Bridged Polycyclic Compounds. XL.
The Catalyzed Addition of Acetic Acid to Norbornadiene[1]

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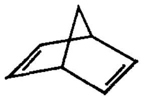
An investigation of the acid-catalyzed addition of acetic acid to norbornadiene (I) to form *exo*-dehydronorbornyl acetate (II) and nortricyclyl acetate (III) has been carried out. Catalysis by sodium perchlorate was similar that of sulfuric acid and perchloric acid. The addition of acetic acid-O-d_1 resulted in a larger degree of "scrambling" of deuterium in the acetates when catalyzed than when uncatalyzed.[2] The ratio of esters (II/III) was essentially constant in the product when perchloric acid was the catalyst. When sulfuric acid was the catalyst, the product ratio was variable, and favored the olefinic acetate more than when perchloric acid was the catalyst. Both sulfuric acid and perchloric acid catalyzed reactions exhibited sensitivity to solvent effects as shown by rate and product-ratio variations.

The acid-catalyzed addition of acetic acid to norbornadiene (I) to form *exo*-dehydronorbornyl acetate (II) and nortricyclyl acetate (III) has been extensively studied in this laboratory and others. Winstein and Shatavsky[3] reported that *p*-toluenesulfonic acid catalysis resulted in a product ratio (II/III) of *ca.* 15/85. Experiments in this laboratory showed that the product ratio with sulfuric acid was 26/74.[4] More recent work indicated that perchloric acid catalysis gave a ratio of 15/85.[5] It, therefore, appeared that a preponderance of nortricyclyl acetate (III) was a characteristic of acid-catalyzed additions of acetic acid to norbornadiene (I), although it is clear from the published data that product ratios varied with the catalyst and/or with the conditions of the addition experiments. This paper reports a continuation of studies on acid-catalyzed additions.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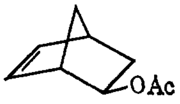

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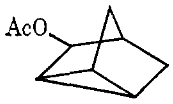

III

Sulfuric Acid Catalysis.—When addition catalyzed by sulfuric acid was scrutinized more closely, it was noted that it did not display a constant product ratio (II/III, see Table I). The ratio was seen to vary during the progress of the reaction, favoring the olefinic acetate at greater degrees of completion.

TABLE I
TIME DEPENDENCE OF THE PRODUCT RATIO FROM THE SULFURIC ACID CATALYZED ADDITION OF ACETIC ACID TO NORBORNADIENE (I)[a]

Expt	Time, hr	Ester yield, %	II/III
1	4.5	3	24/76
2	7.5	5	30/70
3	19	13	34/66
4	43	31	36/64

[a] The reactions were carried out at 23 ± 1°, the sulfuric acid concentration was 0.017 *M*, and the mole ratio of acetic acid/diene was 33.5/1.0.

A simple "product-ratio extent of reaction" correlation was eliminated by the data of Table II. Higher temperatures were observed to favor the tricyclic acetate (III) in the product mixture. The product ratios obtained at higher temperatures closely paralleled the ratios obtained in the case of perchloric acid catalysis at all temperatures (Table III).

TABLE II
THE SULFURIC ACID CATALYZED ADDITION OF ACETIC ACID TO NORBORNADIENE (I) UNDER A VARIETY OF CONDITIONS

Expt	Time, hr	Temp, °C	$[H_2SO_4]$, *M*	Ester yield, %	II/III
1[a]	16	23	0.016	9	32/68
2[a]	4	43	0.016	15	27/73
3[a]	8	23	0.032	11	34/66
4[b]	1	130	0.017	54	19/81
5[c]	20.5	23	0.009	4.9	28/72
6[c]	20.5	23	0.018	10.2	32/68
7[c]	20.5	23	0.045	39.0	39/61
8[c]	20.5	23	0.090	63.5	41/59

[a] Mole ratio of acetic acid/olefin was 16/1.0. Mole ratio of acetic acid/olefin was 28/1.0. [c] Mole ratio of acetic acid/olefin was 34/1.0.

We have also shown that product ratio variations were not due to formation of diadduct preferentially from one isomer. The half-life of the addition reaction of the first mole of acetic acid to norbornadiene at 23° in 0.018 *M* sulfuric acid was about 60 hr. Experiments with the monoacetates have shown that both isomers II and III were still present (95 ± 5%) at the end of 100 hr at 23° in 0.018 *M* sulfuric acid. Data for the addition reactions at these conditions have originated from experiments that were carried out for less than the half-life of the addition.

Perchloric Acid Catalysis Compared to Sulfuric Acid Catalysis and the Effect of Added Salts.—The relative abilities of sulfuric acid and perchloric acid for catalyzing the addition were observed by comparing (Table III) expt 5c–e (both 0.001 *M* acid concentrations) and 5b–d (both 0.01 *M* acid concentrations). In the comparison of the experiments involving added acids only (5c and e), it was noted that perchloric acid was *ca.* 300 times more effective a catalyst for the reaction.

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[1] Previous paper in series: S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *J. Org. Chem.* **31**, 2719 (1966). This work was presented in part in papers presented at the First International Symposium on Organic Reaction Mechanisms in Cork, Ireland, and at the Symposium on Electrophilic Addition Reactions at the 148th National Meeting of the American Chemical Society in Chicago, Ill., Sept 1964.

[2] Paper XLI: S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *ibid.*, **31**, 2733 (1966).

[3] S. Winstein and M. Shatavsky, *Chem. Ind.* (London), **56** (1956).

