an unsymmetric distribution of charges in an ylide structure is essential for them to react effectively with alcohols.

Experimental Section

The preparation of 2-naphthyloxiranes is described in a previous paper.[15] They were purified by multiple crystallization from solvents shown in the parentheses: **1a** (benzene), **1b** (2-propanol), **2a** (1:1 benzene:methanol), and **2b** (1:9 H_2O:methanol). The solvents were of spectral grades. The source and purification of the reagents used in this study are given in previous publications.[13,14,25]

The absorption spectra were recorded on a Cary 219 spectrophotometer (1-nm bandpass). For laser flash photolysis, nitrogen laser pulses (337.1 nm, 8 ns, 2–3 mJ) from a Molectron UV-400 system were used for excitation. For a few experiments, excitation was carried out with laser pulses at 320 nm (~6 ns, 1–2 mJ); the latter were obtained in a Quanta-Ray WEX system by frequency doubling the output (640 nm) from a Quanta-Ray PDL-1 dye laser system containing DCM dye (Exciton); the dye laser was pumped by the output (second harmonic, 532 nm) from a Nd-YAG laser system (Quanta-Ray, DCR-1A). The description of the kinetic spectrophotometer and the computer controlled data collection/processing system is available in previous publications[25] from the Radiation Laboratory. The laser flash photolysis experiments were performed in rectangular quartz cells of 2–3-mm pathlengths. Unless otherwise mentioned, the solutions were deaerated by purging with oxygen free argon (15–30 min).

Acknowledgment. The authors gratefully acknowledge stimulating discussions with Prof. A. M. Trozzolo at the preliminary stage of this work.

Registry No. **1a**, 81052-72-4; **1b**, 81052-73-5; **2a**, 81052-70-2; **2b**, 81052-71-3.

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[25] (a) Das, P. K.; Encinas, M. V.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 6965–6970 and references therein. (b) Chattopadhyay, S. K.; Das, P. K.; Hug, G. L. *Ibid.* **1982**, *104*, 4507–4514 and references therein.

The Chemistry of the *trans*-Trimethylenenorbornene Ring System. 3. Effects of a *trans*-5,6-Trimethylene Bridge on the Norbornyl Cation[1]

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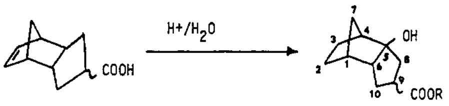
Hydration of the epimeric mixture 9-carboxy-*trans*-5,6-trimethylene-2-norbornene (**1**) in dilute aqueous acid afforded the 9-carboxy-*endo,cis*-5,6-trimethylene-5-norborneols (**2a**) as sole product. Initial protonation of **1** was shown to be regiospecific. The rearrangement to **2a** was found to occur solely by way of a 6,2-type hydride shift, while Wagner–Meerwein rearrangement and 3,2-type hydride shift were completely suppressed in the intermediate cation. It was concluded that the high degree of strain associated with the *trans*-trimethylene bridge in **1** was responsible for the unusual behavior of the intermediate.

As part of our continuing exploration of the synthesis[4] and reactions[1a] of the *trans*-trimethylenenorbornenes, we have initiated an investigation of the effects of the *trans*-trimethylene bridge on the behavior of norbornyl cations in this system. The acid-catalyzed hydration of the unsaturated acids **1**[4] was selected for exploratory study because of the ready availability of these compounds in this laboratory[4] and because the hydration reactions of closely related endo,cis and exo,cis systems have previously been investigated.[5] Thus, any differences in behavior among the isomeric intermediate cations would immediately be evident.

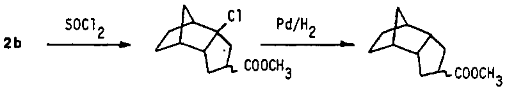
Results and Discussion

Hydration of **1** in dilute phosphoric acid at reflux temperature afforded the rearranged hydroxy acids **2a** as sole product as shown by ^{13}C NMR spectroscopy of the esterified crude product (**2b**). The tertiary nature of the alcohol moiety was revealed by the absence of a downfield signal in the ^1H NMR spectrum, and the endo,cis geometry of the ring system was established by the following reaction sequence.[6a] Treatment of **2b** with thionyl chloride gave **3** which on hydrogenolysis over 30% palladium on carbon in the presence of potassium carbonate gave the esters **4**.[6b,c]



1

2a, R = H
b, R = CH_3



3 **4**

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[1] (a) Part 2. Clemans, G. B. *J. Org. Chem.* **1973**, *38*, 3459. (b) Presented at the National Meeting of the American Chemical Society, Washington, D. C., 1983. (c) Taken in part from the M.S. Thesis of J. G. Samaratoni, Bowling Green State University, 1981.

