874145, in 1973. The author wishes to thank Professor Terukiyo Hanafusa for his helpful advice and encouragement. The author is also indepted to Messrs. Hiroyuki Kato and Kazushi Hanaoka for their experimental assistance.

Registry No.—**4s**-OH, 58692-29-8; **4s**-OPNB, 58692-30-1; **4a**-OH, 58717-76-3; **4a**-OPNB, 58717-77-4; **4a**-OAc, 58692-31-2; **5**-OH, 58692-32-3; **5**-OBs, 58692-33-4; **6**-OH, 58692-34-5; **7**, 10386-81-9; **8**, 58692-35-6; **9**, 58692-36-7; **10**, 58692-37-8; **11**, 58692-38-9; **12**, 58692-39-0; **13**, 58692-40-3; **14**, 58692-41-4; **15**, 58692-42-5; **17**, 58692-43-6; **18**, 58692-44-7; **19**, 58692-45-8; **20**, 58692-46-9; **21**, 58692-47-0.

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Mechanism and Stereochemistry in Addition of Acetic Acid to Quadricyclane

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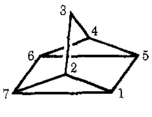
Addition reactions of carboxylic acids (**5a–d**) to tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (**1**, quadricyclane) at 20 °C gave corresponding esters (**6** and **7**) of *exo*-2-norbornenyl alcohol and nortricyclyl alcohol. Solvent effect on the product distribution and the rate of the addition reaction excluded the mechanism involving norbornenyl cation (**4**) as a sole intermediate. A six-centered addition mechanism is presented by the authors to account for both the solvent effects and deuterium distribution in labeled **6** obtained from addition of acetic acid-*O*-d_1 or dichloroacetic acid-*O*-d_1.

Tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (**1**, quadricyclane) allowed several physical organic approaches to a possible conjugation between two cyclopropane rings arranged nearly parallel and in close proximity. Regiospecificity and stereospecificity shown in [$2\sigma + 2\sigma + 2\pi$] cycloaddition reaction[1] of **1** strongly suggest concerted fissions of C_1–C_7 and C_5–C_6 cyclopropane bonds and, therefore, an existence of a kind of "conjugation" in **1**.[2] The conjugation contributed to at least one-fourth (ca. 3.5 kcal/mol) of the stabilization of 1-quadricyclylcarbinyl cation **2**,[2] which exhibited 1.2×10^8 times rate enhancement (14.0 kcal stabilization) compared with cyclopropylcarbinyl cation.

Protonation of quadricyclane with a cleavage of the C_1–C_7 or C_5–C_6 bond could be assumed to give an incipient nortricyclyl cation **3** which is known to be prone to rearrange to norbornenyl cation **4**[3] from solvolysis studies.



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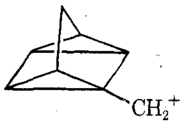

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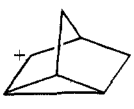

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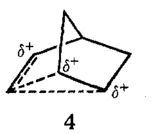


4

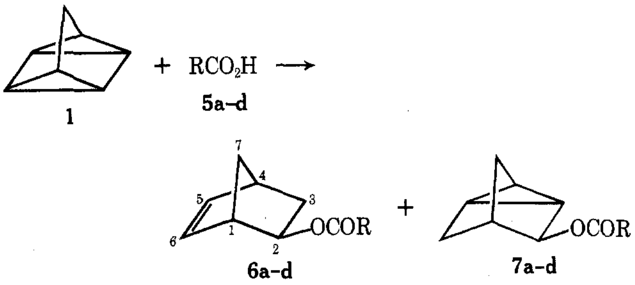
Table I. Product Ratio (6/7) in Addition of 5a–d to Quadricyclane

