Bridged Polycyclic Compounds. XLI. The Uncatalyzed Addition of Acetic Acid to Norbornadiene[1]

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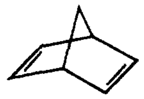
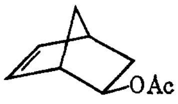
The uncatalyzed addition of acetic acid to norbornadiene (I) to give mixtures of *exo*-dehydronorbornyl acetate (II) and nortricyclyl acetate (III) was studied. Rates of addition and ratios of II/III (degree of homoallylic rearrangement) were found to be quite sensitive to solvent changes. Addition of acetic acid-O-d_1 permitted a study of the stereochemistry of addition and a measure of the accompanying Wagner–Meerwein rearrangement. An examination of the relationship between homoallylic and Wagner–Meerwein rearrangements has been made.

The uncatalyzed addition of acetic acid to norbornadiene (I) to form *exo*-dehydronorbornyl acetate (II) and nortricyclyl acetate (III) has been reported previously. This addition is slow relative to catalyzed additions and favors the olefinic acetate (II) in the product mixture.[2-4]


I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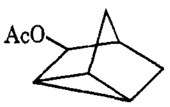
III

TABLE I

EFFECT OF SODIUM ACETATE UPON THE ADDITION OF ACETIC ACID TO NORBORNADIENE[a]

Time, hr	[NaOAc],[b] M	Esters, % yield	10^6k_1[c] sec^{-1}	II/III
43	0	19.4	1.4	75.1/24.9
87	0	38.5	1.5	74.4/25.6
110	0.52	48.9	1.7	74.4/25.6
155	0.52	55.2	1.4	73.6/26.4

[a] Initial mole ratio of acetic acid/norbornadiene was 35/1. [b] The sodium acetate was added after 87 hr at reflux and the reaction continued. [c] The values of the pseudo-first-order rate constants are reliable to about 10%.

TABLE II

SOLVENT EFFECT ON THE UNCATALYZED ADDITION

Expt	Solvent (mole %)[a]	Temp, °C	Time, hr	II/III	Esters, % yield
1	Ether (61)	100 ± 5	49	98/2	0.3
2	Dioxane (56)	100 ± 5	49	97/3	0.4
3	Toluene (55)	100 ± 2	92	95/5	0.3
4	Acetic acid (100)	100 ± 2	22	74/26	0.7
5	Methanol (15)[b,c]	95 ± 3	25	70/30	2.0
6	Methanol (15)[b]	100 ± 3	73.5	70/30	13
7	Methanol (15)[b]	100 ± 2	92	70/30	24
8	Water (17)	100 ± 3	73.5	52/48	93

[a] Mole percentages of solvent were calculated not considering norbornadiene as a solvent. Norbornadiene was present in the above mixtures to an extent of 10 vol %. The carboxylic acid to olefin mole ratio for expt 1–3 was 5.4/1.0 and the ratio for expt 4–8 was 14.3/1.0. [b] Ethers IV and V formed in negligible amounts. [c] The possibility of methyl acetate formation exists, but the solvent polarity of methyl acetate would also be higher than that of acetic acid.

TABLE III

THE EFFECT OF ADDITIONAL METHANOL UPON THE UNCATALYZED ADDITION REACTION[a]

Expt	Mole % methanol	II/III	Ester, % yield	IV/V	Ether, % yield
1[b]	15	70/30	2.0	. . .	. . .
2	26	69/31	1.7	83/17	0.1
3	41	67/33	0.6	81/19	0.2
4	52	68/32	0.2	88/12	0.2
5	64	65/35	0.1	87/13	0.3

[a] Reactions run for 25 hr at 95 ± 3°. The carboxylic acid/olefin mole ratio was 14/1.0 in each experiment. [b] Experiment 5 of Table II.

Sodium Acetate Catalysis.—The effect of sodium acetate, upon rate or product ratio, was investigated (Table I). No significant effects were noted.