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

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

TABLE III

SALT EFFECTS IN ACETIC ACID ADDITIONS TO NORBORNADIENE (I)[a]

Expt	Concn of added salt or acid, *M*	Temp (°C)–time	II/III[b]	Ester yield, %
1a	. . .	48–92 hr	70/30	*ca.* 0.4
b	0.1 $NaClO_4$	48–92 hr	14.5/85.5	41
c	0.1 NaOAc	48–92 hr	. . .	*ca.* 0.2
d	0.1 $NaClO_4$ and 0.1 NaOAc	48–92 hr	*ca.* 75/25	*ca.* 0.3
2a	0.1 $NaClO_4$	62–5 hr	15/85	17
b	0.01 H_2SO_4	62–5 hr	15/85	21
c	0.1 H_2SO_4	62–5 hr	15/85	71
3a	0.0001 $NaClO_4$	62–75 min	. . .	*ca.* 0.01
b	0.001 $NaClO_4$	62–75 min	. . .	*ca.* 0.02
c	0.01 $NaClO_4$	62–75 min	14/86	1.1
d	0.1 $NaClO_4$	62–75 min	15/85	2.9
e	0.1 $NaClO_4$ and 0.01 NaOAc	62–75 min	. . .	*ca.* 0.01
f	0.1 $NaClO_4$ and 0.01 H_2SO_4	62–75 min	14/86	*ca.* 90
4a	0.05 $NaClO_4$	64–100 min	15/85	4.4
b	0.005 H_2SO_4	64–100 min	15/85	5.3
c	0.05 $NaClO_4$ and 0.005 H_2SO_4	64–100 min	14/86	*ca.* 100
5a	0.01 $NaClO_4$	50–35 min	*ca.* 18/82	*ca.* 0.2
b	0.01 H_2SO_4	50–35 min	18/82	1.1
c	0.001 H_2SO_4	50–35 min	*ca.* 20/80	*ca.* 0.1
d	0.01 $HClO_4$	50–35 min	12/88	*ca.* 90
e	0.001 $HClO_4$	50–35 min	13/87	36
f	0.01 $NaClO_4$ and 0.001 H_2SO_4	50–35 min	13/87	8.5
g	0.01 $NaClO_4$ and 0.001 $HClO_4$	50–35 min	13/87	36

[a] The carboxylic acid/diene I mole ratio was 42.5/1.0 in all experiments. [b] Experiments 5b and d should not be used for other than qualitative comparisons as diadduct formation would significantly mar the validity of the result of 5d.

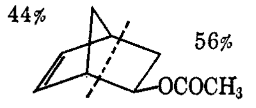
It has been observed[2,6] that sodium acetate does not catalyze the addition reaction, nor does it change the product composition, compared with the uncatalyzed reaction. Experiment 1c is consistent with the previous work. On the other hand, sodium perchlorate (0.1 *M*) increases the rate by about 100 over the uncatalyzed addition experiment (compare 1a and b). Experiments 3a–d indicated that the effects associated with added sodium perchlorate increased with increasing concentration of the salt. When sodium acetate was included with the sodium perchlorate (expt 1b and 3d compared with 1d and 3e, respectively) the accelerative effect was largely eliminated.

The catalytic effect of sodium perchlorate was observed to be very similar to the effect of a sulfuric acid solution one-tenth as strong (compare expt 2a and b and 5a and c).

That the roles of perchlorate salts and strong acids are very similar was seen by data of Table III.

The sulfuric acid catalyzed additions were accelerated substantially by added perchlorate (compare expt 4b and c, 5c and f, and 3d and f).

The Addition of Labeled Acetic Acid–Perchloric Acid Catalysis.—In our initial work on the addition of acetic acid to norbornadiene,[4] we used sulfuric acid as catalyst. Winstein and Vogelfanger[5] reported a somewhat different ratio of products using perchloric acid catalysis. We have now shown the product ratio of olefinic II and tricyclic III acetates, using perchloric acid catalysis, to be relatively constant (Table III). We decided to investigate the addition more intensively, using acetic acid-O-d_1. The gas chromatographic analyses are displayed in Table IV. Note that there was no observable effect upon the rate of reaction or upon the ratio of products when the addend was changed from acetic acid to acetic acid-O-d_1. Mass spectral analysis of the olefinic ester[7] indicated that the deuterium distribution was as indicated in IV.

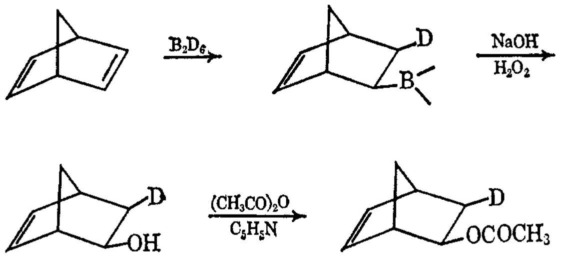


IV

The stereochemistry of the deuterium atom in the acetate was partially established by proton magnetic resonance (pmr) spectroscopy. The complete spectrum of undeuterated *exo*-dehydronorbornyl acetate (II) is described in the experimental section. The *endo*-hydrogen at C_2 (adjacent to the acetoxy group) in the undeuterated olefinic acetate (II) displayed an absorption at τ 5.41 which was a doublet of doublets (Figure 1). The magnitude of coupling was expected to fall within the ranges predicted by work reported previously;[8-10] the *endo–endo* coupling constant was large (7 cps) and the *exo–endo* coupling constant was small (3 cps).

