Rearrangements of α-Hydroxy Ketals and Derivatives of α-Hydroxy Ketals

Xavier Creary* and Anthony J. Rollin

Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556

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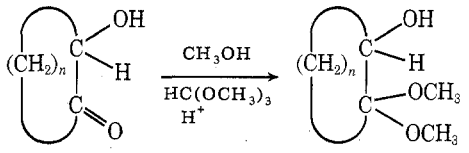
α-Hydroxy ketals are found to rearrange when treated with acid to give alkoxy ketones. The k_H/k_D value of 3.1–3.5 for *endo*-2,2-dimethoxybicyclo[2.2.1]heptan-3-ol (**4**) suggests a mechanism involving rate-limiting hydride migration to an α-alkoxy cation. *exo*-2,2-Dimethoxybicyclo[2.2.1]heptan-3-ol (**5**) gives a dimeric product consistent with the low propensity for *endo*-hydride migration in the norbornyl system. Solvolysis of tosylate and triflate derivatives of α-hydroxy ketals gives rates largely inductively retarded by the dimethoxy grouping. Hydrolysis or acetolysis of 2,2-dimethoxycyclobutyl tosylate (**23**) gave methyl cyclopropanecarboxylate (**32**) via a ring-contraction process. 2,2-Dimethycyclopentyl triflate (**26**) gave 2,3-dimethoxycyclopentene (**38**) on acetolysis and 1,1,2-trimethoxycyclopentane on methanolysis. These products arise from methoxy participation. *endo*-2,2-Dimethoxybicyclo[2.2.1]hept-3-yl triflate (**28**) gave products arising from a k_s process and from methoxy participation. Additionally, methyl cyclohex-3-enecarboxylate (**41**) was produced. A deuterium-labeling study showed that **41** was produced from the rarely observed C_1–C_7 participation in the norbornyl system. The migration is suggested to arise from the increased demand for participation as a result of the inductively destabilizing dimethoxy substituents.

α-Hydroxy ketals are readily available from the corresponding acyloins, which are in turn prepared using the Ruhlmann and Schrapler modification of the acyloin condensation.[1] Complimenting this route is the recently developed procedure involving epoxidation, hydrolysis of silyl enol ethers.[2] The presence of both the alcohol and masked keto functionality makes the hydroxy ketal potentially interesting from a synthetic viewpoint and additionally with respect to potential rearrangement processes. We have undertaken a study of some of the reactions which these acyloin derivatives undergo with the goal of elucidating mechanistic processes. Reported here are the results of these studies.

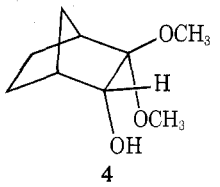
Results and Discussion

Acid-Catalyzed Rearrangements of α-Hydroxy Ketals. α-Hydroxy ketals **1–4** were prepared by ketalization of the appropriate α-hydroxy ketone produced in the acyloin condensation. The *exo*-hydroxy ketal **5** was produced in the unusual reaction of *endo*-keto triflate **6** with sodium methoxide in methanol.[3]