Solvent Effect.—The introduction of solvents to the reaction mixture of the uncatalyzed addition was found to have a very pronounced effect on both the rate of addition and the product ratios. From the data (Table II), it is clear that the inclusion of inert nonpolar solvents (expt 1–4) in the reaction mixture resulted in a slower reaction and a product ratio favoring the olefinic ester (II). The inclusion of polar solvents in small amounts (expt 4–8) had the opposite result: the reaction was more rapid and there was a greater tendency to form the rearranged product, nortricyclyl acetate (III).

The effect of added increments of a single inert solvent was shown to fit a regular trend (Figure 1). Added increments of cyclohexane to acetic acid are expected to fit a regular trend[5] and to cause a nearly linear decrease in solvent polarity. The reaction rate decrease and an alteration of product ratio to favor the olefinic acetate (II) parallels the decrease in solvent polarity.

The effect of *larger amounts* (than added in expt 4 and 5 of Table II) of reactive solvents is illustrated by the data of Table III. A large increase in the proportion of methanol in the solvent mixture is accompanied by a decrease in ester formation rate relative to the expt (Table II, 4–7) in which small amounts of methanol were added and an increase in the amount of ethers IV and V formed. The methanol solvent effect is now combined with the ability of the newly intro-

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[1] Previous papers in series: (a) S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *J. Org. Chem.* **31**, 2719 (1966); (b) S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *ibid.*, **31**, 2726 (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] J. B. Jurale, Ph.D. Thesis, University of Colorado, Boulder, Colo., 1965.

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

[5] At low concentration the dielectric constant of solvent pairs is linear with mole fraction. At higher concentrations, the dielectric constant, although no longer linear, increases with increasing mole fraction of the more polar component: I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).

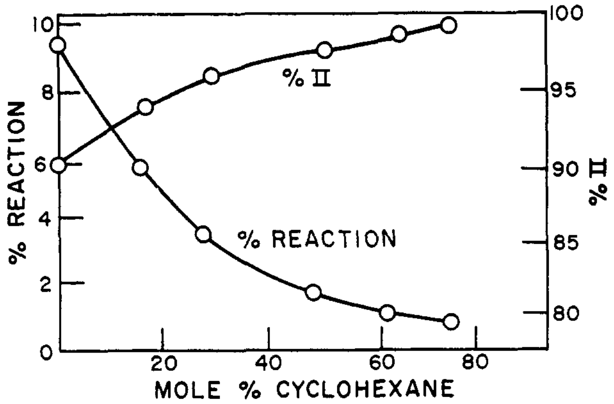


Figure 1.—Addition of acetic acid to norbornadiene in cyclohexane solvent. Reactions carried out for 123 hr at 100°. Data and procedure are described in the Experimental Section.

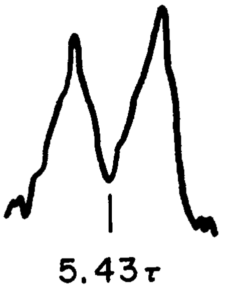
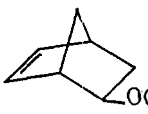
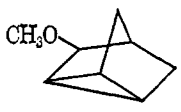


Figure 2.—Nmr spectrum of *exo*-norbornenyl acetate-3-d_1 (Table IV, expt 2).

duced solvent to add to the substrate in competition with the acetic acid. The product ratio of *exo*-dehydronorbornyl methyl ether (IV)/nortricyclyl methyl



IV



V

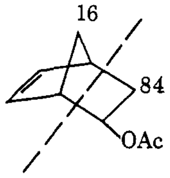
ether (V) indicated that the unrearranged olefinic ether (IV) had been favored more in the ether formation process than had the unrearranged olefinic acetate (II) in the ester formation process.