The absorption of the proton of interest in the deuterated acetate II-D (Figure 2, the product of the addition of acetic acid-O-d_1), showed a fairly clean doublet with a relatively large coupling constant of approximately 7 cps. This value was one which would be expected of vicinal *endo* protons and thus the deuterium in the sample was located primarily in this vicinal *exo* position. Results of such a nature have been discussed before.[9] The olefinic acetate II-D-S, in which the position of deuteration was exactly predictable,[11] was prepared. The method of synthesis is illustrated by Scheme I. The ester synthesized in this way displayed a pmr spectrum as depicted in Figure 3. The chemical shift centered at τ 5.47 was a fairly clean doublet.

SCHEME I



II-D-S

Sulfuric Acid Catalysis.—The addition of acetic acid-O-d_1 catalyzed by sulfuric acid-d_2 was carried out at 23° (Table V). The data of Table VIII compared

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[6] J. B. Jurale, Ph.D. Thesis, University of Colorado, Boulder, Colo., 1965.

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

[8] M. Karplus, *J. Chem. Phys.*., **30**, 11 (1959).

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

[10] P. Laszlo and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **85**, 2709 (1963).

[11] H. C. Brown, *Tetrahedron*, **12**, 117 (1961).

TABLE IV

PERCHLORIC ACID CATALYZED ADDITION OF ACETIC ACID-O-d_1 AND ACETIC ACID TO NORBORNADIENE

Addend	Time, min	Temp, °C	Mole ratio of carboxylic acid/olefin	$[HClO_4]$, M	Ester yield, %	II/III (D)[a]
CH_3CO_2D	39	50	44/1.0	0.02	67	12/88
CH_3CO_2H	39	50	44/1.0	0.02	66	12/88

[a] A general system of notation is used in these papers, II-D = II with deuterium anywhere in the molecule and II-D-S = II specifically labeled with deuterium *cis* and *exo* to the functional group.

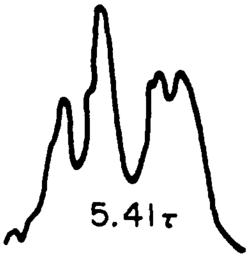

Figure 1.—*exo*-Norbornenyl acetate (II), undeuterated.

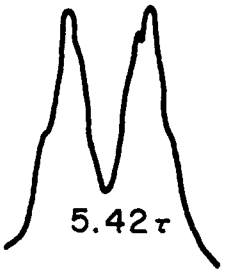

Figure 2.—Deuterio-*exo*-norbornenyl acetate (II-D), Table II, first experiment).

Figure 3.—*exo*-Norbornenyl acetate-*cis*-3-d_1 (II-D-S), J = 7 cps

with the data obtained in the case of perchloric acid catalysis (Table IV) indicated a consistent trend: an increase in the amount of unrearranged II-D acetate paralleled by an increase in the relative amounts of deuteration at the vicinal C_3 position.[12] The data presented in Table V were not complete enough to warrant conclusions about the effect of added ethyl acetate since, although the ethyl acetate affected the product ration, it did not significantly change the deuterium distribution.

In order to investigate more completely the effect of temperature upon the product ratio (see Table II), the addition of acetic acid-d_1 was carried out at 100° (Table VI). Despite the poor reproducibility of yields, a definite trend is noted: an increase in the proportion of (deuterated) nortricyclyl acetate was accompanied by an increase in the degree of deuterium scrambling in the norbornene ring skeleton (compare the results of Table VI with the results of Table V). It also should be noted that there was a significant degree of scrambling of deuterium into the acetoxy methyl group [compared with such a reaction at room temperature (Table V) in which negligible acetoxy methyl group scrambling took place]. There was a slightly greater proportion of ester with nortricyclyl ring skeleton in the experiment using deuterated addend than in the experiment using protic addend (compare Table VI to Table II).

The Effect of Solvent upon the Acid-Catalyzed Reactions.—The effect of the change of reaction mixture composition upon the addition reaction catalyzed by perchloric acid is shown by the data of Table VII. It should be noted that there is a significant over-all rate decrease with an increase in the fraction of hydrocarbon reagent, but little effect on the product ratio.

The aforementioned temperature coefficient of the product ratio (Table II) led to the decision to confine further investigation to temperatures in the vicinity of room temperature. Experiments (Table VIII) were carried out in which a weight of ethyl acetate was added to approximate the weight of ester produced upon conversion of half the norbornadiene used to esters II and III. The reactions employing ethyl acetate (Table VIII) gave much more olefinic acetate than did reactions of comparable ester yields in which no ethyl acetate had been added (Tables I and II).

Further investigation of the effect of solvent upon the rate and product ratio of the acid-catalyzed addition resulted in the data of Table IX. It was clear that the product ratio of the reaction was very much affected by supplementing the acetic acid and norbornadiene with small amounts (5–15%) of other solvents. Rate variations were significant and depended upon the added solvent. There was, however, no simple relation of either rate or product ratio with solvent polarity.

Attempts to equilibrate (or at least achieve a steady-state composition of) a mixture of olefinic II and nortricyclyl III esters in a mineral acid–acetic acid (or mineral acid–inert solvent) mixture were unsuccessful. The problem in acetic acid is associated with the known[4,13] ability of these esters to add a second mole of acetic acid. We have been successful in equilibrating such an ester mixture with boron trifluoride etherate in pentane (Table X). It was found that such an equilibration was unsuccessful in ether.

Experimental Section

The reagents and equipment used in these procedures have been described.[2] The retention times of esters II and III have also been reported.[2]

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[12] Further work is being carried out at this laboratory to determine solvent effects evident in rate, product ratio, and deuterium distribution studies) of the sulfuric acid catalyzed addition.

[13] H. Krieger, *Suomen Kemistilehti*, **B35**, 127 (1962).