[2] Petroleum Research Fund Undergraduate Research Fellow, 1982.

[3] Dreyfus Fund Undergraduate Research Fellow, 1983.

[4] Clemans, G. B.; Essiet, M. N.; Tyson, R. L. *J. Org. Chem.* **1972**, *37*, 2312. All of the compounds prepared in this and in our earlier studies were obtained as mixtures of C9 epimers and were used as such. See also ref 7a and 13.

[5] See: Cristol, S. J.; Seifert, D. W.; Johnson, D. W.; Jurale, J. B. *J. Am. Chem. Soc.* **1962**, *84*, 3918 and references therein cited.

[6] (a) See Experimental Section. (b) For an explanation of the nomenclature used, see: Schleyer, P. von R.; Donaldson, M. M. *J. Am. Chem. Soc.* **1956**, *78*, 5702. (c) That no skeletal rearrangement is to be expected during this reaction sequence is indicated by the lack of such a process in the deuterium exchange reaction observed at carbon 6 (see ref 12). The lack of rearrangement tends to support Schleyer's suggestion[7b] that tertiary ions such as **6** are a "dead end" with respect to endo–exo rearrangements of trimethylene norbornanes.

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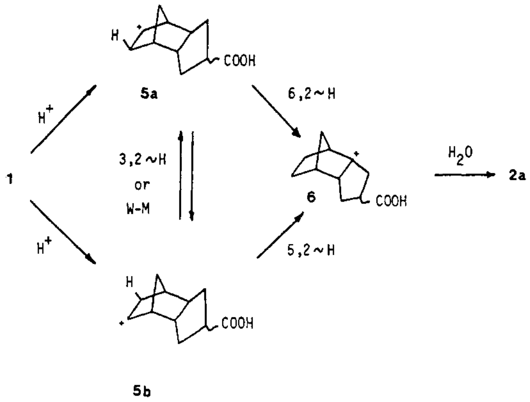
This product was shown to be identical with the same compound prepared previously by Culberson and Wilder[7a] by comparison of gas chromatographic retention times and ^{13}C NMR spectra. The exclusive formation of **2a** is quite unusual, since reports of 5-substituted trimethylenenorbornanes in the literature are rare.[7b]

The mechanistic possibilities for the hydration of **1** to **2a** are more complex than for the isomeric endo,cis and exo,cis compounds.[8a] Thus, protonation of the double bond in **1** can give rise to cations **5a** and **5b** which could interchange either by a 3,2-type hydride shift[8b] or by a Wagner–Meerwein carbon migration. Ion **5a** could rearrange to ion **6** directly by way of a 6,2-type hydride shift. Ion **5b**, on the other hand, could yield **6** only by way of sequential 3,2- (or Wagner–Meerwein) and 6,2-hydride shifts. Another possibility which must be considered in this context is a 5,2-type hydride shift to yield **6** from **5b** directly. Although unprecedented, such a process might be particularly favored in ion **5b**, since the 3,2-shift is known[9] to be slow under solvolytic conditions, and since the geometric distortions caused by the strained *trans*-trimethylene bridge force carbons 2 and 5 close together.[10] In any case the formation of **6** would be favored not only because of its tertiary nature, but also because of the relief of the considerable internal strain associated with the trans bridge.[4,10] Once formed, solvent capture of **6** would afford the observed products **2a**.



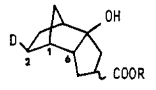
In an effort to distinguish among these mechanistic possibilities the reaction was carried out in the same manner, but in deuterated medium. It was anticipated that the location of the deuterium initially incorporated into the product could be determined by ^{13}C NMR techniques,[11] thereby differentiating between the two possible modes of protonating the double bond.

Table I. Calculated and Observed ^{13}C NMR Chemical Shifts in ppm for 2b

C	multiplicity	chemical shifts	
		calcd[a]	found
1	d	41.0	41.5, 39.1
2	t	21.6 (21.5)[b]	22.0, 20.6
3	t	20.8 (25.7)[b]	24.4, 23.7
4	d	48.0	48.7, 47.1
5	s	89.7[c]	89.6, 89.3
6	d	55.6[c]	57.2, 55.2
7	t	40.3	41.9, 40.6
8	t	40.2[b,d]	39.5, 37.4
9	d	44.0[b,d]	46.7, 46.5
10	t	28.6[b,d]	29.8, 29.3
C=O	s		176.6, 175.6
OMe	q		51.7, 51.5

[a] Base values for *endo*-trimethylenenorbornane taken from ref 14a, and norbornyl hydroxyl substituent parameters from ref 14b. [b] Calculated by using tertiary hydroxyl increments taken from ref 14b. [c] Substituent parameters for cyclopentylcarbomethoxy taken from ref 14c. [d] Substituent parameters for cyclopentyl hydroxyl taken from ref 14d.