Until the solvent effect upon the neutral addition was known, the only methods used for preparative scale ester synthesis of each of the isomers involved subsequent separation procedures.[3,4,6] The addition of large amounts of inert nonpolar solvents caused nearly complete formation of the olefinic acetate (II) and the exclusion of nortricyclyl acetate (III) as shown in Figure 1. The fact that nonpolar solvents caused a reaction rate decrease can be compensated for by the use of sealed glass tubes and high reaction temperatures. The use of this procedure is exemplified by expt 1 of Table V. A good yield of ester was obtained which was almost entirely the olefinic acetate.

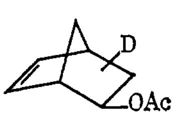
Addition of Labeled Acetic Acid.—Results of a study of the addition of labeled acetic acid-O-d_1 to norbornadiene are given in Table IV. The reaction was done, in this case, at a large enough hydrocarbon concentration to alter substantially the product ratio from the value that is observed when the acetic acid is in large excess (II/III, 75/25).[3] The data indicate a correspondingly large degree of vicinal deuteration in the olefinic acetate (II-D) compared with that observed in the acid-catalyzed addition.[1] The assignment of a *cis*-3-*exo* position for the deuterium was consistent with the pmr spectrum (Figure 2). The confirmation of this assignment was made by comparison of the spectrum of the addition product (Figure 2) with that of the authentically *cis*-*exo*-deuterated olefinic acetate and the arguments associated with these spectra.[1]

TABLE IV

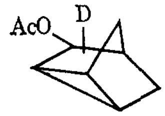
ADDITION OF ACETIC ACID-O-d_1 TO NORBORNADIENE (I)

Expt	Time, hr[a]	Esters, % yield	II-D/III-D[b]	Deuterium distribution[c]
1	15	0.5	85/15	
2	94	1.7	84/16	

[a] The reaction was conducted at reflux (*ca.* 110°). The carboxylic acid/olefin ratio was 4.5/1.0 for both experiments. [b] For D notation see footnote *a* of Table IV of ref 1b. [c] The mass spectral analysis was upon the sample from expt 2.



II-D



III-D

The effect of solvent was further illustrated by the results of the experiments listed in Table V. Experiments 2 and 3 were carried out with the intent of preparing specifically labeled *cis*-*exo*-deuterated olefinic acetate (II-D). Such a labeled product might be expected from concerted addition and is consistent with the low yield of deuterated nortricyclyl acetate (III-D). The pmr spectra (Figures 3a–c) were consistent with the assignment of a *cis*-*exo* position to any significant vicinal deuteration. The more sensitive mass spectral analysis indicated (Table V) predominant vicinal deuteration. The analysis indicated an additional problem, "scrambling" of deuterium into the acetoxy methyl group. Despite the fact that tentative conclusions could be drawn regarding the mechanism of the reaction, the procedure was not useful as a preparation of specifically labeled olefinic acetate. The data of Table V indicate that more severe reaction conditions (heating at higher temperature) resulted in more scrambling of the deuterium into the acetoxy methyl group.

Solvent effects upon the deuterium distribution associated with the addition reaction were shown to be regular (Table VI). The trends clearly indicated that *cis* (vicinal) deuteration and percentage of olefinic acetate (II-D) increased with increasing amounts of inert nonpolar solvent. In addition, the rate of reaction decreased with an increase in the amount of nonpolar solvent. Finally it should be pointed out that the degree of deuteration of the acetoxyl methyl group increased with a greater extent of reaction. In relation to the above, the degree of "scrambling" of deu-

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

Table V

The Addition of Acetic Acid and Acetic Acid-O-d_1 to Norbornadiene (I) in Varying Norbornadiene/Acetic Acid Ratios

Expt	Mole ratio, diene/acid	Addend	Yield, %	II/III (D)	% mono-deuteration[a]	% vicinal deuteration[a]	% mono-acetoxy deuteration[a]
1[b]	1.82/1	CH_3CO_2H	83.7	98.5/1.5	. .	. .	. .
2[b]	1.82/1	CH_3CO_2D	42.7	98/2	45	82	31
3[c]	2.14/1	CH_3CO_2D	77.5	99/1	47	93	37

[a] Reference 7. [b] Reaction was run for 22.3 hr at 188 ± 5°. [c] Reaction was run for 18 hr at 200 ± 5°.

