in the following way. Protonation of I gives XV and XVI; XV isomerizes to VII with the anchimeric assistance associated with the carbon–carbon bond migration. Compound XVI, on the other hand, is more susceptible to attack by nucleophiles than XV and is less ready to isomerize to VII or to VIII, as no anchimeric assistance is possible in this isomerization; XVI then may lead to products related to VI directly, maintaining the *endo* ring system, or may yield an *exo* solvated VIII ion, which can collapse to products VI or isomerize to VII (or to IX). Similar reaction schemes can be devised beginning with V. Under conditions where the sum of the lifetimes of the cationic states is high, for example, in water, where the stability of ions is inherently great, or in acetic acid or formic acid (where the nucleophilicity of the solvent is low) there will be time for rearrangement to intermediates which lead largely to *exo* ring systems. When the reaction is conducted under conditions where cationic species are captured relatively rapidly (for example, in methanol), rearrangements are relatively less complete and products with original ring skeletons may be obtained by direct reaction of π-complexes or by transformation of these to selectively solvated cations.

A comparison of results of solvolysis in methanol and in acetic acid of the *p*-bromobenzenesulfonates of *exo*-dehydronorborneol XI and nortricyclenol XII (Y = OBs) with addition of these solvents to norbornadiene (X) and quadricycloheptane (XIV)[13] also seems to require the intermediacy of several different cationic species. Solvolyses of XI and XII brosylates in methanol give mixtures of XI and XII that appear to differ slightly, although the differences lie just on the edge of experimental error estimates; in acetic acid, however, the differences are well outside experimental error. The differences are of such a nature as to indicate that each isomer isomerizes (in ring skeleton) slightly less than the average; these differences would, of course, be increased were the isomeric brosylates not isomerizing to each other.[12] Thus the cationic species seems to remember its origin. Addition of solvents to the diene X or the tetracyclic compound XIV[13] gives mixtures of products XI and XII (Y = OCH_3 or $OCOCH_3$) that differ substantially from those obtained in the solvolysis experiments.

Winstein and Kosower[6d] have discussed the rates and products of solvolyses of XI and XII derivatives and similar compounds in an extensive and elegant paper, and have suggested that the slight differences in product composition may be due to solvolysis in one case to a symmetrical homoallylic mesomeric ion XXII and in the other case to an unsymmetrical ion XXIII.[18] Here it must

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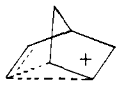
[16] K. Alder, F. H. Flock and H. Wirtz, *Ber.*, **91**, 609 (1958).

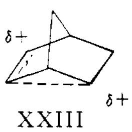
[17] It has been observed that the ring opening of the epoxide XXI with lithium aluminum hydride is very difficult (D. W. Johnson and L. K. Gaston, private communication). This may be analogous to the reaction of XV.

[18] Winstein and Kosower[6d] suggest that norbornenyl *p*-bromobenzenesulfonate (XI) gives the unsymmetrical ion XXIII in the solvolysis, while the nortricyclyl bromobenzenesulfonate XII gives the symmetrical ion XXII. In view of the marked stereochemical requirement generally observed for anchimeric assistance to solvolysis (*anti*-coplanarity of neighboring and leaving group seem required[19]),

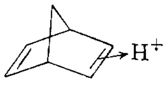
be assumed that capture by nucleophile competes with transformation of XXII to XXIII or *vice versa*. An alternative possibility is that both bromobenzenesulfonates give the same cationic species, which react at least in part with solvent in the "solvent-separated ion pair" stage,[9] in such a way that solvent reacts somewhat more readily in that position closest to the departing counter anion. A distinction between these unsymmetrically solvated species and classical non-mesomeric carbonium ions cannot be drawn from product data such as are available.