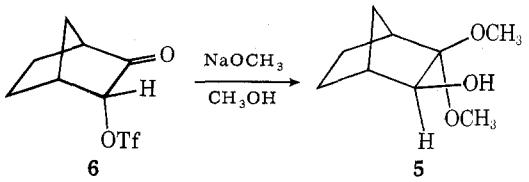


n = 2,3,4

1, n = 2
2, n = 3
3, n = 4



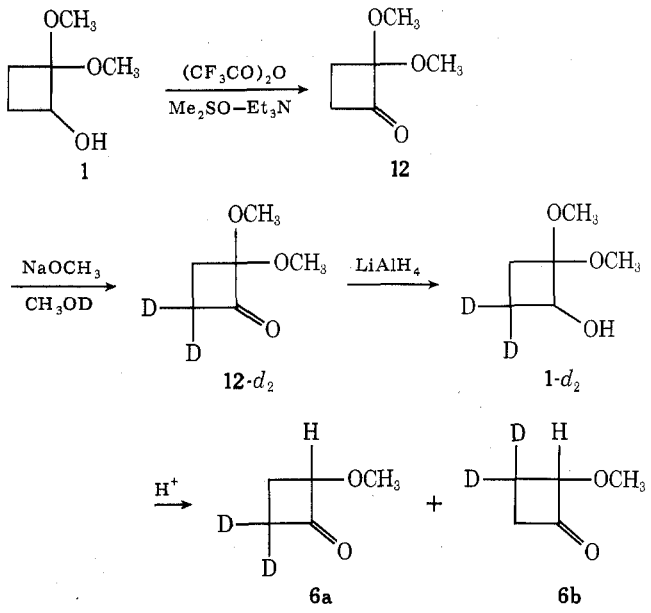
4



6 **5**

Ketal alcohols **1–5** undergo rearrangement when treated with hydrochloric acid vapors. Table I gives the products and reaction conditions employed for these transformations. Conia has previously reported rearrangement of **1** under thermal conditions at temperatures greater than 200 °C and has suggested mechanisms ranging from entirely concerted to acid catalyzed.[4] We have found that **1** is thermally stable in base-washed glassware and that the reaction of **1** is truely acid catalyzed. The mechanism of rearrangement of **1** remains open to question and we therefore sought to shed further light on this process.

Scheme I

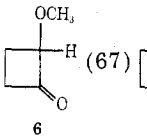
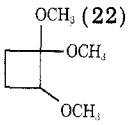
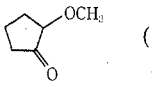
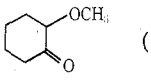
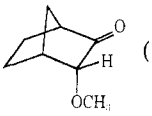
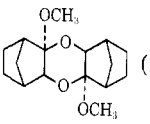


Among other mechanisms, Conia has suggested that aldehyde **16** is involved in formation of **7**. Aldehyde **16** was shown to rapidly rearrange to **7** on treatment with acid.[4c,d] We therefore prepared deuterated alcohol **1**-d_2 by the route shown in Scheme I to evaluate the importance of the rearrangement processes shown in Scheme II.

After many attempted alternate oxidations, 2,2-dimethoxycyclobutanone (**12**) was prepared in 83% yield by oxidation of **1** with the trifluoroacetic anhydride–dimethyl sulfoxide–triethylamine reagent.[5] Exchange of **12** in methanol-d_1 with sodium methoxide followed by lithium aluminum hydride reduction gave **1**-d_2.

Acid-catalyzed rearrangement of **1**-d_2 gave, by NMR determination, equal amounts of **6a** and **6b**. This observation suggests the complete involvement of a symmetrical intermediate **16** in the rearrangement of **1**. The mechanism most consistent with this and Conia's observed acid-catalyzed re-

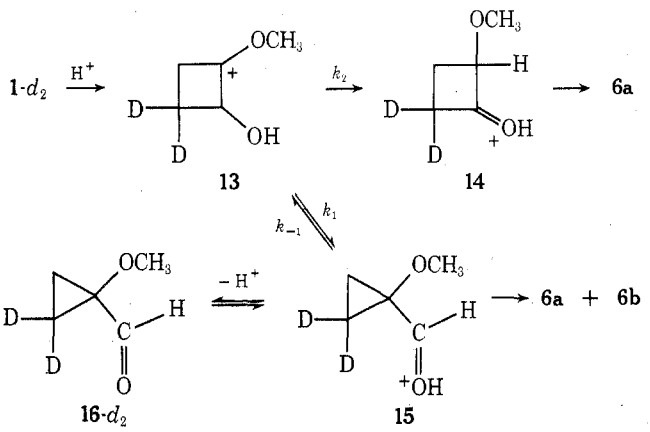
Table I. Acid-Catalyzed Rearrangement of α-Hydroxy Ketals

Alcohol	Registry no.	Temp, °C	Reaction time, min	Products (% yield)
1	42082-99-5	100	50	 (67)  (22)
				6 7
2	63703-33-3	120	18	 (89)
				8
3	63703-34-4	100	18	 (87)
				9
4	63703-35-5	110	20	 (89)
				10
5	63703-36-6	120	45	 (95)
				11

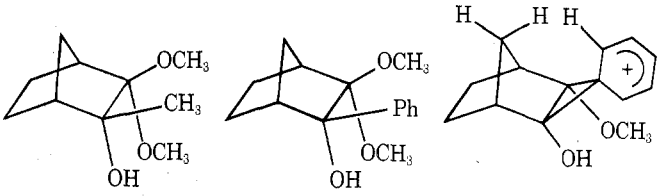
arrangement of **16** involves ring contraction of **13** (k_1) occurring at a rate much *faster* than hydride migration (k_2). The acid-catalyzed conversion of **16** to **6** probably proceeds via reprotonation of **16** leading to **13** and subsequent hydride migration. Concerted thermal rearrangements of **1** and **16** now appear improbable under the current reaction conditions.