Table VI

Solvent Effect in the Addition of Acetic Acid-O-d_1 to Norbornadiene

Expt	Vol % heptane	Ester, % yield	II-D/III-D	% D on C-3 of II-D[a]	% mono-deuterated species[b]
1[c]	0	40	78/22	83	68[d]
2[c]	20	22	84/16	86	72
3[c]	50	7	89/11	90	77
4[c]	80	0.9	93/7	95	84
5[c]	90	0.3	. . .	. . .	. . .
6[e]	80	3	95/5	95	77

[a] Based on vicinal deuteration of species with one deuterium in bicyclic ring skeleton. [b] Reference 7. [c] Reaction carried out at 145 ± 2° for 16.5 hr. The carboxylic acid/olefin mole ratio was 9.9/1.0. [d] *The remaining species are largely polydeuterated (in the* acetoxy methyl group) rather than undeuterated. [e] Reaction carried out at 145 ± 2° for 48 hr. The carboxylic acid/olefin mole ratio was 9.9/1.0.

terium was much smaller in the catalyzed addition reactions at room temperature at comparable yields.[1,7]

A plot (Figure 4) of % *cis* addition *vs.* the percentage of olefinic acetate (II-D) in the product mixture shows an intersection of 100% *cis* addition with 100% olefinic acetate upon extrapolation.

Addition under Extreme Conditions.—The results of the addition of acetic acid and acetic acid-*O*-d_1 to norbornadiene (I) under extreme conditions of pressure and temperature were investigated (Table VII). It was shown that the addition at elevated temperatures and at "low" (0.06 *M*) concentrations of diene in acetic acid gave a product ratio similar to that reported by Vogelfanger[3] (expt 4, II/III, 75/25).

The vapor phase addition (expt 2, Table VII) greatly favored the olefinic acetate (II). The amounts of nortricyclyl acetate (III) observed in the vapor phase addition were, however, larger than one might expect from such a reaction and may possibly be attributed to "wall reactions" on the glass surface of the sealed tube.

The results of the vapor phase addition using acetic acid-O-d_1 (expt 3, Table VII) indicated that the reaction was largely *cis*. The data were limited by the fact that under these relatively severe conditions the deuterium was significantly "scrambled" into the acetoxy methyl group.[7] The pmr spectrum (Figure 5) verified the "scrambling" of deuterium into the acetoxy methyl group. Despite the fact that the reaction gave mostly olefinic acetate II-D, implying *cis* addition, the pmr spectrum was similar to that observed for acetate without *cis-exo* deuterium (Figure 3a). This is the result of exchanging the hydrogen atoms with deuterons in the acetoxy methyl group which effectively places a hydrogen atom upon the vicinal *cis-exo* position.

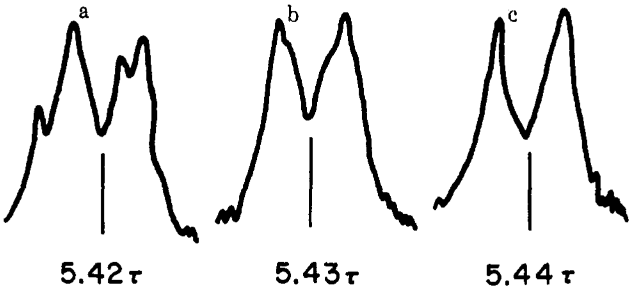

Figure 3.—Nmr spectra: (a) *exo*-norbornenyl acetate from expt 1, Table V; (b) *exo*-norbornenyl acetate from expt 2, Table V; (c) *exo*-norbornenyl acetate from expt 3, Table V.