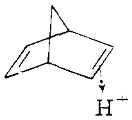
XXII



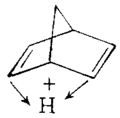
XXIII



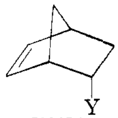
XXIV



XXV



XXVI



XXVII

Again it can be assumed that the addition reactions to X involve different intermediates from solvolysis reactions. Several π-complexes (or hydrogen-bridged cations) may be postulated for the addition reaction represented by eq. 1. It is clear that, as *no* significant amount of *endo* product XXVII is observed in addition of either methanol or acetic acid, any XXIV which is formed either reverts to starting diene or is transformed to one of the carbonium ion species (XXII, XXIII or "classical" ions). Presumably XXII or XXIII would lead largely to nortricyclyl products as are found in solvolyses. On the other hand, an *endo*-π-complex, which might be represented as XXV, if one double bond is involved, or as XXVI, if it is assumed that the hydrogen orbital overlaps with the π-orbitals of both double bonds,[20] might be involved. It would be anticipated that either XXV or XXVI would lead by *trans* ring opening to the *exo* products XI or, of course, could rearrange to carbonium ions.

There is, of course, the possibility that addition to norbornadiene and to dihydrodicyclopentadiene involves some simple *cis* addition mechanism, similar perhaps to those postulated for the *cis* addition of chlorine to phenanthrene[22] in acetic acid or for the *cis* addition of acetyl nitrate to olefins.[23] Such *cis* addition mechanisms may be particularly attractive in these norbornene systems where *cis* bimolecular eliminations have been found to be favored over *trans*.[24]

The mechanisms involved in transformation of XIV to an equimolar mixture[13] of acetates XI and XII are even more obscure. Very little information appears to be available on the mechanisms of additions to cyclopropanes. It seems remarkable, however, that this addition gives more olefinic product XI than does addition to the diene.

With the data described herein it is not possible to decide among the various possibilities for reaction paths; in particular, it is not possible to state whether or not the *endo* protonated complexes are involved as intermediates in the addition reactions. However, consideration of the product-composition data in both the *endo*-dihydrodicyclopentadiene case and the norbornadiene case is of interest. In each case, it would appear that about 20% of the "abnormal" product (with I, the *endo* ring skeleton product VI, and with X, the dehydronorbornyl product XI) may be accounted for by the "normal" path—that is, the path assumed by the solvolyses or by addition to V. The remaining 80% of the products VI or XI must come from another path. Studies with deuterium-labeled solvents would appear to promise interesting results, as it is clear that *endo*-protonated intermediates such as XVI, XVIII, XXV and XXVI would lead to *trans* addition of H and Y. This work is in progress.

Acknowledgments.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. In addition, the authors are indebted to the Air Force Office of Scientific Research for partial support of this work, to the Shell Development Co. for samples of norbornadiene and to Professors Paul D. Bartlett, Herbert C. Brown, John D. Roberts and Saul Winstein for critical discussions.

Experimental

Addition of Water to *endo*-Dihydrodicyclopentadiene (I).—A mixture of 2.06 g. (15.3 mmoles) of *endo*-dihydrodicyclopentadiene I (containing about 2% of V and a trace of II or IV) and 17.7 g. of 22 wt. % aqueous sulfuric acid was heated at reflux with magnetic stirring for 4 hours. The cooled mixture was extracted 4 times with 15-ml. portions of ether. The combined ethereal solution was washed with sodium carbonate solution and water and the ether was removed by distillation. After azeotroping the water off with benzene, 1.74 g. of oil remained, which still contained a considerable amount of starting olefin I. The hydrated fraction by analysis showed 2% of VI (Y = OH) and 98% of III (Y = OH) (vapor phase chromatographic analysis).

In another experiment under identical conditions, using a less pure starting material, a mixture of III and VI (Y = OH) melting at 44–49° was obtained in 42% yield after distillation, b.p. 68.5° (0.6 mm.), which gave analysis for 3.2% of VI (Y = OH); m.p. of pure III (Y = OH) reported[2a,j] 53–54°.

Alcohol VI (Y = OH) was found to be stable under these reaction conditions. Olefin I did not isomerize when treated with 10% or 50% aqueous sulfuric acid for 0.5 hour (identification by melting point and infrared spectrum).

Methyl *exo*-5,6-Trimethylene-*exo*-2-norbornyl Ether (III, **Y = OCH_3**).—A solution of 1.52 g. (10 mmoles) of alcohol III[2j] (m.p. 52.8–53°) in 5 ml. of dry benzene was heated to reflux with 0.48 g. (20 mmoles) of sodium hydride for 1 hour. Methyl iodide (1.56 g., 11 mmoles), was added to the cooled mixture and heated for 1 hour at reflux temperature. The

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the opposite products might ordinarily be anticipated from XI and XII *p*-bromobenzenesulfonates.