Hydroxy ketals **2, 3,** and **4** also rearrange to give analogous methoxy ketone products. No evidence is seen for ring-contraction processes. This general type of reaction has some precedent.[6] Certain α-hydroxy ketones produce methoxy ketones when treated with methanolic hydrochloric acid.[6a] Ainsworth has produced a methoxy ketone directly from a bis(trimethylsilyl) enol ether under similar conditions.[6b] However, we are unaware of any studies designed to elucidate mechanistic details of this transformation. Table II gives rate data for rearrangement of **4** and the deuterated analogue **4-*d***. The deuterium isotope effect k_H/k_D is large (3.1 to 3.5) and consistent with carbon–hydrogen bond fragmentation in the rate-controlling step. In view of this isotope effect, we suggest hydride migration to a cationic center generated by acid-catalyzed loss of methoxide is rate determining. The overall mechanistic scheme is reminescent of the pinacol rearrangement in which deuterium isotope effects are also analogous[7] (primary). The rearrangement reaction of α-hydroxy ketals provides a novel route for the preparation of certain α-keto

Scheme II



ethers. However, attempts to rearrange ketals **17** and **18** under more strenous conditions than those in Table I were unsuccessful. Reasons for these failures may lie in the decreased migratory aptitude of the methyl group and steric strain in the transition state **19** necessary for phenyl migration.[8]



Treatment of *exo*-3-hydroxynorcamphor dimethyl ketal **5** with acid gave only **11**.[10] Undoubtedly, the low propensity for *endo*-hydride migration in the norbornyl system[9] accounts for this product, which is suggested to arise as shown in Scheme III. Intermolecular capture of **20** by **5** occurs in pref-

Scheme III

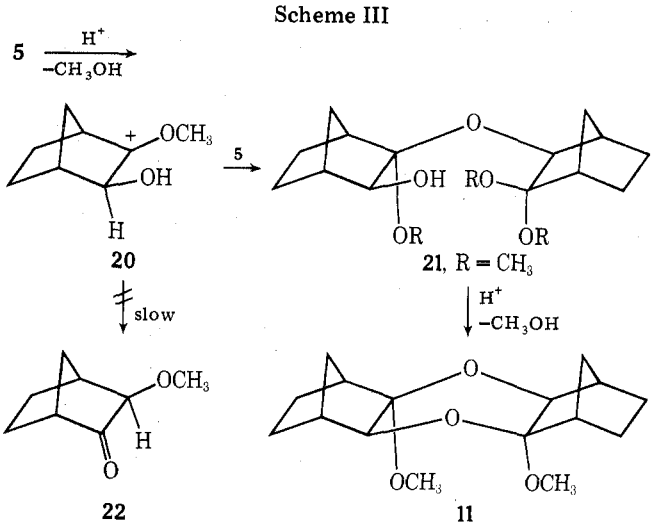


Table II. Rearrangement Rates of 4 and 4-*d* in 0.057 M HCl in Di-*n*-propyl Ether

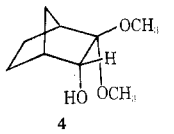
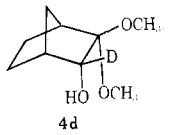
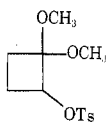
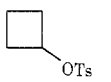
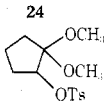
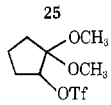
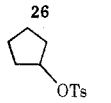
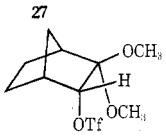
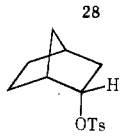
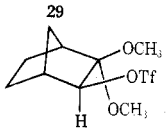
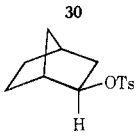
Compound	Temp, °C	k, s^{-1}	$\Delta H^{\ddagger}$, kcal	$\Delta S^{\ddagger}$, eu	k_H/k_D
 4	35.0	$(1.05 \pm 0.03) \times 10^{-4}$			3.5 ± 0.2
	50.0	$(4.68 \pm 0.11) \times 10^{-4}$	19.1 ± 0.8	−15 ± 2	3.1 ± 0.2
 4d	35.0	$(3.05 \pm 0.07) \times 10^{-5}$			
	50.0	$(1.53 \pm 0.03) \times 10^{-4}$	20.6 ± 0.5	−12 ± 2	