TABLE V

RESULT OF THE SULFURIC ACID-d_2 CATALYZED ADDITION OF ACETIC ACID-O-d_1 TO NORBORNADIENE

Expt	Temp, °C	Mole ratio of carboxylic acid/olefin	[D_2SO_4], M	Ester yield, %	II-D/III-D	% d on C_3[a]
1	23 ± 1	15.9/1.0	0.16	20	33/67	67
2	23 ± 1	15.9/1.0	0.18	39	33/67	65
3[b]	23 ± 1	15.3/1.0	0.18	45	41/59	67

[a] The olefinic acetate II-D contained a negligible amount of polydeuterated species. [b] Reaction mixture contained added ethyl acetate.

TABLE VI

THE ACID-CATALYZED ADDITION OF ACETIC ACID-d_1 TO NORBORNADIENE AT 100°

Expt[a]	Mole ratio of carboxylic acid/olefin	[D_2SO_4], M	Ester yield, %[b]	(II/III) (D)	% vicinal deuteration	% monodeuteration (ring skeleton)[c]
1	15.9/1.0	0.18	100	13/87	59.5	28.5
2	15.9/1.0	0.18	61	14/86	56.6	29.7
3	15.9/1.0	0.18	65	13.5/86.5	56.5	29.5

[a] All reactions were carried out for *ca.* 15 min. [b] Differences in yield of duplicate experiments are probably attributable to inconsistencies in times of reaction (due to different lengths of cooling periods) and a deviation of *ca.* ± 2° in oil-bath temperature (see Experimental Section). [c] The remaining species were largely composed of polydeuterated esters.

TABLE VII

THE EFFECT OF CONCENTRATION OF REAGENTS ON THE PERCHLORIC ACID CATALYZED ADDITION OF ACETIC ACID TO NORBORNADIENE (I)

Expt	Mole ratio of carboxylic acid/olefin	[$HClO_4$], M	Ester yield, %	II/III
1[a]	42.5/1.0	0.02	35.5	13/87
2[a]	7.1/1.0	0.02	26.6	12.5/87.5
3[a]	2.9/1.0	0.02	3.7	12/88
4[a]	1.2/1.0	0.02	0.6	12/88

[a] Reaction was run at 28° for 45 min.

The proton magnetic resonance spectrum of *exo*-dehydronorbornyl acetate (II) is a multiplet centered at τ 3.95 (two protons), a doublet of doublets centered at 5.45 (one proton), a doublet centered at 7.23 (two protons), a singlet at 8.07 (three protons), and multiplets centered at 8.45 and 8.60 (total of four protons). This spectrum was determined on a Varian A-60 spectrometer, field strength of 60 Mc with tetramethylsilane (τ 10.00) used as an internal standard.

Sulfuric Acid Catalyzed Addition of Acetic Acid to Norbornadiene (I) (Table I).—Four 25-ml. volumetric flasks were prepared with 1.25 ml (1.13 g, 1.23 mmoles) of norbornadiene (I). These flasks were filled to volume with 0.018 M sulfuric acid in acetic acid. The reactions were allowed to proceed for the indicated times (Table I) at 23 ± 1°. Reaction progress stopped by pouring the solutions into 100 ml of water. These water solutions were extracted three times with 100-ml volumes of pentane. The pentane extracts were washed with 20 ml of 10% aqueous sodium carbonate and 20 ml of water. After drying over anhydrous magnesium sulfate, the solutions were filtered and evaporated to an approximately 3 ml of residue (water bath at *ca.* 50°). Quantitative transfer of the residues to 5-ml volumetric flasks was carried out and analysis was done by gas chromatography (column, silicon oil 710, 7 m × 0.25 in., 140°, helium flow of 100 cc/min). Yields are calculated by comparison of peak areas for the above samples with peak areas for samples of ester solutions of known concentration. Analyses were made upon 50-μl samples of the above solutions.

Experimental Related to Table II.—Three 10-ml flasks were injected with 1.00 ml (0.91 g., 9.8 mmoles) of norbornadiene (I) and were filled to the mark with solutions of the following concentrations of sulfuric acid in acetic acid (experiment and concentration): 1, 0.018 M; 2, 0.018 M; and 3, 0.036 M. Experiments 1 and 3 were carried out at 23 ± 1° for 16 and 8 hr, respectively. Experiment 2 was run at 43 ± 2° for 4 hr. The reaction mixtures were worked up and analyzed as in the preceding Experimental Section.

A glass tube (expt 4) was prepared containing 0.50 ml (0.46 g, 0.49 mmole) of norbornadiene (I) and 8 ml of 0.018 M sulfuric acid in acetic acid. The contents were frozen (Dry Ice) and flushed with nitrogen; the tube was sealed. The tube was warmed gradually (over *ca.* 0.5 hr) to room temperature and then placed in an oil bath at 130 ± 2° for 2 hr. After removal of the tube from the oil bath, it was cooled at room temperature for 5 min and then the contents were frozen (Dry Ice). The tube was opened and work-up and analysis were done as described in the preceding Experimental Section.

Four 10-ml volumetric flasks were prepared containing 0.5 ml. (0.46 g, 4.9 mmoles) of norbornadiene. The flasks were filled to the mark with the following sulfuric acid–acetic acid solutions (experiment and sulfuric acid concentration): 5, 0.009 M; 6, 0.018 M; 7, 0.045 M; and 8, 0.090 M. Reaction time was 20.5 hr at 23° for expt 5–8. The reaction products were worked up and analyzed as described in the preceding Experimental Section.