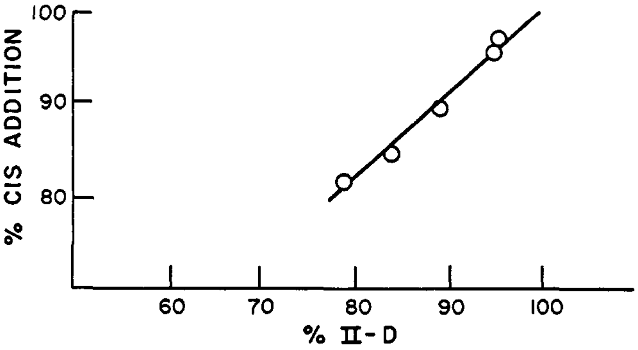

Figure 4.—Variation of per cent *cis* addition with per cent II in the reaction mixture (Table VI).

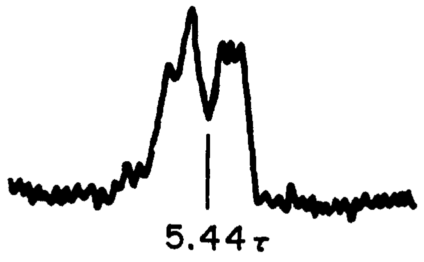

Figure 5.—*exo*-Norbornenyl acetate-d_1 (expt 3, Table VII).

The result of expt 1 was another case in which an inert, relatively nonpolar solvent gave a product ratio favoring olefinic acetate II-D and a large preponderance of *cis-exo* vicinal deuteration.

Experimental Section

Analyses for the ratios of *exo*-dehydronorbornyl (II) and nortricyclyl (III) acetates were done by gas chromatography (Aerograph A-100). Ester yields were determined by gas chromatographic recorder responses to samples of reaction products. These responses were compared to the response from standard ester solution samples. The retention times for the esters on a Carbowax 20M column (2 m × 0.25 in.) on firebrick at 113° (flow rate of 70 cc/min.) were, 39 min II, and, 53 min III.

The acetic acid used for the addition reactions was Du Pont reagent grade (99.7% minimum purity) and was found to be 99.9% anhydrous by Karl Fischer titration.

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

TABLE VII

ADDITION OF ACETIC ACID AND ACETIC ACID-O-d_1 TO NORBORNADIENE UNDER EXTREME CONDITIONS OF TEMPERATURE AND PRESSURE

Expt	Nature of reaction	Time, hr/temp, °C	II/III (D)	Ester, % yield	% D on C-$_3$	Mole ratio, carboxylic acid/olefin
1	Ether solvent[a]	47/123	97/3	0.2	97	1.1/1.0
2	Vapor phase[b]	120/160	97/3	0.4	..	1.7/1.0
3	Vapor phase[a]	46/230	99.8/0.2	10	97	1.0/1.0
4	High temperature[b]	0.5/150–200	75/25	59	..	26/1.0

[a] Addend is acetic acid-O-d_1. [b] Addend is acetic acid.

Norbornadiene was commercially available from Frinton and was distilled at 83° (620 mm) immediately prior to use.

Pentane was technical grade, distilled from anhydrous potassium carbonate.

Proton magnetic resonance spectra were performed on a Varian A-60 spectrometer, field strength 60 Mc, with tetramethylsilane (τ 10.00) used as internal standard. The complete spectrum of *exo*-dehydronorbornyl acetate (II) is described elsewhere.[1b]