Solvent	Catalyst	Temp, °C	ϵ	**6a/7a**	**6b/7b**	**6c/7c**	**6d/7d**
Formic acid		20	58.5				16/84
Acetic acid		20	6.17	55/45			
Acetic acid	$HClO_4$	20	6.17	15/85			
Cyclohexane		20	2.02	55/45			
Cyclohexane		60	1.96	50/50			
Chloroform		20	4.8		68/32	70/30	59/41
Acetonitrile		20	37.5	65/35	71/29	71/29	55/45

Dauben and Cargill reported formations of equal amounts of *exo*-2-norbornenyl and nortricyclyl acetate in acetic acid addition to 1.[4] More recently, from stereochemical study using labeled HCl, Morrill and Greenwald reported that mechanisms of HCl additions to 1 and to norbornadiene are very similar and that neither addition can involve 4 as the sole intermediate to products.[5] As part of a program to investigate the assumed "conjugation" in 1, additions of several carboxylic acids to 1 were carried out by the authors and results of mechanistic and stereochemical studies have been reported in this article.

Results and Discussion

In general, quadricyclane has considerably greater reactivity than cyclopropanes or nortricyclanes toward many reactants,[1,4–6] including electrophiles. In marked contrast to addition reaction of acetic acids to cyclopropanes or nortricyclanes, any strong acid catalyst was not necessary for additions of acetic acids (**5a–c**) and formic acid (**5d**) to **1**. The reaction was practically over in 40 h at 60 °C in 0.7 M solution of 1 in acetic acid. Two products, purified through preparative gas-liquid chromatography (GLC), were identified as *exo*-2-norbornenyl (**6a**) and nortricyclyl acetate (**7a**). Corresponding esters (**6b–d, 7b–d**) of *exo*-2-norbornenyl alcohol and of nortricyclyl alcohol were obtained in additions of chloro- and dichloroacetic acids and formic acid to 1.

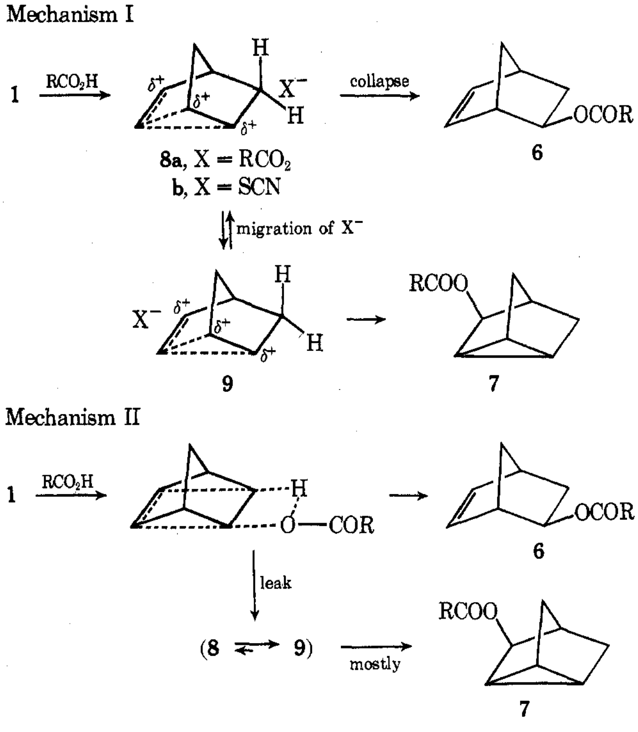


R = a, CH_3; b, CH_2Cl; c, $CHCl_2$; d, H

Table I summarizes the influences of solvents and catalyst on product distributions. These results were ascertained by comparison of the GLC retention time displayed by the component of the reaction mixture with those of relevantly prepared authentic compounds on two columns of different liquid phase. Authentic **6a** and **7a** were prepared by the reported addition of acetic acid to norbornadiene[7] and the products **6b–d** and **7b–d** were compared with **6a** and **7a**, respectively, on the spectroscopic grounds (NMR, ir, and mass spectra), which left no ambiguity in structural assignment of the products. Authentic *endo*-2-norbornenyl acetate was prepared by Diels–Alder reaction of vinyl acetate with cyclopentadiene[8] and little or no formation of the endo isomer in the present reactions was ascertained by GLC analyses.