Table III. Solvolysis Rates of α-Hydroxy Ketal Derivatives

Compound	Registry no.	Solvent	Temp, °C	k, s^{-1}	$\Delta H^{\ddagger}$, kcal	$\Delta S^{\ddagger}$, eu	$k_{rel}^{25°C}$ (HOAc)[b]	$k_{rel}^{60°C}$ (70% acetone)
 23	63703-37-7	HOAc	25.0[a]	3.15×10^{-9}			1.5×10^{4}	
			100.0	$(7.33 \pm 0.05) \times 10^{-5}$	29.1	0.2		
			120.0	$(5.71 \pm 0.10) \times 10^{-4}$				
		70% acetone	60.0[a]	1.53×10^{-6}				
			90.0	4.39×10^{-5}	26.5	−5.8		2.7
			100.0	$(1.19 \pm 0.02) \times 10^{-4}$				
			110.0	3.18×10^{-4}				
 24	10437-85-1	HOAc	25.0[a,c]	6.97×10^{-7}			3.4×10^{6}	
		70% acetone	60.0	$(6.58 \pm 0.03) \times 10^{-4}$				1140
 25	63703-38-8	70% acetone	60.0[a]	5.78×10^{-7}				
			100.0	$(5.80 \pm 0.01) \times 10^{-5}$	27.5	−4.7		1.0
			120.0	$(4.03 \pm 0.01) \times 10^{-4}$				
 26	63703-39-9	HOAc	25.0	$(2.37 \pm 0.05) \times 10^{-4}$			1.2×10^{4} [b]	
 27	3558-06-3	HOAc	25.0[a,d]	1.68×10^{-6}			8.2×10^{6}	
			25.0[a]	2.06×10^{-8}			1.0[b]	
 28	63703-40-2	HOAc	100.0	$(2.21 \pm 0.08) \times 10^{-4}$	26.8	−3.8		
			120.0	$(1.47 \pm 0.08) \times 10^{-4}$				
 29	840-90-4	HOAc	25.0[a,e]	8.3×10^{-8}			3.9×10^{5}	
 30	63703-41-3	HOAc	25.0	$(3.06 \pm 0.05) \times 10^{-5}$	22.8	−2.6	1.5×10^{3} [b]	
			60.0	$(1.97 \pm 0.02) \times 10^{-3}$				
 31	959-42-2	HOAc	25.0[a,e]	2.3×10^{-5}			1.1×10^{8}	

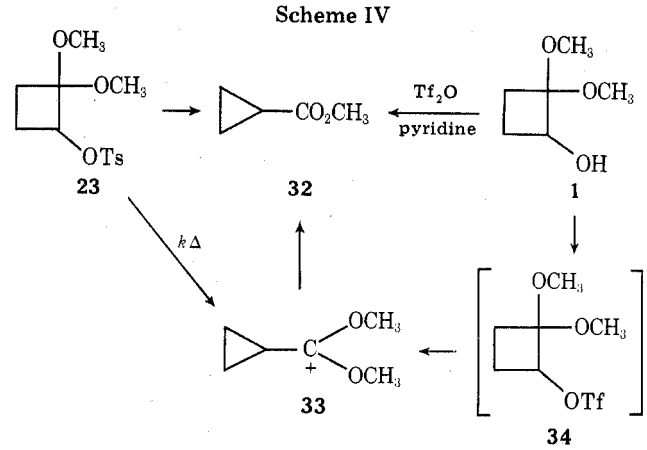
[a] Extrapolated value. [b] For the tosylate derivative assuming $k_{ROTf}/k_{ROTs} = 10^{5}$. [c] Reference 18. [d] Reference 19. [e] Reference 20.

erence to *endo*-hydride migration, leading ultimately to **11** rather than **22.** This reaction provides yet another example of the avoidance of *endo*-2,3-hydride migration in a norbornyl system.