Procedure for Determining the Data for Figure 1.—Small (*ca.* 3.5-ml capacity) Pyrex glass tubes were washed with concentrated ammonium hydroxide and water and were oven dried. To these tubes were added the following volumes of cyclohexane (freshly distilled and technical grade) (experiment and milliliters): 1, 0.00; 2, 0.10; 3, 0.30; 4, 0.60; 5, 1.00; and 6, 2.00. A mixture of 0.20 ml (0.18 g, 1.97 mmoles) of norbornadiene and 0.20 ml (0.21 g, 3.5 mmoles) of acetic acid was added to each tube. The contents of the tubes were cooled (Dry Ice) and the tubes were purged with nitrogen and sealed. These tubes were heated at 100° (±2°) for 123 hr. After cooling, the tubes were opened and 0.5 ml of water was added to each tube. The tubes were resealed (after cooling) and shaken for *ca.* 1 min. After opening the tubes as above, cyclohexane was added to the tubes of expt 1–5 to bring the total volume of each to 2.0 ml (in the organic layer). A small amount of powdered, anhydrous, reagent grade potassium carbonate was added to each and the resulting mixtures were gently shaken. Analyses of these samples on gas chromatography (conditions described at the beginning of the Experimental Section) resulted in the data given in Table VIII.

TABLE VIII

Expt	% II	% III	Ester, % yield	Mole percentages Cyclohexane	 Norbornadiene	 Acetic acid
1	89.5	10.5	9.55	0.00	36.0	64.0
2	92.6	7.4	5.83	14.5	30.8	54.7
3	95.5	4.5	2.76	33.8	23.8	42.4
4	96.9	3.1	1.55	50.5	17.8	31.7
5	97.8	2.1	0.92	62.9	13.4	23.7
6	99	<1	0.57	77.2	8.2	14.6

Effect of Sodium Acetate on the Addition of Acetic Acid to Norbornadiene (Table I).—A mixture of 4.50 g. (0.049 mole) of norbornadiene and 100.0 ml of acetic acid was heated in a reflux appparatus in an oil bath maintained at 111 ± 2°. A 5.00-ml aliquot was removed (*via* syringe) at the end of 43 hr and quenched by injection into cold water. The water solution was extracted four times with 20-ml portions of pentane. The combined extracts were washed with 10 ml of 10% aqueous sodium carbonate solution and then with 10 ml of cold water. The pentane solution was dried over anhydrous magnesium sulfate, filtered, and evaporated (in a hot-water bath, maximum temperature 70°) to *ca.* 3 ml of residue. This residue was transferred quantitatively to a 5.00-ml volumetric flask. The flask was filled to the mark and the contents were analyzed by gas chromatography. The column used was a 2 m × $^3/_8$ in. 25% TCEP on Chromosorb W, regular 60–80 mesh, and was maintained at 118°. Retention times for a flow rate of 100 cc/min on this column were, 35 min II, and, 49 min III. The results of this and other analyses are shown in Table I.

A similar aliquot was removed at the end of 87 hr, and worked up and analyzed as described above.

The reaction vessel was cooled and 4.00 g (0.049 mole) of anhydrous reagent sodium acetate was added. The vessel was then replaced in the oil bath and reflux was continued as above.

Aliquots were removed and worked up (in the aforementioned manner) at the end of an additional 23 and 68 hr.

Procedure for Determining the Data of Table II.—Pyrex glass test tubes (25 × 200 mm, flame drawn to a narrow neck) were filled with 1.0 ml (0.91 g, 9.8 mmoles) of norbornadiene and the acetic acid–solvent compositions described in Table IX. The contents of the test tubes were then frozen in Dry Ice, treated briefly with a nitrogen stream, and sealed. The tubes were removed at appropriate times, frozen in Dry Ice, and opened. The work-up and analysis method was that employed in the case of the addition reactions under the influence of sodium acetate.

TABLE IX

Expt	Acetic acid, ml	Solvent	Volume, ml
1	3.0	Ether	7.0
2	3.0	Dioxane	7.0
3	3.0	Toluene	7.0
4	8.0	...	...
5	8.0	Methanol	1.0
6	8.0	Methanol	1.0
7	8.0	Methanol	1.0
8	8.0	Water	0.5

Procedure for Determining Data of Table III.—Glass tubes (as described in the preceding section) were prepared with methanol contents as described (experiment and milliliters of methanol): 2, 2.0; 3, 4.0; 4, 6.0; and 5, 10.0. To each of these tubes was added 1.0 ml (0.91 g, 9.8 mmoles) of norbornadiene and 8.0 ml of glacial acetic acid. The tubes were sealed as described previously (experimental results for Table I) and heated in an oil bath at 95 ± 3° for 25 hr. The reactions were stopped as described in the previous section and worked up according to the experimental results for Table I.