Rate of Disappearance of *exo*-Dehydronorbornyl Acetate (II) and Nortricyclyl Acetate (III) in 0.018 M Sulfuric Acid in Acetic Acid at 23°.—A standard (pentene solvent) solution (2-ml volumetric flask) was prepared containing 43 mg (0.28 mmole) of II, 44 mg (0.29 mmole) of III, and 30 mg (0.10 mmole) of bromobenzene. The molar responses were determined for 50-μl samples (gas chromatography)[2] of the solution (Table XI). This gave the ratio of the response of II and III relative to an equimolar amount of bromobenzene (1.17 and 1.12, respectively).

Two 10-ml volumetric flasks were prepared as shown in Table XII. These flasks were filled with 0.018 M sulfuric acid in acetic acid. The reactions were carried out at 23 ± 1° and 0.25-ml aliquots were removed at the end of times ranging from 50 to 1000 hr. These aliquots were injected into 5-ml vials containing a two-phase system of 0.50 ml of cyclohexane and *ca.* 2.5 ml of 10% aqueous sodium carbonate. The vials were gently shaken, and allowed to stand (to allow the layers to separate). Analysis of the organic layer (gas chromatography)[2] gave a measure of the amount of disappearance of the ester in each sample. This method indicated that 95 ± 5% of the esters remained for at least 100 hr under the above conditions.

An approximate rate constant was determined for the appearance of esters II and III by preparing a series of 10-ml volumetric flasks containing 0.1 ml (0.08 g, 0.98 mole) of norbornadiene (I) and filling them to the mark with 0.018 M sulfuric acid in acetic acid. The reactions were run at 24.0 ± 0.1° for a series of times (0–48 hr). The resulting times and percent reaction (by ester appearance) were 5.33 hr, 1.5% reaction; 18.5 hr, 11.8% reaction; and 30.5 hr, 21% reaction. The pseudo-first-order rate constant was $3.0 \pm 0.1 \times 10^{-6}$ sec^{-1} which indicated a half-life of *ca.* 60 hr for the addition reaction under these conditions.

Salt Effects in Acetic Acid Additions to Norbornadiene (I) (Table III) Expt 1a–d.—All salts used were dried for at least 24 hr at 120°. To clean and dry 100-ml volumetric flasks were added the substances listed in Table XIII. The flasks were filled with *ca.* 80 ml of acetic acid. To the flasks were added 4.0-ml (3.62 g, 39 mmoles) portions of norbornadiene. Each flask was then filled to the mark with acetic acid, stoppered, and placed in an oil bath at 48 ± 2°.

TABLE VIII

THE ETHYL ACETATE SOLVENT EFFECT UPON THE SULFURIC ACID CATALYZED ADDITION OF ACETIC ACID TO NORBORNADIENE (I)

Expt	Time, hr	Temp,[a] °C	Ester yield, %	II/III	Mole ratio of carboxylic acid/olefin	[H_2SO_4], *M*	Vol (ml) of added ethyl acetate[b]
1	7	23	3.8	29/71	34/1.0	0.017	0.00
2	7	23	4.6	35/65	59/1.0	0.017	0.41
3	7	23	3.5	40/60	59/1.0	0.016	1.00
4	20.75	23	14	46/54	59/1.0	0.016	0.41
5	24.1	23	18	44/56	59/1.0	0.016	0.41
6	47	23	40	47/53	59/1.0	0.016	0.41

[a] ±1°. [b] The total volume for all experiments was 10 ml.

TABLE IX

THE EFFECT OF VARIOUS SOLVENTS UPON THE SULFURIC ACID CATALYZED ADDITION OF ACETIC ACID TO NORBORNADIENE (I)[a]

Solvent (mole %)	II/III[b]	Ester yield,[c] %	Dielectric constant[d]
Dioxane (6.4)	47/53	3.3	2.2
Cyclohexane (5.8)	34/66	3.2	2.1
Acetone (8.5)	34/66	4.5	21.2
Chlorobenzene (6.3)	28/72	3.0	5.7
1-Butanol (6.8)	25/75	1.4	17.8
Acetic acid (100)	24/76	4.6	6.2
Ethanol (10.8)	20/80	0.4	25.1
Methanol (14)	24/76	0.2	33.6
Nitrobenzene (6.3)	24/76	3.9	35.7
Acetonitrile (10)	20/80	4.3	37.5
Nitromethane (10)	17/83	5.5	37.5
Water (28.6)	19/81	0.1	80.4

[a] The carboxylic acid/olefin mole ratio was 14/1.0 and the sulfuric acid concentration was 0.014 *M*. All reaction mixtures contained 10 vol % added solvent. [b] Contains small (1–3%) amount of *endo*-dehydronorbornyl acetate. [c] The reactions were carried out for 21.7 hr at 23°. [d] This value is for a pure sample of the added solvent. The reference for all values except dioxane is J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 39. Dioxane: "Handbook of Chemistry and Physics," 40th ed, Chemical Rubber Publishing Co., Cleveland, 1958–1959, p 2515.

TABLE X

EQUILIBRATION OF *exo*-DEHYDRONORBORNYL (II) AND NORTRICYCLYL (III) ACETATES WITH BORON TRIFLUORIDE ETHERATE[a]

	Expt		
	1[b]	2[b]	3[c,d]
Time, hr	II/III	II/III	II/III
0	54/66	54/46	54/46
32.0	...	7/93	53/47
52.5	6/94	4/96	54/46
68.5	4/96	3/97	53/47
98.0	...	4/96	...