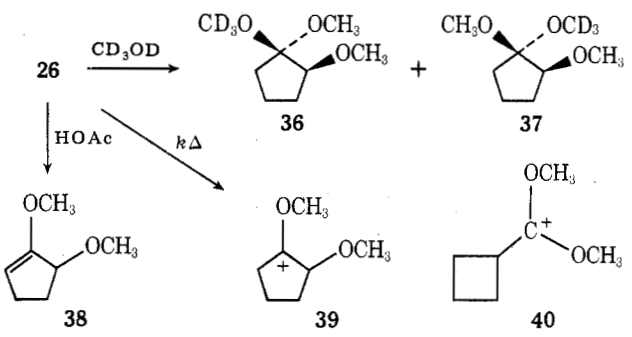
Solvolysis of α-Hydroxy Ketal Derivatives. Hydroxy alcohols **1** and **2** were converted to the tosylate derivatives **23** and **25,** respectively, and **2, 4** and **5** were converted to the corresponding triflates. Solvolytic rate data are given in Table III. Immediately apparent are the decreased rates (10^{2} to 10^{5}) of solvolysis of the α-ketal derivatives relative to their unsubstituted analogues. This rate retardation is a result of the electron-withdrawing α-dimethoxy grouping adjacent to the ionization center. Product analyses were therefore carried out to evaluate the effect of increasing inductive destabilization on neighboring-group participation as reflected by rearranged products.

Solvolysis of 2,2-dimethoxycyclobutyl tosylate (**23**) in 70% aqueous acetone gave only methyl cyclopropanecarboxylate (**32**). The same product was observed in the pyrolysis of 1-bromo-2,2-dimethoxycyclobutane[4a] and was suggested to arise via a concerted process.[4b] In the solvolytic reaction, the rearranged ester **32** suggests an assisted ionization leading to **33.** Attempts to prepare the triflate derivative of **1** by reaction with trifluoromethanesulfonic anhydride in pyridine gave only ester **32** apparently by the in situ ionization of **34.** No products

Scheme IV



Scheme V



of retained cyclobutyl structure or homoallylic rearrangement products were produced.

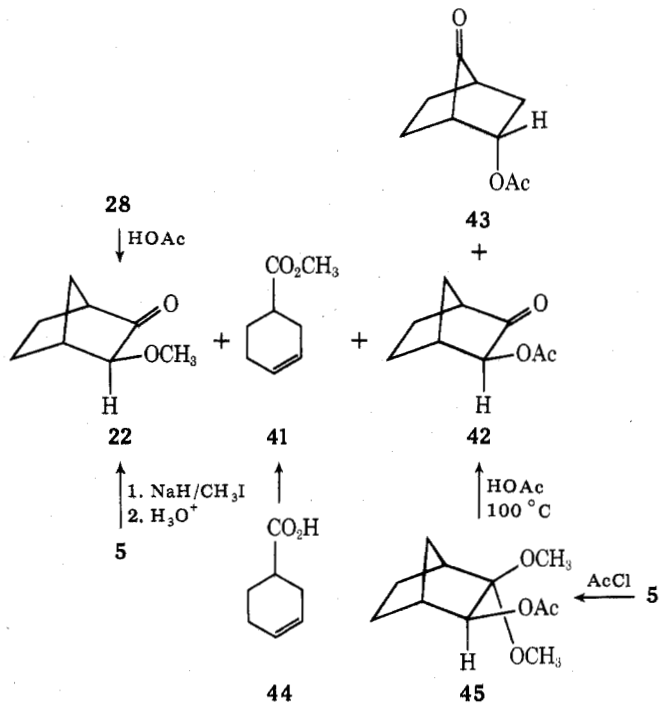
Despite the expected stability of cation **33**, the rate of solvolysis of **23** is less than cyclobutyl tosylate **24**. Apparently, the transition state for ionization of **23** still reflects some of the inductive effect of the dimethoxy grouping. The relative stability of **33** vs. that of the much debated intermediate in the solvolysis of cyclobutyl tosylate **24**[11] is not the only factor influencing the rate of solvolysis of **23**. However, by any method of estimation, there is still substantial anchimeric assistance in the ionization of **23**.