Preparation of Acetic Acid-O-d_1.—Reagent grade acetic anhydride was distilled through a 30-in. Vigreux column and a center cut was removed, bp 130° (627 mm).

To 132 g (1.30 moles) of anhydride was added rapidly, with minimal air contact, freshly opened ampoules of deuterium oxide (Consolidated Electrodynamics, 20 g, 1.0 mole). The reaction was carried out under drying tube (Drierite) protection and the mixture stirred for 15 hr at room temperature.

The solution was placed in the apparatus used for the anhydride distillation and fractionated. A center cut was removed for additions and analysis, bp 110° (629 mm). Mass spectral analysis, accomplished after several purgings of the mass spectrometer, indicated 83% deuteration.

Neutral Addition of Acetic Acid-O-d_1 to Norbornadiene (Table IV).—To 10.0 ml (9.05 g, 0.0985 mole) of norbornadiene in a reflux system protected by a drying tube (Drierite) was added 25.0 ml of acetic acid-O-d_1 (prepared as described in the preceding section). The solution was stirred under reflux (*ca.* 110°) for 93.5 hr. The work-up used was that employed in the experimental results for Table I, except that the volumetric flasks used contained 25.00 ml. The gas chromatographic analyses were carried out as described in the experimental section for Table I. A sample of the olefinic ester (II-D) was collected by gas chromatography and subjected to mass spectral analysis. The results of these analyses are given in Table IV.

A completely analogous reaction was run for 15 hr, the results of which are given in Table IV.

Addition of Acetic Acid to Norbornadiene in an Excess of Hydrocarbon Substrate (Expt 1, Table V).—To 38.4 ml (40.4 g, 0.672 mole) of acetic acid was added 125.0 ml of norbornadiene. The mixture was placed in a 3-ft glass tube and sealed in the manner described in the experimental results of Table II. The tube was heated for 22.3 hr at 188 ± 5°. The resulting reaction mixture was poured into a flask and treated with 10 g of potassium carbonate powder. A pentane solution of this mixture was filtered into a 250-ml distilling flask. The pentane was removed under reduced pressure, and the acetate mixture was distilled. The principal fraction (44.0 g) boiled at 72–74° (12 mm). Results of gas chromatographic analyses are listed in Table V. A pmr spectrum was taken of a neat sample and is depicted in Figure 3a.

Addition of Acetic Acid-O-d_1 to Norbornadiene in an Excess of Hydrocarbon Substrate (Expt 2, Table V).—Into a 3-ft glass tube was placed 41.5 g (0.680 mole) of acetic acid-O-d_1 (prepared as described previously) and 125.0 ml of norbornadiene. The tube was sealed, the reaction was run, the reaction mixture was worked up, and the analyses were made by the method of the preceding section. Olefinic acetate (II-D) samples were collected and subjected to mass spectral analyses, the results of which are presented in Table V. Pmr analysis of this type of sample resulted in a spectrum, a portion of which is presented in Figure 3b.

Addition of Acetic Acid-O-d_1 to Norbornadiene in a Large Excess of Hydrocarbon Substrate (Expt 3, Table V).—To 4.0 ml (4.2 g, 0.070 mole) of acetic acid-O-d_1 (from previously described synthetic procedure) was added 15.0 ml of norbornadiene. The mixture was placed in a glass tube, prepared, and sealed as described in the experimental results of Table II. The tube was heated at 200 ± 5° for 18 hr. The tube was opened, worked up, and analyzed as described in the two preceding Experimental Sections. The distillation procedure yielded 8.28 g (77.5%) of acetates. The analytical results are described by Table V.