[19] (a) D. H. R. Barton and R. C. Cookson, *Quart. Revs.*, **10**, 44 (1956); (b) S. J. Cristol and R. P. Arganbright, *J. Am. Chem. Soc.*, **79**, 3441 (1957).

[20] The possible interactions of the two double bonds in norbornadiene and norbornadiene derivatives have been discussed as has the structure of silver ion π-complexes.[21]

[21] (a) J. G. Traynham and J. R. Olechowski, *J. Am. Chem. Soc.*, **81**, 571 (1959); (b) C. F. Wilcox, Jr., S. Winstein and W. G. McMillan, *ibid.*, **82**, 5450 (1960); (c) C. F. Wilcox, Jr., and R. R. Craig, *ibid.*, **83**, 4258 (1961).

[22] P. B. D. de la Mare and N. V. Klassen, *Chemistry & Industry*, 498 (1960).

[23] F. G. Bordwell and E. W. Garbisch, Jr., *J. Am. Chem. Soc.*, **82**, 3588 (1960).

[24] S. J. Cristol and E. F. Hoegger, *ibid.*, **79**, 3438 (1957).

TABLE I

PRODUCTS OF ADDITION OF METHANOL AND WATER TO OLEFINS I, II AND V IN METHANOL SOLVENT

Reaction	Reactants	Yield, %	Ratio[a] of methoxyln. to hydran. prod.	Composition of products, %[d]				
				Found				Calculated
				Y = OCH_3		Y = OH		Y = OCH_3
				III	VI	III	VI	VI
1	II	89^e	$12^{c,e}$	85.2^e	14.8^e	83.2^e	16.8^e	...
2	I^f	81	33^b	85.5^f	14.5^f	87.9	12.1	...
3	V^g	90	$11^{c,e}$	96.5^c	3.5^e	97.3^c	2.7^e	...
4	29% I^h 71% V	88	..	94.0	6.0	...	...	$6.7^{h,i}$

[a,b,c] This ratio depends on the amount of water present in the methanol reaction mixture and on the method of isolation of the alcohols III and VI (Y = OH) (fractionation by distillation[b] or vapor phase chromatography[c]). [b] The low hydration yield is due to hold-up in the distillation flask of this small scale run and therefore the 12.1% of VI (Y = OH) is not as good as the corresponding data of run 1. [d] Percentages are calculated as ethers III and VI (Y = OCH_3) being 100% and alcohols III and VI (Y = OH) being 100%. [e] After hydrogenation of the addition product. [f] The starting material (m.p. 0–2°)[2j] contains about 2% of V and a trace of II or IV. The latter is the reason for the presence of about 1% or less of unsaturated ethers in the 14.5% of isolated VI (infrared). [g] The starting material contains about 7% of a mixture of II and IV. [h] The preparation of the starting material is described in ref. 2j (Table I, expt. 10); it is free of II and IV. [i] Calculation based on values of reactions 2 and 3; an additional error is introduced into this calculation by the analytically[2j] determined composition of the reactants. Therefore, the calculated value is considered to be in excellent agreement with that observed.

solution was filtered; the inorganic solid was washed with benzene, dissolved in water and the aqueous solution extracted with ether. The combined ether and benzene solutions were washed with water, potassium hydrogen sulfate solution and water. The solution was dried over calcium sulfate and the solvents were removed under reduced pressure. Distillation gave 0.95 g. (57% yield) of product, $n^{22}\mathrm{D}$ 1.4867, b.p. 43–44° (0.2 mm.). The product gave analysis for 96.3% of III (Y = OCH_3). Pure III (Y = OCH_3) was isolated by preparative gas phase chromatography; infrared spectrum in carbon disulfide: 9.10 (strong) and 7.34 μ; there are weak absorptions at 7.95, 9.65 and 12.63 μ which are not present in the *endo* isomer VI (Y = OCH_3).

Anal. Calcd. for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.65; H, 11.03.