When the reaction was carried out under these conditions, only the monodeuterated products **7a** were formed[12] as evidenced by the fact that the absorptions[13] of but a single carbon in the ^{13}C NMR spectrum of **7b** showed splitting arising from deuterium coupling. This was the highest field pair[13] in the spectrum which was assigned to carbon 2 on the following basis.



7a, R = H
b, R = CH_3

Peak assignments were initially made by using chemical shift estimations from measured substituent effects in model compounds. The expected chemical shifts of the ring carbons of **2b** were calculated by using the reported[14a]

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(7) (a) Culberson, C. F.; Wilder, P., Jr. *J. Org. Chem.* **1961**, *26*, 4289. The ^{13}C NMR spectra of the two products indicated that they differ slightly in epimeric composition. That material obtained from **1** contained essentially equal amounts of both epimers, while that obtained via cyclization consisted of an approximately 65:35 mixture. The equilibration results Culberson and Wilder suggest that the major isomer has the syn configuration. The isomers were not separated. (b) Schleyer, P. von R.; Donaldson, M. M. *J. Am. Chem. Soc.* **1960**, *82*, 4645.

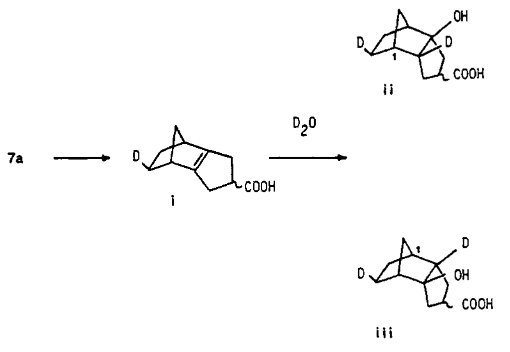
(8) (a) For a general discussion of hydration mechanisms, see: Lowry, T. H.; Richardson, K. S. "Mechanism and Theory in Organic Chemistry", 2nd ed.; Harper and Row: Cambridge, 1981; pp 508–513. For a discussion of the chemistry of norbornyl cations, see: Brown, H. C. "The Nonclassical Carbonium Ion Problem"; Plenum Press: New York, 1977. (b) These rearrangements are characterized with reference to the numbering of the parent norbornyl system rather than to the numbering of the trimethylenenorbornenes used here (see ref 6b).

(9) (a) Stothers, J. B.; Tan, C. T.; Nickon, A.; Huang, F.; Sridhar, R.; Weglein, R. *J. Am. Chem. Soc.* **1972**, *94*, 8581. (b) Lee, C. C.; Lam, L. K. M. *Ibid.* **1966**, *88*, 2831. (c) Lee, C. C.; Hahn, B. S.; Lam, L. K. M. *Tetrahedron Lett.* **1969**, 3049.

(10) That a high degree of strain is associated with the *trans*-trimethylene bridge is evident from the thermal rearrangement of **2b** to the tricyclo[5.3.0]decane system which we reported earlier.[1a] The direction of this facile process is exactly opposite that observed by Berson in the absence of the trans bridge (see: Berson, J. A. *Acc. Chem. Res.* **1972**, *5*, 406). As we have shown,[4] 6 kmol/mol represents a lower limit for this strain. The rearrangement also confirms the close approach of carbons 2 and 5, since in this reaction bond formation between them actually occurs.

(11) Wehli, F. W.; Wirthlin, T. "Interpretation of Carbon-13 NMR Spectra"; Heyden: New York, 1976.

(12) Two dideuterated products were also formed by way of exchange at carbon 6. This process occurs by a dehydration of **7a** to the symmetric unsaturated acid **i** and subsequent nonselective rehydration to **ii** and **iii**. A similar reaction has been observed in a closely related system (see: Paquette, L. A.; Ohkata, O.; Carr, R. V. C. *J. Am. Chem. Soc.* **1980**, *102*, 3303).



(13) All ^{13}C NMR spectra were obtained on the esterified products because of their greater solubility in deuteriochloroform compared to the hydroxy acids. Since the products are formed as mixtures of C9 epimers, each carbon gives rise to a pair of signals.