[a] The reactions were carried out at 23°. The ratio (volume) of esters/boron trifluoride etherate was 1/1 with a 50-fold (volume) excess of solvent. [b] Pentane solvent. [c] Ether solvent. [d] Comparable experiments, using a nortricyclyl acetate sample of >99% purity, in ethyl acetate and ether solvents, showed no isomer ratio change (III/II >99/1) after 76 hr at 23°.

TABLE XI

Compd	Area, cm²	m*M* response, cm²/mmole
I	33.7	476
II	33.2	458
Bromobenzene	19.5	402

TABLE XII

Sample	Ester, mg	Bromobenzene, mg
1	II, 261	150
2	III, 273	148

TABLE XIII

Expt	Amount, g	Added salt
1a	...	...
b	1.225	Sodium perchlorate
c	0.820	Sodium acetate
d	1.225 and 0.820, resp	Sodium perchlorate and sodium acetate, resp

Samples (25.0 ml) were withdrawn after 92 hr and quenched by injection into water. Each water solution was extracted with a 50-ml portion of pentane. These pentane solutions were each washed consecutively with 15-ml portions of 10% aqueous sodium bicarbonate and water. Drying of the pentane solutions was carried out for at least 24 hr over sodium sulfate at reduced temperatures (*ca.* −10°). The pentane solutions were filtered and washed into 100-ml flasks and evaporated (water bath, *ca.* 45°) to approximately 3-ml residues. These residues were than transferred quantitatively to 5.00-ml. volumetric flasks. The flasks were filled to the mark with pentane and samples were analyzed by gas chromatography. Yields were determined by comparison of peak areas to the areas of samples from standard ester solutions. Solutions of esters II and III were prepared in a method completely analogous to expt 1b and c. Analyses of these solutions, after treatment as described above for 92 hr, showed no appreciable change in concentration. The gas chromatographic column conditions that were used have been described.[2]

Expt 2a–c.—Volumetric flasks (100 ml) were prepared (in the manner of expt 1a–d) as shown in Table XIV. The flasks were stoppered and placed in an oil bath at 62 ± 2°. Aliquots were removed, worked up, and analyzed as in the preceding section with the following modifications: (a) two 50-ml pentane portions were used for extractions, and (b) 20-ml portions of 10% aqueous sodium bicarbonate solutions and water were used for the washings.

TABLE XIV

Expt	Amount of added substance
2a	1.225 g of sodium perchlorate
b	0.561 ml (1.03 g, 0.01 mole) of concd sulfuric acid
c	0.056 ml (0.10 g, 0.001 mole) of sulfuric acid

Expt 3a–f.—Six 50-ml volumetric flasks were prepared as in expt 1a–d. In each of the flasks were placed 2.0 ml (1.81 g, 19.5 mmoles) of norbornadiene and the substances of Table XV. The flasks were filled to mark with acetic acid, stoppered, and heated for 75 min in an oil bath at 62 ± 2°. The resulting reaction mixtures were worked up and analyzed as described in 1a–d. The only modification of the work-up was that three 50-ml pentane extractions were performed per sample.

Expt 4a–c.—Three volumetric flasks (prepared as described above)containing 1.0 ml (0.91 g, 9.8 mmoles) of norbornadiene (I) and the substances of Table XVI. The flasks were filled to the

TABLE XV

Expt	Amount, of added substances
3a	0.6 mg of sodium perchlorate
b	6.13 mg of sodium perchlorate
c,d	61.3 mg of sodium perchlorate
e	41.0 mg of sodium acetate
f	0.0285 ml of concd sulfuric acid

TABLE XVI

Expt	Amount of added substance
5a	30.7 mg of sodium perchlorate
b	0.25 ml of 1.0 M sulfuric acid in acetic acid
c	0.025 ml of 1.0 M sulfuric acid in acetic acid
d	2.5 ml of 0.1 M perchloric acid in acetic acid
e	0.25 ml of 0.1 M perchloric acid in acetic acid
f	30.7 mg of sodium perchlorate and 0.025 ml of 1.0 M sulfuric acid in acetic acid
g	30.7 mg of sodium perchlorate and 0.25 ml of 0.1 M perchloric acid in acetic acid

mark with acetic acid, stoppered, and placed in an oil bath at 50 ± 2° for 35 min. The reaction mixtures were worked up and analyzed exactly as in the procedure for expt 3a–f.

Preparation of Deuterium Perchlorate.—A solution of 5.00 ml of 70% (by weight) with water) perchloric acid and 5.00 ml of 55% deuterium oxide solution (45% water) was prepared. The solution was evaporated to its original volume (*ca.* 5.00 ml) under vacuum in a boiling-water bath. This was repeated three times and performed a final time with 99.5% deuterium oxide.[2] This procedure was calculated to result in *ca.* 80% deuteration.

Titration of the final sample with a sodium hydroxide solution to a phenolphthalein end point indicated the acid concentration was 7.17 M. The original perchloric acid was 11.6 M.

Addition of Acetic Acid-O-d_1 and Acetic Acid to Norbornadiene (I) as Catalyzed by Deuterium Perchlorate (Table IV).—A 10-ml (9.1 g, 9.8 mmoles) sample of norbornadiene (I) was placed in a 50-ml flask. To this flask was added 25.0 ml of acetic acid-O-d_1 and 0.098 ml of deuterium perchlorate solution (preparation described above). The flask was placed in a reflux apparatus and the solution was heated for 39 min at 50 ± 2°. The reaction mixture was worked up and analyzed just as described in the experimental results for Table I. Deuterated olefinic acetate (II-D) samples were collected from the gas chromatograph and subjected to mass spectral analysis. A completely analogous reaction was carried out with the only modification being the use of acetic acid as the addend.