The product ratios exhibited no appreciable change with increase in conversion, which supported that the present addition reaction was not contaminated with a competing or successive process such as isomerization of 1, 6, or 7. The product ratio in a single run was measured at varied conversion, and values listed in Table I are the averages of three or four runs.

Scheme I



Utilization of perchloric acid as a catalyst resulted in a substantial change in the ratio **6a/7a** to 15/85. This fact strongly supports the idea that the protonated quadricyclane was identical with norbornenyl cation, **4**, the accepted intermediate of solvolysis.[3] The reported ratio **6a/7a** for acetolysis of norbornenyl or nortricyclyl *p*-bromobenzenesulfonate was 17/83.[3a] Therefore, the quite different product distribution observed in uncatalyzed additions (**6** predominating, Table I) indicated that the rate-determining step could not be the protonation of the quadricyclane.

The most plausible mechanisms, I and II, are shown in Scheme I. In mechanism I, norbornenyl cation was assumed as the intermediate, the formation of which should be considered at least in the case of $HClO_4$ catalysis (loc. cit.). Ion pair **8a** seems to be distinguished from ion pair **9a** as was shown for analogous ion pairs **8b** and **9b**, which were distinguished in the case of thiocyanate.[9]

In mechanism II, a six-centered transition state with far less charge separation was assumed as the major path leading to the predominant formation of **6**. The minor formation of nortricyclyl products **7** is explained as the result of leak from the six-centered addition path to the norbornenyl cation.[7]

The authors were led to a conclusion that for the present specific system, mechanism II is much more likely to operate than mechanism I on the basis of the following observations: (1) quite small solvent effect on the addition rate (vide infra), (2) increased portion of **6** in products with the increased solvent polarity, (3) increase in **6** with the decreased nucleophilicity of the acyloxyl anion (Table I). If the rate of the migration happened to be comparable to the collapse rate in acetic acid addition to **1** in cyclohexane (the rate ratio of collapse/migration equals the product ratio **6a**/**7a** = 55/45), the collapse/migration ratio should decrease in a more polar solvent (acetonitrile) with a less nucleophilic counterion ($ClCH_2COO^-$ or Cl_2CHCOO^-). Observations 2 and 3 were apparently incompatible with the deductions. Therefore, the present results strongly suggest that the mechanism II predominates.

Formation of norbornenyl product in concerted addition (II) may be the result of electron removal from a quadricyclane molecule making the C_1–C_7 (C_5–C_6) bond easily broken. Experiments and calculations[10] based on this idea are now in progress.

Small solvent effects on the rate of the addition reaction also excluded to **1** was measured in cyclohexane or in acetonitrile by GLC analysis using cyclododecane as an internal standard. The second-order rate constants obtained are

$$\left.\begin{array}{l} k_2 = 6.28 \times 10^{-7}\ \mathrm{M^{-1}\ s^{-1}}\ \text{in cyclohexane} \\ \qquad\qquad (\epsilon\ 2) \\ k_2 = 3.35 \times 10^{-6}\ \mathrm{M^{-1}\ s^{-1}}\ \text{in acetonitrile} \\ \qquad\qquad (\epsilon\ 37.5) \end{array}\right\} 60.1 \pm 0.05\ ^\circ\mathrm{C}$$

$$\frac{k_2\ (\epsilon\ 37.5)}{k_2\ (\epsilon\ 2)} = 5.3$$

This is in marked contrast to the rate of acetic acid addition to norbornadiene (via **8**).

$$k_2 = 3.4 \times 10^{-9}\ \mathrm{M^{-1}\ s^{-1}}\ \text{in ether–acetic acid (61/39)}\quad (\epsilon\ 5)$$

$$k_2 = 7.2 \times 10^{-7}\ \mathrm{M^{-1}\ s^{-1}}\ \text{in acetic acid–water (83/17)}\quad (\epsilon\ 10)$$[11]