Table II. Lanthanide-Induced Shifts for Carbons 2 and 3 of Alcohols 10

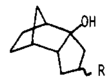
C	chemical shift, ppm	induced shift,[b] ppm	std dev
2	anti[a] 20.6	−18.1	0.10
	syn[a] 22.3	−16.9	0.07
3	syn[a] 23.8	−20.4	0.08
	anti[a] 24.3	−21.8	0.11

[a] Epimeric assignments are made on the assumption that the alcohol with the *anti*-methyl group will be less sterically hindered and will thus experience the greater induced shift. [b] Extrapolated to a 1:1 reagent–substrate ratio.

chemical shifts of *endo,cis*-trimethylenenorbornane and adding the norbornyl hydroxyl substituent parameters of Lippmaa et al.[14b] supplemented by additional parameters derived from carbomethoxycyclopentane[14c] and cyclopentanol.[14d] The results of these calculations are summarized in Table I. With the exception of carbon 3, the agreement between calculated and observed values is quite good. This is somewhat surprising and helps to define the limits within which such parameters may be applied to closely related systems (see below). Assignments that were not evident from off-resonance decoupling and chemical shift data were then confirmed by other means. Thus, base-catalyzed deuterium exchange at carbon 9 via the enolates from **2b** unambiguously established the assignment of its signals as a result of the observed deuterium coupling in the ^{13}C NMR spectrum of the product. Further, the detection of the expected isotope-induced shifts in the positions of the signals of the adjacent carbons 8 and 10 confirmed[11] their assignments as well. Similarly, the acid-catalyzed deuterium exchange observed[12] at carbon 6 of the acids **2a** allowed these assignment to be made, and the isotope-induced shifts in the adjacent carbons (1 and 10) confirmed these also.[15] Carbon 4 is the only remaining methine carbon, while carbon 7 is the only methylene carbon unaffected by any of the deuterium incorporations made.

The key distinction between carbons 2 and 3 which give rise to the two high-field pairs of signals thus remains. Although the calculations (Table I) indicate that the signals of carbon 3 occur at higher field than those of 2 as expected,[14e] the results of a lanthanide shift reagent study suggested that this assignment should be reversed. In order to avoid ambiguities resulting from the presence of two potential complexation sites, the ester functions of **2b** were reduced to methyl (see Experimental Section) to yield the mixture of epimeric alcohols **10**. A similar conversion was carried out by using the deuterated product **7b** to assure that correct chemical shift correspondences were maintained. The alcohol mixture **10** was subjected to increasing concentrations of $Pr(FOD)_3$ and the changes in chemical shifts for each signal determined. A least-squares extrapolation of the data to a 1:1 substrate–reagent ratio was then made, and the results for carbons 2 and 3 are given in Table II.

As can be seen the highest field pair of signals (those of the methylene carbon deuterated in the addition reaction) are shifted less than the pair of next highest field (the adjacent nondeuterated methylene). If the reagent–substrate complex is axially symmetric[16] then a simple $1/r^3$ dependence[17] of the induced dipolar shifts[18] suggests that these high-field signals be assigned to carbon 2 rather than to carbon 3 as indicted by the calculations in Table I. Drieding models do not reveal a single preferred geometry for the complex. This makes it difficult to apply a $3\cos^2\chi - 1$ correction factor for the angular dependence of the shifts. It seems likely, however, that in any case the angles for carbons 2 and 3 will not differ greatly. Under such circumstances, an approximate proportionality of the induced shift to $1/r^3$ is to be expected.[17,18]



8, R = CH_2OH

9, R = CH_2OTs

10, R = CH_3

The alternative assignments of carbons 2 and 3 are confirmed by the observation that in tertiary 2-norborneols the substituent effect of the hydroxyl group on the chemical shift of carbon 6 is reversed, the signal of that carbon being shifted to lower fields. This change in the "γ-trans effect" does not appear to have been commented upon in the literature,[19] but it is nonetheless evident in the reported data[14b] as well as in our own. For instance, if the chemical shift of carbon 6 in *endo*-2-methyl-*exo*-2-norborneol is compared to that of the corresponding carbon in *endo*-2-methylnorbornane, the substituent effect of the hydroxyl group is seen to be +2.6 ppm.[20a] This compares with an effect of −5.2 ppm in norborneol itself.[14e] The reason for this change is not known.[20b] If the chemical shifts of carbons 2 and 3 are recalculated by using substituent parameters based on a tertiary hydroxyl, the results (Table I) are seen to be in good agreement both with the observed values and the shift reagent study above.

It is thus concluded that the products obtained from the hydration of **1** in deuterated medium are **7a**, with the deuterium selectively incorporated at carbon 2. This indicates that the initial protonation is highly regioselective and that the formation of the observed products **2a** occurs by way of a 6,2-type hydride shift in the intermediate ion **5a**.