In order to determine whether an analogous ring contraction could occur in a cyclopentyl system, the tosylate and triflate derivatives **25** and **26** of alcohol **2** were prepared. Methanolysis of **25** gave 1,1,2-trimethoxycyclopentane (**35**) which could be prepared independently by treatment of **2** with sodium hydride followed by methyl iodide. However, the origin of the methoxy groups in **35** was uncertain due to the high temperature necessary to methanolize **25**. Triflate **26** was therefore prepared. Methanolysis in methanol-d_4 gave **36** and **37** with the deuterium incorporated in the ketal function (Scheme V). The structural assignments on **36** and **37** were based on NMR. A mixture of **36** and **37** showed a three-proton methoxy signal at δ 3.29, as well as signals at δ 3.14 and 3.21, having a combined integral of three protons. The signal at δ 3.29 is assigned to the ether methoxy group. The signals at δ 3.14 and 3.21 (ketal protons) exchange rapidly when 1,1,2-trimethoxycyclopentane is treated with methanol-d_4 and a trace of toluenesulfonic acid, while the signal at δ 3.29 does not exchange.

The isolation of **36** and **37** shows that methoxy group migration giving **39** must have occurred. The k_s process does not appear to be important in this system. A similar methoxy participation process is suggested to occur in the acetolysis of **26** which gave exclusively enol ether **38**. Apparently, the driving force for ring contraction is insufficient in **26** to produce **40**, despite its expected stability. The increased demand for stabilization in the solvolysis of **26** results in methoxyl participation giving **39** rather than σ participation giving **40**.

Attention was next turned to the bicyclo[2.2.1]heptyl system. Solvolysis of triflate **28** gave *exo*-2-methoxynorcamphor (**22**), 4-carbomethoxycyclohexene (**41**), and keto acetates **42** and **43**. The structure of **22** was based on its spectral properties as well as its independent synthesis, as shown in Scheme VI. Methylation of alcohol **5** followed by hydrolysis gave authentic **22**. Ester **41** could be prepared independently from the acid **44**. The structure of keto acetate **42** was inferred from its spectral properties and proven by its alternate preparation from **5**. Conversion of **5** to the corresponding acetate **45** followed by treatment of **45** under the reaction conditions resulted in its complete conversion to **42**. The structure of **43** was inferred from its spectral properties. Spectral comparison with *exo*-2-acetoxy-7-ketonorbornane showed the solvolysis

Scheme VI

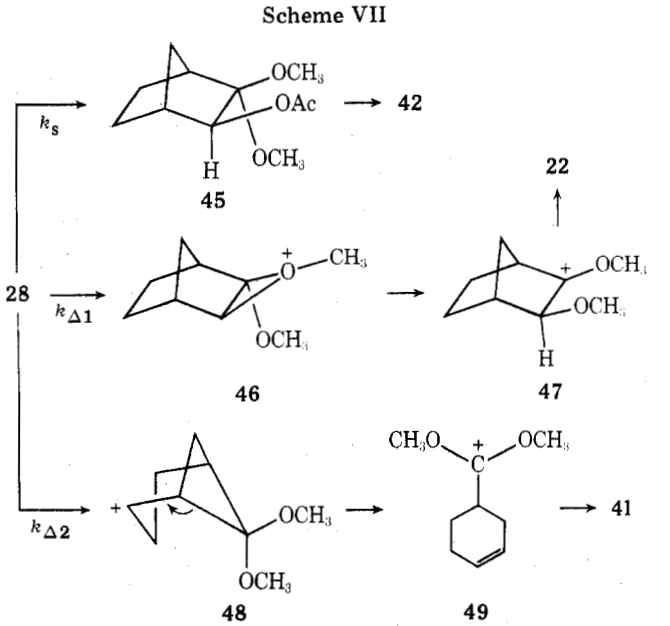


product to be different and therefore, in all probability, the endo epimer.

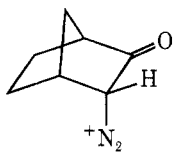
Keto acetate **42** is suggested to arise via ketal acetate **45** which has been shown to deketalize under the reaction conditions. The source of **45** may be a solvent-assisted process or may involve a classical 2-norbornyl cation, which captures solvent from the exo side. The *endo*-2-acetoxy-7-ketonorbornane (**43**) would be a Wagner–Meerwein rearrangement product of such a cation. Such products have been seen in the solvolysis of 7,7-dimethoxy-2-norbornyl tosylate.[12]

A second process is a methoxy-assisted pathway ($k_{\Delta 1}$) which leads to **47**[13] and ultimately to **22**. This 1,2 type of methoxy participation in solvolytic displacement reactions is a well-documented phenomenon.[14] However, such participation usually leads to onium-type ions.[14b,c] The fact that complete migration occurs to give **47** as an intermediate can be attributed to the cationic stabilizing influence of the second methoxy group.