Methyl *endo*-5,6-Trimethylene-*exo*-2-norbornyl Ether (VI, Y = OCH_3).—One gram (6.6 mmoles) of alcohol VI,[2j] (m.p. 81–82.5°) was treated with 0.48 g. (20 mmoles) of sodium hydride as described above. After reaction with 2.8 g. (19 mmoles) of methyl iodide, in an additional 2 ml. of benzene for 2 hours at reflux temperature, the mixture was worked up as described for III (Y = OCH_3); b.p. 40–43° (0.2 mm.). The yield was 230 mg. (21% of theor., 50% of the starting alcohol was recovered by distillation), $n^{22}\mathrm{D}$ 1.4924; vapor phase chromatography shows the absence of any III (Y = OCH_3). Infrared spectrum in carbon disulfide was 9.14 (strong) and 7.27 μ; there is a weak absorption at 12.20 μ, which is not present in III (Y = OCH_3).

Anal. Calcd. for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.58; H, 10.70.

Addition Reactions of Methanol to *endo*-1,2-Dihydrodicyclopentadiene (I), *exo*-1,2-Dihydrodicyclopentadiene (V), *endo*-Dicyclopentadiene (II) and a Mixture of I and V.—A mixture of 5 to 20 mmoles of olefin and an amount of 22 wt. % methanolic sulfuric acid (96%), which corresponds to a 50-fold molar ratio of methanol to olefin, was heated at mild reflux for 4 hours. Two volumes of water was added and the mixture was extracted four times with five 10-ml. portions of ether. The combined ethereal solution was washed with water, sodium carbonate solution and water. The excess of the ether was distilled off and the water was removed by azeotroping with benzene at normal pressure. The last trace of benzene was removed at 25° (10 mm.). The hydration products III and VI boil about 15° higher at 0.08 mm. than the ethers III and VI and therefore can be separated by distillation. However, in small scale runs the preferred method was to distil alcohols and ethers together and separate them by vapor-phase chromatography. No fractionation of VI from III (Y = OH or OCH_3) in excess of the experimental error of their analyses occurred during distillation, since the forerun and the afterrun contained the stereoisomers III and VI in the same ratio as the main fraction; the *endo* isomers VI (Y = OH and OCH_3) were found to have slightly higher boiling points than their corresponding *exo* isomers III (Y = OH and OCH_3); the data in Table I represent the average of duplicate analyses.

Reactions 2 and 3 were repeated several times with described results. In all reactions the identity of VI (Y = OCH_3) with authentic VI (Y = OCH_3) synthesized as described above was proven by isolation of VI (Y = OCH_3) from the addition products by preparative gas phase chromatography and comparison of infrared spectra. At the same time any amount of unsaturated ethers (these have slightly shorter retention times on Carbowax than VI (Y = OCH_3), but are not separated from VI) originating from small amounts of II and IV present in the starting olefins, were detected by their infrared absorption at 14.35 μ.[2j]

In reaction 1 of olefin II these unsaturated ethers are the primary products. Their infrared spectra show bands of approximately equal intensity at 14.35 and 9.10 μ. Thus amounts of unsaturated ethers present in isolated VI (Y = OCH_3) of reactions 2, 3 and 4 can be estimated, since the absorption at 14.35 μ is absent in pure VI (Y = OCH_3).

Since the mixture of unsaturated ethers and alcohols (reaction 1) could not be separated into stereoisomers with a Carbowax column, it was hydrogenated quantitatively with platinum dioxide in ethyl acetate solvent at room temperature for 2.5 hours giving a mixture of III and VI (Y = OCH_3). The hydrogenated product was isolated by filtration, washing of the catalyst with ethyl acetate and removal of the solvent by distillation.

In reaction 3 the sum of VI (Y = OCH_3) and unsaturated ethers was 10.8% by analysis. The value of 3.5% (Table I) for VI (Y = OCH_3) obtained after hydrogenation as described above was confirmed by treating 32 mg. of the crude methanol adduct of V (reaction 3) with excess bromine in carbon tetrachloride for several hours at room temperature; the vapor phase chromatogram showed a ratio of III:VI (Y = OCH_3) = 96:4. In another addition of methanol to 99% pure[2j] V an amount of 3.5% of VI (Y = OCH_3) was found.