In an alternative approach to elucidating this mechanism, the dideuterated derivative **11** was prepared and hydrated under the same conditions used previously. Rearrangement via a 6,2-type shift of deuterium in this

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(14) (a) Nakagawa, K.; Iwase, S.; Ishii, Y.; Hamanaka, S.; Ogawa, M. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2391. (b) Lippmaa, E.; Pehk, T.; Paasivirta, J.; Belikova, N.; plate, A. *Org. Magn. Reson.* **1970**, *2*, 581. (c) Gordon, M., Grover, S. H.; Stothers, J. B. *Can. J. Chem.* **1973**, *51*, 2092. (d) Christl, M.; Reich, H. J.; Roberts, J. D. *J. Am. Chem. Soc.* **1971**, *93*, 3463. (e) Grutzner, J. B.; Jautelat, M.; Dence, J. B.; Smith, R. A.; Roberts, J. D. *J. Am. Chem. Soc.* **1970**, *92*, 7107.

(15) We have never observed a similar induced shift in the signals of carbon 5 which would also be expected in this case. We have no explanation for this, but similar results have been obtained by others (see ref 11, p 109).

(16) Hawkes, G.; Leibfritz, D.; Roberts, D.; Roberts, J. D. *J. Am. Chem. Soc.* **1973**, *95*, 1659.

(17) Hawkes, G.; Leibfritz, D.; Roberts, D.; Roberts, J. D. *J. Am. Chem. Soc.* **1971**, *93*, 4295.

(18) Both carbons 2 and 3 are sufficiently removed from the site of complexation that contact shifts should be minimal, see: Hawkes, G.; Marzin, C.; Johns, S.; Roberts, J. D. *J. Am. Chem. Soc.* **1973**, *95*, 1661.

(19) For a summary, see: Marchand, A. P. "Stereochemical Applications of NMR Studies in Rigid Bicyclic Systems"; Verlag Chemie International: Deerfield Beach, 1982.

(20) (a) The carbon 6 parameter is the only one altered to such an extent nor are the calculated chemical shifts of Table I changed significantly for any other ring carbon if tertiary hydroxyl parameters are used. (b) A similar reversal is not observed for secondary trimethylenenorborneols such as **16** and **17** (X = OH), the effect of the hydroxyl group being diamagnetic in both cases (see: Dawson, B. A.; Stothers, J. B. *Org. Magn. Reson.* **1983**, *21*, 217). The mechanism of this particular shift in substituted norbornanes is not known, although two possibilities have been suggested (see ref 14e and Eliel, E. L.; Bailey, W. F.; Kopp, L. D.; Willer, R. L.; Grant, D. M.; Bertrand, R.; Christensen, K. A.; Dalling, D. K.; Duch, M. W.; Wenkert, E.; Schell, F. M.; Cochran, D. W. *J. Am. Chem. Soc.* **1975**, *97*, 322). We are actively investigating this point at the present time.

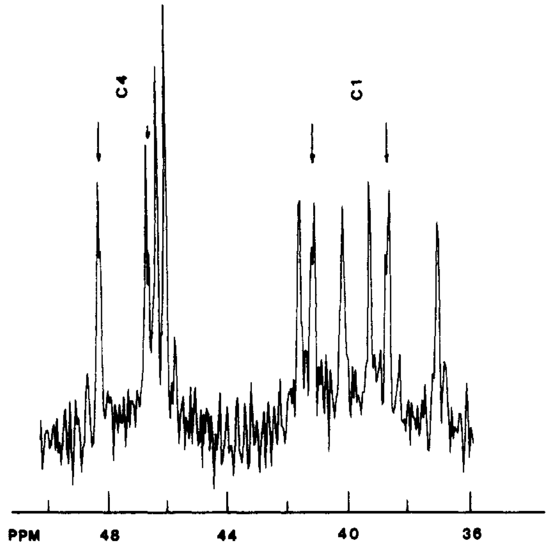
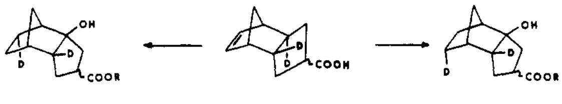


Figure 1. Partial ^{13}C NMR spectrum of an equimolar mixture of dideuterated hydroxy ester **12b** and undeuterated material **2b**.

case would yield **12a** in which both carbons 1 and 4 are flanked by deuterium-bearing atoms. A 5,2-type shift, on the other hand, would yield **13a** in which the two deuteriums flank carbon 1 only. Thus, a determination of the number of methine carbons experiencing an isotope-induced shift,[11] in the ^{13}C NMR spectrum of the esterified product obtained (either **12b** or **13b**) would permit a distinction between these two pathways independently of specific chemical shift assignments. As shown in Figure 1, an induced shift of approximately 0.1 ppm is observed for the signals previously assigned to carbons 1 and 4. Thus, the 6,2-type hydride shift route is again established.