Preparation of *exo*-3-Deuterio-*exo*-dehydro-2-norbornyl Acetate (II-D-S).—An apparatus was constructed consisting of a 2-neck, 500-ml, round-bottom flask supplied with a reflux condenser (water cooled) and a pressure line equipped dropping funnel. Prepurified nitrogen gas was admitted through a drying tube fitted to the top of the condenser. A solution of 31.0 g (0.336 mole) of norbornadiene (I) in 100 ml of anhydrous reagent grade ether was stirred (in the above flask) with a magnetic stirring bar. The system was thoroughly flushed with nitrogen and 1.0 g (0.0226 mole) of lithium aluminum deuteride was immediately added. The system was flushed again with nitrogen and 3.2 ml (3.55 g, 0.025 mole) of boron trifluoride etherate (freshly distilled) was slowly added (dropwise) over a period of 35 min. This mixture was stirred for 17 hr at room temperature. At the end of this time 2.0 ml of water were slowly added to decompose the remaining hydrides.

The mixture was evaporated under reduced pressure (*ca.* 15 mm) to a relatively involatile residue of *ca.* 10 ml. The residue was diluted, under a nitrogen atmosphere, with 100 ml of ether. A solution of 1.1 g (0.0275 mole) of sodium hydroxide in 8.0 ml of water was added. To this stirred solution was slowly added, over a 45-min period, 10.5 ml of 30% hydrogen peroxide. This mixture was stirred for 2 hr at room temperature.

The ether solution was separated from the milky aqueous layer and this aqueous layer was extracted with 60 ml of ether. The combined ether extracts were dried over anhydrous sodium sulfate at 0°. Gas chromatographic analysis indicated a yield of 4.3 g. (57%) of alcohol. This result was obtained by comparison of peak areas of the sample with areas for samples of known alcohol concentration.

This alcohol–ether solution was distilled (water bath, 50°) to a thin syrup residue. Recrystallization of the alcohol from pentane was unsuccessful and the pentane solution was distilled to a thin, syrupy residue. This residue was treated with 7.0 ml of reagent grade acetic anhydride (which contained *ca.* 50 mg of sodium acetate) for 18 hr at room temperature. Heating of this mixture was carried out on a steam bath for 2 hr. To the solution was added 20 ml of water and this mixture was stirred for 2 hr at room temperature. Extraction of the mixture was done twice with 30-ml portions of pentane. These extracts were combined, washed with 5 ml of aqueous sodium carbonate and 10 ml of water, and dried over anhydrous magnesium sulfate.

Gas chromatographic analysis of the pentane solution showed greater than 95% conversion of alcohols to acetates. The acetate mixture was primarily *exo* acetate II-D-S with contamination to *ca.* 30% by deuterio-*endo* acetate (gas chromatography). The pentane solution was evaporated to a residue and gas chromatographic collections of pure *exo*-deuterio-*exo*-dehydro-2-norbornyl acetate (II-D-S) were carried out at column conditions that have been described.[2] The pmr spectrum (Figure 3) and mass spectrum[8] of this sample have been given.

Experimental Results of Table V.—All glassware for these reactions was oven dried and cooled in a desiccator. Norbornadiene (I, 2.50 ml, 2.38 g, 24.5 mmoles) was added to a 25-ml. volumetric flask (expt 1); the flask was filled within *ca.* 1 ml of the mark with acetic acid-O-d_1.[1] To this solution was added 0.25 ml of sulfuric acid-d_2 (Merck, of Canada). The flask was filled to the mark with acetic acid-O-d_1, stoppered, and shaken. This flask was kept at 23 ± 1° for 91.5 hr. Work-up and analysis were by the methods described in the experimental results for Table I. Samples of the olefinic acetate II-D were collected by preparative gas chromatography (Aerograph-Autoprep-A-700, column, Carbowax 20M (25%) on Chromosorb W regular 60/80 mesh, 5 m × 3/8 in. o.d., temperature = 150°, flow rate of 200 cc/min) and subjected to mass spectral analysis.

Two volumetric flasks (expt 2, 10 ml; expt 3, 25 ml) were prepared containing 1.0 ml (0.91 g, 9.8 mmoles) of norbornadiene and to the 25-ml flask was added 0.41 ml of reagent grade ethyl acetate. Each flask was partially filled by addition of 8.6 ml (to the 25-ml flask) and 9.0 ml (to the 10-ml flask) of acetic acid-O-d_1 (Merck of Canada, 99% deuterated). To each flask was added 0.10 ml of sulfuric acid-d_2 (Merck of Canada). The flasks were shaken and allowed to stand for 114.5 hr at 23 ± 1°. Work-up and analysis were carried out as in the experimental results of Table IV. Samples were collected for mass spectral analysis as described in the preceding paragraph.

Catalyzed Addition of Acetic Acid-d_1 to Norbornadiene at 100° (Table VI).—Three 25 × 200 mm Pyrex glass test tubes were prepared containing 1.00 ml (0.91 g, 19.5 mmoles) of norbornadiene, 9.0 ml of acetic acid-d_1 (Merck of Canada), and 0.1 ml of sulfuric acid-d_2 (Merck of Canada). Experiments 2 and 3 were run simultaneously, attempting to duplicate the conditions of expt 1. After the reagents were mixed, freezing of the tubes' contents (Dry Ice) was carried out immediately and the tubes were sealed. The tubes were placed over the oil bath (100°) and allowed to warm for *ca.* 3–4 min and then they were immersed in oil. Fluctuation of oil-bath temperature was *ca.* ±2°. After 15 min in the oil bath, the tubes were removed and allowed to stand for *ca.* 5 min. After the tubes' contents were refrozen, the tubes were opened and the reaction mixtures were worked up and analyzed as described in the experimental results for Table I. Samples of deuterated *exo*-dehydronorbornyl acetate were collected from the gas chromatograph (conditions in experimental results for Table I) and subjected to mass spectral analysis.