In run 4 an olefinic by-product (5% yield) was isolated, which had absorption at 14.35 and 3.30μ and did not yield a phenyl azide adduct. The yield and composition of the hydration product in reaction 4 was not determined.

When the pure methyl ethers III and VI were treated under addition reaction conditions, only slight isomerization was observed. Analyses indicated that VI isomerized to a mixture containing 1.7% of III, while III gave a mixture containing 0.2% of VI. Neither ether gave any alcohol, while alcohol III gave a slight conversion to 2% of ether III.

Addition of Formic Acid to *endo*-1,2-Dihydrodicyclopentadiene (I).—A mixture of 1.37 g. (10.2 mmoles) of I and 1.41 g. (30.6 mmoles) of formic acid was heated at 93–103° for 45 minutes. The excess formic acid was distilled at reduced pressure and then 950 mg. (52%) of formate ester, b.p. 57–65° (0.15 mm.), $n^{23}\mathrm{D}$ 1.4910 (lit.[2j] 1.4911), was obtained. The ester was reduced with lithium aluminum hydride to a mixture of alcohols III and VI (Y = OH). This mixture was analyzed by various procedures and gave results indicating a content of 4.4 to 7.2% of III. Good analytical procedures were not yet developed at the time of this preliminary experiment, so these results are not as precise as those for hydration or methanol addition.

Addition of Acetic Acid to *endo*-1,2-Dihydrodicyclopentadiene (I).—A solution of 2.68 g. (20.0 mmoles) of I, 0.1 ml. of 96% sulfuric acid and 12.1 g. of glacial acetic acid was heated at reflux for 1.2 hr. The solution was then cooled, diluted with two parts of water and extracted several times with ether. The combined ethereal extracts were washed with water, aqueous sodium carbonate, and water again and then dried over anhydrous calcium sulfate. Distillation gave 2.15 g. (55%) of ester,[2j] b.p. 64–70° (0.14 mm.), n^{23}D 1.4934. The ester was saponified with ethanolic potassium hydroxide and the resulting alcohol isolated. The alcohol product was analyzed by infrared estimation of the product urethanes (a procedure now known to be less satisfactory than vapor-phase chromatography) and contained 4 ± 2% of III and 96 ± 2% of VI.

Vapor phase chromatographic determinations were conducted on a Perkin–Elmer vapor fractometer, model 154-C, or a Beckman GC-2 gas chromatograph using helium as carrier gas. The isomeric alcohols and their methyl ethers were determined quantitatively on a 3-meter by 6-mm. copper column packed with approximately 25% Carbowax 20M on C-22 firebrick purchased from Wilkens Instrument and Research, Inc.

The ethers were analyzed at 124 ± 1° and at a flow rate of 97–99 cc./min.

The analyses of the isomeric alcohols were generally conducted at 60 cc./min. and 150 ± 2°. The compositions of *exo*- and *endo*-dihydrodicyclopentadiene (I and V) mixtures were determined on a 4-meter Ucon polyglycol LB-550-X (two Perkin–Elmer "R" columns in series). The analyses were carried out at 125 ± 2° with a helium flow of 50–55 cc./min.

A 3 microliter sample normally was used for the quantitative determinations. Larger samples were used when material was to be collected, but in these cases a poorer separation of the isomers was obtained.

The percentage compositions of a mixture were generally determined by planimeter measurement of the peak areas of the vapor-phase chromatogram. In some cases the areas were measured by the method of triangularization. When both methods were used on the same chromatogram, they gave values differing by less than 1%.

To determine that the relative thermal conductivities of the olefins and ethers are close enough to one to give accurate percentage composition data by peak area calculations, a synthetic mixture was prepared and analyzed. The prepared sample was 47.4% in olefin and 52.6% in the corresponding ethers. Calculation of the peak areas of the chromatogram indicated a composition of 48.0% olefins, 52.0% ethers, thus showing that the thermal conductivities are nearly the same and the peak areas are proportional to the weight percentage composition.

The ethers and alcohols showed the following order of retention volumes: VI (Y = OH) > III (Y = OH) > VI (Y = OCH_3) > III (Y = OCH_3). The isomeric unsaturated ethers had a slightly shorter retention time than VI (Y = OCH_3) and were not resolved well from each other or from VI.