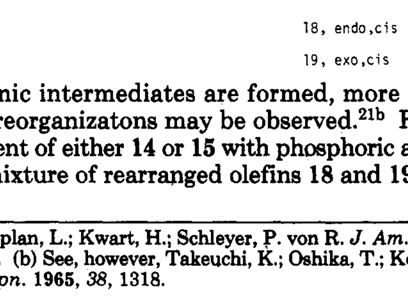


12a, R = H
b, R = CH$_3$

11

13a, R = H
b, R = CH$_3$

Ionic additions to either *endo,cis*-**14**[5] or *exo,cis*-trimethylenenorbornene (**15**)[21a] are usually accompanied by Wagner–Meerwein rearrangement, although there is often a tendency to favor the adduct with the more stable exo,cis bridge **17**. In related reactions in which presumably the same cationic intermediates are formed, more extensive molecular reorganizatons may be observed.[21b] For example, treatment of either **14** or **15** with phosphoric acid yields the same mixture of rearranged olefins **18** and **19**.[22] Even more remarkable, of course, is the rearrangement, catalyzed by Lewis acids, of *endo,cis*-trimethylenenorbornane (**16**, X = H) first to the exo,cis isomer (**17**, X = H) and finally to adamantane.[7b] The marked tendency of these compounds toward rearrangement has thus clearly been documented.



16, endo,cis
17, exo,cis

14, endo,cis
15, exo,cis

18, endo,cis
19, exo,cis

It is evident that the trans bridge in **1** has drastically restricted the reactivity of the norbornyl cation shown here to be generated at carbon 3. Questions of regiospecificity do not arise in the protonation of the endo,cis and exo,cis olefins (**14** and **15**) because of their higher symmetry. However, the formation of **5a** in preference to **5b** is surprising in view of the bond angle distortions induced by the trans bridge,[4] since it places the electron-deficient site at the more highly compressed angle. Exclusive reaction by way of a transannular hydride migration is also quite striking, such processes being rare among addition reactions of the endo,cis and exo,cis analogues.[7b] It thus appears that the dominating factor in the trans system is the great relief of internal strain[10] on rearrangement to **6**.

Equally remarkable is the complete absence of Wagner–Meerwein rearrangement of ion **5a**, even though this process is common in both norbornyl[8a] and dicyclopendadienyl[5] cations. Such a rearrangement in the present case would place a deuterium at carbon 7, contrary to observation. This lack of carbon migration is, however, consistent with the formation of the cation at carbon 3. The downward force that the trans bridge exerts on the 5,8 bond in **5a** pulls the 4,5-bond up and away from the electron-deficient site at carbon 3, thus sharply reducing the possibility of orbital overlap and hence the tendency toward rearrangement as well.

It is seen that protonation of the double bond in **1** does not produce the isomeric ion **5b** and that an alternative ion-generating process will have to be used if it is to be observed. It would be most interesting to compare the behavior of the ions **5a** and **5b**. These studies are under way and will be reported shortly.

Experimental Section

General Methods. Infrared spectra were obtained with a Perkin-Elmer Model 337 spectrophotometer. Nuclear magnetic resonance spectra were obtained with either a Varian Model EM-360L or a Varian Model CFT-20 spectrometer using tetramethylsilane as internal reference. Mass spectra were run on a Varian-MAT CH 7 spectrometer, and gas chromatographic analyses were obtained with a Hewlett-Packard Model 5790A instrument using packed 6 ft by $^1/_4$ in. columns of either 10% DEGS or 30% silicone rubber at the indicated temperatures. Microanalyses were performed by either MHW Laboratories, Garden City, MI, or by Spang Laboratories, Eagle Harbor, MI. All melting and boiling points are uncorrected.

Hydration of 1. To a 0.4 M solution of phosphoric acid (prepared from 1100 mg of phosphorous pentoxide and 40 mL of water) was added 1200 mg (6.8 mmol) of the unsaturated monoacids **1** and the mixture was refluxed for 12 h under nitrogen. The reaction mixture was then cooled, saturated with sodium chloride, and extracted with three 50-mL portions of ether. The combined extracts were washed once with saturated brine, dried over $MgSO_4$, and concentrated to yield 1330 mg (100%) of a white solid. Recrystallization from ethyl acetate afforded the hydroxy acids **2a** as white crystals: mp 153–155 °C; IR (KBr) 3590–2300, 3400, 1696 cm^{-1}; mass spectrum, *m/e* 196 (M^+).

Anal. Calcd for $C_{11}H_6O_3$: C, 67.32; H, 8.22. Found: C, 67.25; H, 8.13.