Addition of Acetic Acid-O-d_1 to Norbornadiene in Varying Amounts of Heptane Solvent (Table VI).—Base-rinsed, water-rinsed, and dried Pyrex glass test tubes (50-ml capacity) were filled with mixtures containing the amounts of heptane and acetic acid/norbornadiene (1/10, volume ratio) solutions listed in Table X. The tubes were flushed with helium gas, sealed, and heated for 16.5 (expt 1-5) and 48 (expt 6) hr at 145 ± 2°. The tubes were then cooled, opened, and analyzed by gas chromatography. Samples of the olefinic acetates (II-D) collected by gas chromatography were subjected to mass spectral analyses. The results of all of these analyses are displayed in Table VI.

TABLE X

Expt	Vol of acid–diene soln, ml	Vol of heptane, ml
1	10.0	0.0
2	8.0	2.0
3	5.0	5.0
4	2.0	8.0
5	1.0	9.0
6	3.0	12.0

Addition of Acetic Acid-O-d_1 to Norbornadiene in Ether Solvent (Expt 1, Table VII).—To 2.00 ml (1.84 g, 0.0196 mole) of norbornadiene in a glass tube was added 2.00 ml of acetic acid-O-d_1 and 15.0 ml of ether (anhydrous reagent grade). The tube was sealed as in the experimental results of Table II and heated for 47 hr in an oil bath at 123 ± 3°. The tube was then cooled and opened and the contents were worked up as described in the experimental results of Table I. Mass spectral samples were collected as above and the results of these and analytical gas chromatographic determinations are listed in Table VII.

Addition of Acetic Acid to Norbornadiene in the Vapor Phase (Expt 2, Table VII).—An 11-in.-long, thick-walled glass tube was washed with base (aqueous potassium hydroxide), then with water, and finally oven dried. Into the *bottom* of this tube were injected (*via* syringe) 70 μl (64 mg, 1.2 mmoles) of norbornadiene and 40 μl (42 mg, 0.70 mmoles) of acetic acid. The introduction of liquid was such that it was deposited on the bottom with a minimum of material on the upper walls. The tube was then cooled in a Dry Ice–acetone bath, evacuated to 0.10 mm and sealed by flame. Heating of the tube was carried on for 119.8 hr, at 160 ± 3°. Preparation of the tube for opening was accomplished by cooling in the Dry Ice–acetone bath. The contents of the tube were removed and worked up in the manner described in the experimental results of Table I. In addition, the analytical samples were evaporated down to a smaller volume to check the product ratios more accurately. The results of these gas chromatographic analyses are listed in Table VII.

Addition of Acetic Acid-O-d_1 to Norbornadiene in the Vapor Phase (Expt 3, Table VII).—To a thick-walled glass tube (*ca.* 400-ml capacity, prepared as described in preceding section) was added 0.51 ml (0.46 g, 5 mmoles) of norbornadiene and 0.29 ml (0.31 g, 5 mmoles) of acetic acid-O-d_1. The tube was prepared and sealed as described in the preceding section and heated for 46 hr at 230 ± 10°. The tube was opened and the reaction mixture was worked up as in the preceding experiment. Gas chromatographic analyses were carried out and the results of these are listed in Table VII. Deuterated olefinic acetate II-D was collected from the gas chromatograph and subjected to mass spectral and pmr spectroscopic analyses (Table VII).

Addition of Acetic Acid to Norbornadiene at High Temperatures (Expt 4, Table VII).—An excess (15.0 ml) of acetic acid was added to 1.00 ml (0.91 g, 9.9 mmoles) of norbornadiene in a 3-ft glass tube. The tube was prepared for heating as described in the experimental results of Table II. The reaction vessel was heated for 0.5 hr at a temperature that rose gradually from 150 to 200°. The tube was cooled and opened as described in expt 1 of this series. The tube contents were worked up and analyzed by the procedure described in the experimental results of Table I. The results of analytical gas chromatography are given in Table VII.

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