Solvolysis of *endo*-5,6-Trimethylene-*exo*-2-norbornyl *p*-Toluenesulfonate (VI, Y = OTs).—The toluenesulfonate ester, m.p. 49.0–50.5° (lit.[8] 48–49°), was prepared from alcohol VI, m.p. 81.5–82.5°.[2j] A solution of 323 mg. (1.05 mmoles) and 90 mg. (1.1 mmoles) of anhydrous sodium acetate in 25 ml. of anhydrous methanol was heated at gentle reflux. After 11 hours the solution was allowed to cool, water was added, and the mixture was extracted with 4 portions of ethyl ether. After the solution was dried over magnesium sulfate, the ether was removed by distillation, benzene was added to the residue, then distilled to remove any remaining water. Calculation of the peak areas of the vapor-phase chromatogram indicated the presence of 3.3% (two analyses, 3.0% and 3.6%) of VI (Y = OCH_3) in III (Y = OCH_3).

The solvolysis was repeated on 30 mg. (0.13 mmole) of the tosylate in 3.0 ml. of absolute methanol. After the usual work-up vapor-phase chromatographic analysis showed 3.4% of VI ether.

Solvolysis of *exo*-5,6-Trimethylene-*exo*-2-norbornyl *p*-Toluenesulfonate (III, Y = OTs).—The *p*-toluenesulfonate ester was prepared from *exo*-trimethylene-*exo*-norborneol (III, Y = OH),[2j] and then was hydrogenated to remove any unsaturation which had been present in the parent alcohol. Recrystallization from ligroin gave product melting at 65.3–67.5° (lit.[8] 60–61°). A solution of 701 mg. of this material in 70 ml. of absolute methanol was heated at reflux for 12.5 hr. and then cooled. Water was added, the solution was extracted with ether and the ethereal solution was dried over calcium sulfate. The solvent was removed by distillation and residual water was azeotroped off with benzene. Gas chromatographic analysis of the residue showed 2.7% of VI ether. After vacuum distillation, analysis of the product showed 3.2% of VI. A repeat experiment gave a product with 2.8% of VI, while one with sodium acetate present gave a product containing 3.0% VI and 97.0% of III (Y = OCH_3).

Acid-catalyzed Addition of Methanol to Norbornadiene (X).—Norbornadiene (5 g., 0.0545 mole) was added to absolute methanol (70 g., 2.18 moles) containing 8.11 g. of 96% sulfuric acid (10% sulfuric acid solution in methanol) which had been cooled to 0°. The reaction mixture was stirred for 0.5 hr. at 0° and then for 5 hours at room temperature. The reaction mixture was poured into water and extracted with pentane. The pentane solution was washed once with water, then with 10% sodium carbonate and then dried over anhydrous magnesium sulfate. Most of the pentane was removed, and the methyl ethers formed were analyzed by vapor-phase chromatography (modified Aerograph, master A-100, equipped with a 1 mv. Brown recorder) on a 2-meter × 6-mm. Carbowax 20M column. Analysis showed 65.5% of nortricyclyl methyl ether (XII) and 34.5% of *exo*-dehydronorbornyl methyl ether (XI). The addition had proceeded a few per cent. and no diadduct was formed.

In another experiment the addition was carried out at 5° for 5.5 hr. and allowed to stand at room temperature for 26 hr. Analysis showed that the reaction had proceeded approximately 64% to completion and a small amount of diadduct was formed. Analysis of the monoadduct showed 70% of XII and 30% of XI.

Analysis of a reaction mixture which had been allowed to stand at room temperature for 1 week gave 33% of XI and 67% of XII.

The nortricyclene ether XII was saturated to 2% potassium permanganate solution and had n^{25}D 1.4638. It had the characteristic nortricyclene peak at 12.35 μ.[25] The nuclear magnetic resonance spectrum (Varian A-60 spectrometer) showed no peaks below 6.7 τ, indicating no unsaturation. Compound XII was not extractable from pentane into aqueous silver nitrate, and did not isomerize to XI under addition conditions.