Esterification of this compound in methanol at room temperature by the same procedure used earlier[4] afforded the esters **2b** in quantitative yield as a colorless oil after evaporative distillation: IR (neat) 3400, 1734 cm^{-1}; mass spectrum, *m/e* 210 (M^+);

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(21) (a) Kaplan, L.; Kwart, H.; Schleyer, P. von R. *J. Am. Chem. Soc.* **1960**, *82*, 2341. (b) See, however, Takeuchi, K.; Oshika, T.; Koga, Y. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 1318.

(22) Wilder P., Jr.; Cash, D. J.; Wheland, R. C.; Wright, G. W. *J. Am. Chem. Soc.* **1971**, *93*, 791.

^1H NMR ($CDCl_3$) δ 3.68 (s, 3, methoxyl protons). The ^{13}C NMR spectrum of this product is given in Table I.

Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.55; H, 8.62. Found: C, 68.47; H, 8.53.

At reflux temperature a small amount of the corresponding methoxy methyl esters are also obtained. This product is not formed at the lower temperature.

Structure Proof of Hydroxy Ester 2b. The hydroxy esters (**2b**) were treated with thionyl chloride by the procedure of Fuson and Walker[23] to yield the intermediate chlorides **3** (mass spectrum, *m/e* 228, M^+).[6c] Hydrogenolysis of this intermediate then gave the esters **4**. An authentic sample of **4** was prepared by the method of Culberson and Wilder[7a] except that the procedure of Mariella and Raube[24] was followed for the cyclization with malonic ester. Except for minor differences due to slight variations in the epimer ratio, the two samples were found to have identical mass spectra, ^{13}C NMR spectra,[7a] and gas chromatographic retention times on the two columns indicated at 165 °C.

Reaction of 1 in Deuterated Medium. Formation of 7a. In a dry flask were placed 534 mg of the unsaturated acids **1** and 20 mL of a 0.3 M solution of D_3PO_4 in D_2O (prepared from 450 mg of P_2O_5 and 20 mL of D_2O), and the mixture was refluxed for 12 h under nitrogen. After the usual workup the product (**7a**) was obtained as a white solid. Esterification in methanol as before[4] then gave the esters **7b** along with minor amounts of dideuterated material as a colorless oil after evaporative distillation.

The ^{13}C NMR spectrum of this product revealed that the carbon giving rise to the highest field signals was largely deuterated. These signals appeared as a pair of triplets arising from coupling with deuterium. However, when the reaction product was resubjected to the reaction conditions for 12 h, a second deuterium was incorporated as indicated by the fact that the carbon 6 signal and to a lesser extent that of carbon 8 were also split. This is expected as a result of isotope exchange by a dehydration–rehydration mechanism, similar to processes that have been observed in closely related systems.[12] Further, in the ^{13}C NMR spectrum of an equimolar mixture of this dideuterated and undeuterated material a 0.1 ppm upfield shift was observed for carbons 1, 2, 3, 4, and 10. A shift of 0.2 ppm was also observed for carbon 1. This is the pattern of shifts expected (except for the lack of shift in the carbon 5 signals as noted[15]) for the product mixture obtained by the mechanism proposed.

That incorporation of the second deuterium had not occurred at carbon 9 via enolization of the carboxyl group was established as follows. Treatment of the esters **2b** with methoxide in methanol-*d*[25] afforded a product that clearly revealed deuterium coupling in that signal assigned to carbon 9. Further, when mixed with an equimolar amount of undeuterated material, the expected 0.1 ppm isotope shifts[11] of the signals of carbons 8 and 10 were also observed.

9-Carboxy-5,6-dideuterio-5,6-*trans*-trimethylene-2-norbornene (11). The intermediate diester *trans*-5,6-dicarbomethoxy-2-norbornene was dideuterated with methoxide in methanol-*d* by the same procedure used above. The mass and ^1H NMR spectra of this material indicated that it was essentially completely dideuterated. This product was then converted to the dideuterated monoacid **11** by the same synthetic pathway reported earlier.[4] The unsaturated acids **11** were obtained after sublimation as a white crystalline solid, mp 65–66 °C.

Hydration of Dideuterated Acids 11. The acids **11** (532 mg, 3.0 mmol) were refluxed in 20 mL of 0.3 M phosphoric acid (prepared from 455 mg P_2O_5 and 20 mL of H_2O) under nitrogen for 3 h. The reaction mixture was then worked up as before, and the crude products **12a** were esterified in methanol. After the usual workup, the hydroxy esters **12b** were purified by evaporative distillation. They were obtained as a colorless oil in 66% yield. The ^{13}C NMR spectrum of this product clearly showed collapse of the signals assigned to carbons 3 and 6 due to deuterium coupling. Further, a spectrum of an equimolar mixture of this product and undeuterated material showed a 0.1 ppm upfield shift in the signals of both carbons 1 and 4 (see Figure 1).