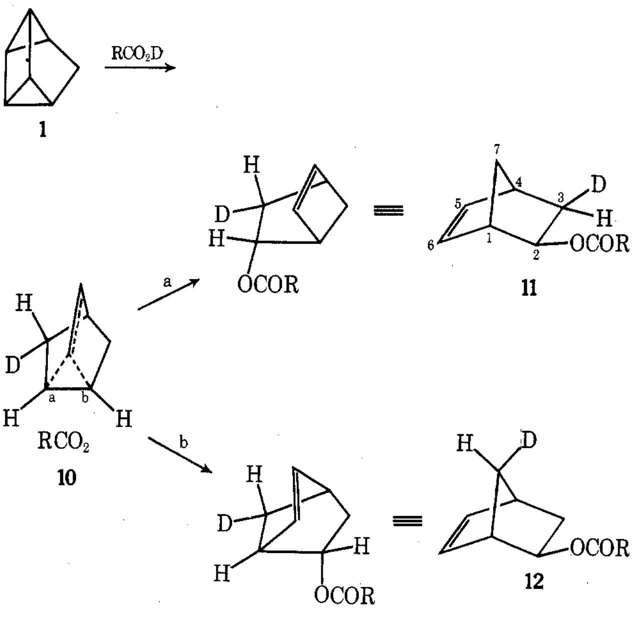
$$\frac{k_2\ (\epsilon\ 10)}{k_2\ (\epsilon\ 5)} = 212$$

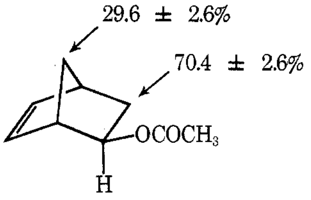
$$\frac{k_2\ (\epsilon\ 37.5)}{k_2\ (\epsilon\ 5)}\ \text{(extrapolated)} = 4 \times 10^6$$

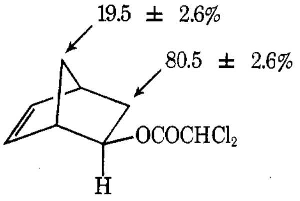
Addition of acetic acid-*O*-d_1 or dichloroacetic acid-*O*-d_1 to quadricyclane was also investigated in order to gain further insight. Employment of 65 mol % of tris(dipivaloylmethanato)europium [$Eu(DPM)_3$] to the CCl_4 solution of **6a** resulted in successful separation of H_{3x} and H_{7s} resonances (Figure 1) and the deuterium distribution in labeled *exo*-2-norbornenyl acetate was measured by repeated (at least seven times) integrations of the peak areas in 100-MHz spectra B and C (Figure 1). The same procedure was also successful in determining the deuterium distribution in labeled **6c**.

Nucleophilic attack to the symmetrically bridged norbornenyl cation by the acyloxyl anion can occur at two positions (a and b in Scheme II). Captures at a and b positions give *exo*-3-*d*-*exo*-2-norbornenyl acetate (**11**) and *syn*-7-*d*-*exo*-2-norbornenyl acetate (**12**), respectively. Therefore, indiscriminate deuterium distribution at exo-3 and syn-7 positions is reasonably expected from the (approximately) equal possibility of the cation captures at a and b positions, if norbornenyl cation (**4**) or ion pair (**10**) is the sole intermediate to norbornenyl products (**6**).