Effect of Excess Hydrocarbon on the Perchloric Acid Catalyzed Addition of Acetic Acid to Norbornadiene (I) (Table VII, Expt 1–4).—To thoroughly cleaned and dried 25-ml volumetric flasks were added the following volumes of norbornadiene (experiment and milliliters of norbornadiene): 1, 1.0; 2, 5.0; 3, 10.0; and 4, 15.0. To each of these was added to a 5.0-ml portion of 0.1 M perchloric acid in acetic acid. Each flask was filled to the mark with acetic acid, stoppered, and shaken. The reactions were allowed to proceed at room temperature (28 ± 2°) for 45 min. The reactions were quenched by pouring the mixtures into cold water. Each solution was treated with *ca.* 250 mg of powdered potassium carbonate. Extraction of the aqueous solutions was carried out three times with 100-ml volumes of pentane. The pentane extracts were combined, washed once with 20 ml of 10% aqueous sodium carbonate, and dried over anhydrous magnesium sulfate. After filtration, the pentane solutions were evaporated (water bath, 50°) to residue which were transferred quantitatively to 25-ml volumetric flasks. Gas chromatographic analyses were carried out as described in the experimental results for Table I.

A sample of olefinic acetate II was subjected to the above reaction and analytical conditions and was recovered in 92% yield.

Experimental Results of Table VIII.—Into three 10-ml volumetric flasks were introduced the volumes of norbornadiene (I) and ethyl acetate (distilled, reagent grade) as shown in Table XVII. The flasks were then filled to the mark with 0.018 *M* sulfuric acid in acetic acid. All of the reactions were carried out for 7 hr at 23 ± 1°. The work-up and analysis were those used in the experimental results for Table I.

TABLE XVII

Expt	Norbornadiene, ml	Ethyl acetate, ml
1	0.50	0.00
2	0.25	0.41
3	0.25	1.00

Three 10-ml volumetric flasks (expt 4–6) were each injected with 0.25 ml (0.23 g, 2.4 mmoles) of norbornadiene and 0.41 ml of ethyl acetate. The flasks were filled to the mark with 0.018 *M* sulfuric acid in acetic acid. Times of the reaction (at 23 ± 1°) were as follows (experiment and time): 4, 20.75 hr; 5, 24.1 hr; and 6, 47 hr. The work-up and analysis were by the method described in the Experimental Section for Table IV.

Experimental Results of Table IX.—Seven (expt 1–5, 7, 12) clean, dry 10-ml volumetric flasks were prepared containing 1.00 ml (0.91 g, 9.8 mmoles) of norbornadiene (I) and 1.00 ml of the solvent listed in Table XVIII.

Five, clean, dry (expt 6, 8–11) 25-ml volumetric flasks were prepared with 2.50 ml (2.38 g, 2.45 mmoles) of norbornadiene (I) and 2.50 ml of the solvent listed in Table XVIII. The flasks were filled to the mark with 0.018 *M* sulfuric acid in acetic acid and allowed to stand at 23 ± 1° for 21.7 hr. The work-up procedure was the same as the one used in the experimental results for Table I.

TABLE XVIII

Expt	Solvent	Solvent purification procedure
1	Dioxane	Passed through alumina column
2	Cyclohexane	Distilled
3	Acetone	Reagent grade
4	Chlorobenzene	Reagent grade
5	1-Butanol	Distilled from calcium chloride
6	Acetic acid	Reagent grade[a]
7	Ethanol	Reagent grade
8	Methanol	Reagent grade
9	Nitrobenzene	Distilled from calcium chloride
10	Acetonitrile	Distilled from calcium chloride
11	Nitromethane	Reagent grade
12	Water	Distilled

[a] See ref 2.

TABLE XIX

Expt	Vol flask size, ml	Vol of ester sample, μl	Vol of $BF_3O(C_2H_5)_2$, μl	Solvent
1	10.00	100	100	Pentane
2	10.00	100	100	Pentane
3	5.00	50	50	Ether

Equilibration of *exo*-Dehydronorbornyl (II) and Nortricyclyl (III) Acetates with Boron Trifluoride Etherate (Table X).—A sample (>99.5% ester by gas chromatography) composed of 54% II and 46% III was used for this experiment. The flasks employed were prepared containing the noted amounts of ester sample. Each flask was partially filled with the indicated solvents (Table XIX) and the appropriate amount (1/1 vol ratio to ester) of boron trifluoride etherate was added. Each flask was filled to the mark with the correct solvent, and the flasks were shaken for *ca.* 5 sec and allowed to stand in a room thermostated at 23 ± 1° for the indicated (Table X) lengths of time. The solutions of expt 1 and 2 developed a small, heavier, brownish second phase. No such second phase developed in the case of ether solvent. At the end of the times described (Table X), 0.5-ml aliquots were removed (syringe) and injected into water. These organic solvent–water mixtures were shaken, allowed to separate, and 50-μl samples of the organic phase were analyzed by gas chromatography (conditions have been described).[2]

Experiments were carried out as described for expt 1, the differences being that a sample of >99% nortricyclyl acetate (III) was employed and ethyl acetate and ether were each substituted for pentane. Work-up and analysis were as described above. Both experiments gave the same results: no product ratio change (III/II, >99/1) after 76 hr at 23°.

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