Reduction of the Hydroxy Esters 2b to the Alcohols 10. A solution of 900 mg (4.3 mmol) of **2b** in 20 mL of ether was added dropwise to a cold solution of 810 mg (21 mmol) of lithium aluminum hydride in 60 mL of ether, and the resulting mixture was refluxed with stirring for 4 h. The reaction was then cooled in an ice bath and was decomposed with 25 mL of water followed by 20 mL of cold 20% sulfuric acid. The aqueous layer was then saturated with sodium chloride and was extracted with three 75-mL portions of ether. The combined ether extracts were washed with 25 mL of saturated sodium bicarbonate and 20 mL of saturated sodium chloride and dried ($MgSO_4$). The dessicant was removed by filtration, and the solvent was distilled to yield 750 mg (96%) of crude diols **8**: IR (neat) 3312 cm^{-1}.

To a cold solution of the above product in 7 mL of pyridine was added 840 mg of *p*-toluenesulfonyl chloride over a period of about 0.5 h, and the resulting mixture was allowed to stand at 5–10 °C for 48 h. The mixture was then taken up in 250 mL of ether and was washed with three 20-mL portions of 10% hydrochloric acid, 20 mL of saturated sodium bicarbonate, and 20 mL of saturated sodium chloride. The resulting ether solution was dried ($MgSO_4$) and concentrated to yield 850 mg of an oil whose ^1H NMR indicated reaction was incomplete. It was therefore retreated with *p*-toluenesulfonyl chloride (750 mg, 3.1 mmol) as above. After an identical workup, there was obtained 1060 mg of crude hydroxy tosylates **9**: ^1H NMR ($CDCl_3$) δ 2.43 (s, 3, $ArCH_3$), 3.90 and 3.96 (d, J = 6 Hz, 2, CH_2OTs), and 7.23–7.80 (m, 4, ArH).

This product was dissolved in 30 mL of ether and was added to a cold solution of 550 mg (15 mmol) of lithium aluminum hydride in 40 mL of ether, and the reaction mixture was refluxed with stirring for 24 h. The reaction was cooled in an ice bath and was decomposed with 35 mL of cold water followed by 10 mL of cold 30% sulfuric acid. The aqueous layer was saturated with sodium chloride and was extracted with three 100-mL portions of ether. The combined organic layers were washed successively with 10 mL of saturated sodium bicarbonate and 10 mL of saturated sodium chloride, dried ($MgSO_4$), and concentrated to yield 420 mg of the alcohols **10** as a white solid. Recrystallization of this material from hexane yielded the pure product: mp 71–72 °C; IR (KBr) 3290 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 19.2, 21.3 (q, CH_3), 90.2, 90.5 (s, COH); ^1H NMR ($CDCl_3$) δ 1.01 (d, J = 5 Hz, CH_3); mass spectrum, *m/e* 165 $(M - H)^+$, 151 $(M - CH_3)^+$, 137 $(M - H_2O)^+$.

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.54; H, 11.02.

Lanthanide Shift Reagent Study of the Alcohols 10. A weighed amount of the alcohol mixture **10** was transferred under a nitrogen atmosphere by using a glove bag to an NMR tube and was dissolved in deuteriochloroform to a constant volume mark. After an initial ^{13}C NMR spectrum was obtained, a small amount of the solvent was evaporated under nitrogen, a weighed amount of $Pr(FOD)_3$ was added, and the solution diluted to mark. Another spectrum was obtained and the changes in chemical shift measured. This procedure was repeated five times until an approximate reagent/substrate ratio of 0.25 was obtained. For each peak a least-squares extrapolation to a reagent/substrate ratio of 1.0 was then made, and the results for carbons 2 and 3 are given in Table II.

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Registry No. **1** (isomer 1), 34599-27-4; **1** (isomer 2), 34599-26-3; **2a** (isomer 1), 91295-15-7; **2a** (isomer 2), 91382-86-4; **2b** (isomer 1), 91295-16-8; **2b** (isomer 2), 91382-87-5; **7a** (isomer 1), 91295-17-9; **7a** (isomer 2), 91295-23-7; **8** (isomer 1), 91295-22-6; **8** (isomer 2), 91382-91-1; **9** (isomer 1), 91295-21-5; **9** (isomer 2), 91382-90-0; **10** (isomer 1), 91295-20-4; **10** (isomer 2), 91382-89-7; **11** (isomer 1), 91295-18-0; **11** (isomer 2), 91295-24-8; **12b** (isomer 1), 91295-19-1; **12b** (isomer 2), 91382-88-6.

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