Anal. Calcd. for $C_8H_{12}O$: C, 77.43; H, 9.68. Found: C, 77.67; H, 9.51.

The unsaturated ether XI reacted rapidly with potassium permanganate and had n^{25}D 1.4611. The nuclear magnetic resonance spectrum showed two almost mirror image quartets centering at 3.9 and 4.2 τ, showing two different olefinic protons. This compound was extractable into 30% aqueous silver nitrate. It was stable under addition conditions and did not isomerize to XII.

Anal. Calcd. for $C_8H_{12}O$: C, 77.43; H, 9.68. Found: C, 77.40; H, 9.71.

Acid-catalyzed Addition of Acetic Acid to Norbornadiene (X).—Norbornadiene (16.7 g., 0.182 mole) was added to 43.5 ml. of glacial acetic acid containing 1 ml. of 40% sulfuric acid. The mixture was stirred for 1.5 hr. at room temperature. The reaction mixture was worked up in the same manner as the methanol-addition reactions and analyzed in an identical manner except for column temperature. The mixture showed 76% of nortricyclyl acetate (XII) and 24% of *exo*-dehydronorbornyl acetate (XI).

The nortricyclyl acetate XII did not react with potassium permanganate and was not extractable into aqueous silver nitrate. It had the infrared peak at 12.3 μ characteristic of nortricyclenes,[25] and had n^{25}D 1.4677. The n.m.r. spectrum had no peaks below 5.4 τ, indicating no unsaturation. Neither XII nor XI rearranged under addition conditions.

Anal. Calcd. for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 71.15; H, 7.93.

The unsaturated ester XI reacted with aqueous potassium permanganate and was extractable from pentane with 25%

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(25) G. T. Youngblood, C. D. Trivette, Jr., and P. Wilder, Jr., *J. Org. Chem.*, **23**, 684 (1958).

aqueous silver nitrate. It had n^{25}_{D} 1.4639. The n.m.r. spectrum showed two different olefinic proton multiplets centering at 3.85 and 4.11 τ.

Anal. Calcd. for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 70.89; H, 7.90.

Acetolysis of *exo*-Dehydronorbornyl *p*-Bromobenzenesulfonate.—*exo*-Dehydronorbornyl *p*-bromobenzenesulfonate, m.p. 79–81°[26] (prepared from alcohol, with analysis as 99% pure, 500 mg., 1.8 mmoles), was added to 50 ml. of glacial acetic acid and allowed to stand in the dark at room temperature for 24 hr. The solvolysis mixture then was poured into ice-water and extracted five times with 50-ml. portions of pentane. The combined pentane solution was then extracted once with water and once with 5% sodium carbonate, and dried over anhydrous magnesium sulfate. The pentane was removed by distilling through a fractionating column to minimize loss of product. The products then were analyzed by gas chromatography as 92.0% nortricyclyl acetate (XII) and 8.0% dehydronorbornyl acetate (XI). Results were essentially identical (92.2% XII and 7.8% XI) when potassium acetate was present in the solvolysis mixture.

Acetolysis of Nortricyclyl *p*-Bromobenzenesulfonate.—The procedure was as above except that the reaction time was 3 days.

The *p*-bromobenzenesulfonate, m.p. 80–82°,[26] was prepared from nortricyclyl alcohol of 99% purity by analysis (vapor-phase chromatography). The solvolysis products contained 95.4% of nortricyclyl acetate (XII) and 4.6% of dehydronorbornyl acetate (XI). With potassium acetate present, the product was 95.0% nortricyclyl acetate and 5.0% dehydronorbornyl acetate.

Methanolysis of Nortricyclyl *p*-Bromobenzenesulfonate.—The methanolysis reactions were run in the same fashion as the acetolyses except that the reaction time was 10 hr. at room temperature. Analysis showed 93.0% of nortricyclyl methyl ether (XII) and 7.0% of dehydronorbornyl methyl ether (XI). In the presence of pyridine, the product analysis was 93.5% XII and 6.5% XI.

Methanolysis of *exo*-Dehydronorbornyl *p*-Bromobenzenesulfonate.—The reaction time was 3.2 hr. at room temperature. The methyl ether product was 92.0% of XII and 8.0% of XI in the presence or absence of pyridine.