Scheme II







The results shown below, however, indicate that much more deuterium was incorporated at exo-3 than syn-7 position in labeled *exo*-2-norbornenyl acetate and labeled *exo*-2-norbornenyl dichloroacetate. Thus cis-exo addition accounts for more than 70% of the norbornenyl product from quadricyclane. Deuterium incorporation into exo-3 and syn-7 positions was also determined by mass spectroscopy as was described by Cristol et al.[7] A characteristic fragment peak, *m/e* 66, in the mass spectrum of norbornenyl acetate (**6a**) was attributed to cyclopentadienyl cation ($C_5H_6^+$) produced by a retro-Diels–Alder reaction.[11] Deuterium distribution was calculated by the relative peak intensity at *m/e* 66 and 67 in the mass spectrum, which was measured at the ionization potential of 5 eV. Thus incorporation of 62% deuterium at exo-3 and 38% at syn-7 positions in the labeled norbornenyl acetate (**6a**) was concluded.

Thus, mass spectroscopy gave the results of somewhat more scrambling than the NMR. These small but noticeable discrepancies between the results of the deuterium distributions in labeled **6a** and **6c** determined by NMR and mass spectroscopies must be taken into consideration. The NMR spectroscopy, which is free from any error brought by undesirable excess energy in the mass spectroscopy, seems to be more suitable and gives more reliable results than mass spectroscopy for the cases like the present system.

Therefore, it is concluded that norbornenyl cation cannot be the sole precursor to labeled **6** and that the primary process to give *exo*-2-norbornenyl acetates (**6a–c**) is the six-centered cis-exo addition of acetic acid to quadricyclane (mechanism II). The predominant cis-exo addition via a six-centered transition state requires the existence of an interaction between two cyclopropane rings in **1**, although the interaction had only a limited effect on the cyclic process which resulted in the limited ratio of **6**/**7** = 71/29.

Experimental Section

Preparation and common purification of quadricyclane were reported in our previous paper.[1] Commercially available acetic acid-*O*-d_1 was used to prepare labeled *exo*-2-norbornenyl acetate by applying a similar procedure described for addition of unlabeled acetic acid to **1** at 60 °C (vide infra). Dichloroacetic acid-*O*-d_1 was prepared from dichloroacetic anhydride and commercially available deuterium oxide (minimum assay 99.75%) according to the reported procedure.[12] Cyclododecane used for an internal standard in kinetic study was purified through recrystallization from benzene. Acetic acid, chlo-