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(26) S. Winstein, H. M. Walborsky and K. Schreiber, *J. Am. Chem. Soc.*, **72**, 5795 (1950).

[CONTRIBUTION FROM THE ORGANIC CHEMISTRY DIVISION, U. S. NAVAL ORDNANCE LABORATORY, WHITE OAK, SILVER SPRING, MD.]

Steric Enhancement of Resonance. I. Absorption Spectra of the Alkyltrinitrobenzenes

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The absorption spectra of the alkyltrinitrobenzenes between 214 and 400 mμ are considered as comprising bands deriving from two non-equivalent N → V transitions and over-all substituent effects are regarded as summations of the effects on the individual bands. The influence of alkyl group bulk on one band is consistent with steric inhibition of resonance in the classical sense, but to explain effects on the second transition the existence of a hitherto undescribed phenomenon, termed "steric enhancement of resonance," is suggested.

Progressive hypsochromic–hypochromic spectral displacements in the series [nitrobenzene, *o*-nitrotoluene, *o*-nitrocumene, *o*-nitro-*t*-butylbenzene (Table I)][1] and [trinitrobenzene, trinitromesitylene, trinitro-*t*-butylxylene][2] have been ascribed to steric inhibition of resonance, *i.e.*, progressively decreasing ring-nitro interaction with increasing bulk of *o*-alkyl substituents. We wish now to report that in the related series [*sym*-trinitrobenzene (I), 2,4,6-trinitrotoluene (II), 1-ethyl-2,4,6-trinitrobenzene (III), 2,4,6-trinitrocumene (IV), 1-*t*-butyl-2,4,6-trinitrobenzene (V) (Table I, Fig. 1)] steric inhibition of resonance will not alone account for spectra–structure variations and to suggest the operation of a further phenomenon which may properly be termed "steric diminution of electronic suppression of resonance interaction" or, more succinctly, "steric enhancement of resonance."

In comparing the spectrum of II in methanol with that of I, it is observed that the decrease in band-height is accompanied by a *bathochromic* displacement of λ_{max}. More readily noted is the broadening of the spectral envelope toward longer wave lengths with the consequence that the half-band integrated intensity[3] decreases only 17% as compared with a 29% decrease in ϵ_{max} (Table I). With III a further decrease in ϵ_{max} is accompanied by a further small bathochromic shift, a slight broadening of the band toward longer wave lengths and no significant change in half-band integrated intensity. Of interest is the appearance of an inflection at ~255 mμ. In the spectrum of IV the original band-maximum persists only as an inflection at ~230 mμ and the inflection at ~255 mμ has grown more pronounced. The spectral envelope in the case of V has broadened further still, the 255 mμ inflection has become a maximum and not even a change in slope remains to mark the original position of λ_{max}. It is noteworthy that the half-band integrated intensity of the newly emerged band of V is of the order observed for *p*-nitrotoluene (Table I) and expected for *p*-nitro-*t*-butylbenzene.[4]

These unusual substituent effects may more readily be rationalized if consideration is first devoted to spectra–structure variations in the series nitrobenzene, *m*-dinitrobenzene, *sym*-tri-

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(1) W. G. Brown and H. Reagan, *J. Am. Chem. Soc.*, **69**, 1032 (1947).

(2) P. Fielding and R. J. W. Le Fèvre, *J. Chem. Soc.*, 2812 (1950).

(3) Since the total transition probability is measured by $\int \epsilon d\nu$ over the band, we feel this to be a better intensity measure for intercomparison purposes than ϵ_{max}. Most of the bands herein described, however, are strongly overlapped by high-intensity shorter-wave length bands. For this reason integrated intensities were taken only from the band maxima toward the red. These half-band integrated intensities undoubtedly still incorporate substantial but undetermined contributitions from the underlying tails of the shorter-wave length transitions, so that intercomparisons are meaningful only in a qualitative sense.

(4) The spectra of *p*-nitrotoluene and *p*-nitro-*t*-butylbenzene in methanol should show no greater differences than have been reported for these compounds in isoöctane (Table I).[1] From an inspection of Fig. 1 of ref. 1, they appear to show closely comparable half-band integrated intensities.