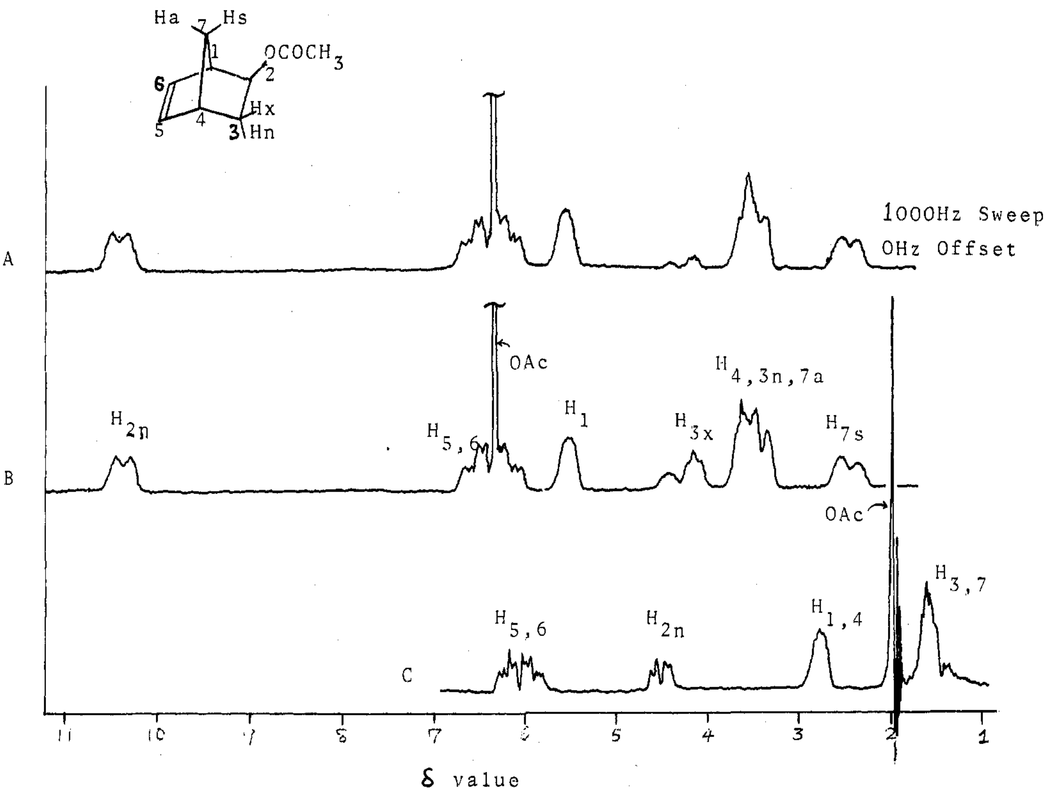


Figure 1. 100-MHz nuclear magnetic resonance spectra of labeled (A) and unlabeled (B, C) *exo*-2-norbornenyl acetate. A, B: 65 mol % of Eu(DPM)$_3$ in CCl$_4$.

roacetic acid, dichloroacetic acid, and formic acid used for addition reactions were reagent grade of more than 99% purity. Spectrograde tris(dipivaloylmethanato)europium was used as a NMR shift reagent to determine the deuterium incorporation in **6a** and **6c**. Nuclear magnetic resonance spectra were recorded on JEOL 60-H and 100-H instruments. Infrared absorption spectra were determined on a Hitachi Model 215 infrared spectrometer.

Analysis for the ratios of *exo*-2-norbornenyl (**6**) and nortricyclyl (**7**) acetates, chloroacetates, dichloroacetates, and formates were carried out by peak integration of gas–liquid chromatography on silicone DC 550 (3.5 m) and polyethylene glycol 20M (3.5 m) columns, assuming equal molar responses of **6** and **7**.

General Procedure of Addition Reaction of Acetic Acid or Formic Acid to Quadricyclane. A reaction vessel (10-ml flask) was washed with ammonium hydroxide (or sodium bicarbonate) solution and water and dried. To the flask were added 0.5 ml of quadricyclane (**1**), 0.05 ml (0.05 g) of carboxylic acid, and 2.0 ml of solvent. The stoppered flask was stirred for appropriate period at 20 °C or at 60 °C. An aliquot was taken from the mixture and was extracted with ether. Analysis of samples on gas–liquid chromatography gave the results shown in Table I.

Kinetics. For pseudo-first-order kinetic study of addition of acetic acid to **1**, samples were prepared at room temperature from 0.534 g of **1**, 37.8 mg of acetic acid, 2.0 ml of acetonitrile (or cyclohexane), and 12.2 mg of cyclododecane (an internal standard). The mixture was divided into ten ampules (2 ml volume, washed with ammonium hydroxide solution and dried), which were sealed and prepared for kinetic study in a bath thermostated at 60.1 ± 0.05 °C. Amount of two products **6a** and **7a** in the mixture were determined by GLC analysis. With appropriate calibration, ratios of products relative to cyclododecane, an internal standard, were estimated from products' peak areas. Up to 55% conversion, the reaction exhibited clean pseudo-first-order behavior. The second-order rate constant was obtained from the pseudo-first-order rate constant divided by the molar concentration of quadricyclane.

Registry No.—**1**, 278-06-8; **5a**, 64-19-7; **5b**, 79-11-8; **5c**, 79-43-6; **5d**, 64-18-6; **6a**, 5257-37-4; **6b**, 58673-07-7; **6c**, 58673-08-8; **6d**, 6997-19-9; **7a**, 6555-48-2; **7b**, 58673-09-9; **7c**, 58673-10-2; **7d**, 21892-95-5.

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