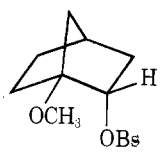
Scheme VII



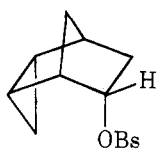
Perhaps the most unusual process which **28** undergoes involves the rare case of C_1–C_7 bond participation ($k_{\Delta 2}$) and resultant migration of C_7. Such processes are quite infrequent in the norbornyl system and occur usually when the intermediate is greatly stabilized or the demand for stabilization in the cationic intermediate is enormous. Examples of such participation include the acid-catalyzed decomposition of diazonorcamphor via **50**,[15] and the solvolyses of **51**[16] and **52**.[17] The deamination of **53** also results in some C_1–C_7 migration.[8]



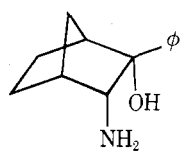
50



51



52

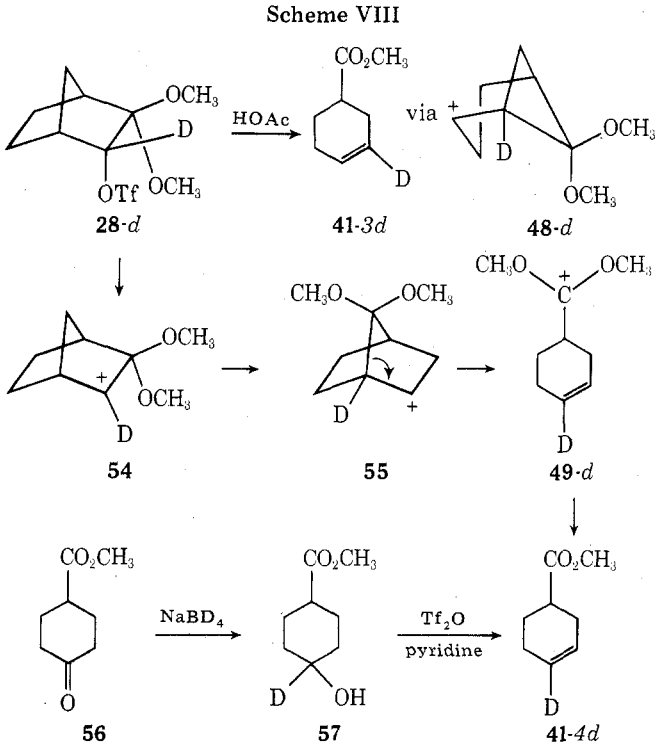


53

The C_1–C_7 bond participation in the solvolysis of **28** probably reflects the enormous demand for stabilization induced by the dimethoxy grouping. Such C_1–C_7 participation is consistent with increased participation as a function of increased electron demand. Fragmentation of the indicated bond in **48** (which may be in concert with C_1–C_7 participation) leads to **49** and ultimately to the monocyclic ester, methyl cyclohex-3-enecarboxylate (**41**).

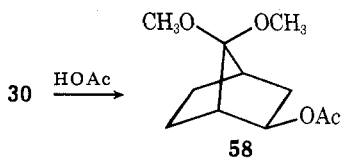
An alternative mechanism that must also be considered for the formation of methyl cyclohex-3-enecarboxylate (**41**) is shown in Scheme VIII. Wagner–Meerwein rearrangement of a classical ion generated from **28** followed by fragmentation of the C_1–C_7 bond of such a rearranged cation could lead in principle to **41**. This mechanism has been *ruled out* as a source of **41**. Solvolysis of **28**-*d* gave exclusively **41**-*3d*, which is consistent with the $k_{\Delta 2}$ process. The Wagner–Meerwein rearrangement–fragmentation mechanism predicts formation of **41**-*4d*.

Scheme VIII



The assignment of the position of the deuterium in the solvolysis product of **28**-*d* was made by ^{13}C NMR spectroscopy. Ester **41** showed olefinic ^{13}C signals at δ 124.9 and 126.4 (vs. Me_4Si). The solvolysis product showed only a signal at δ 126.4. An authentic sample of **41**-*4d* was prepared by sodium borodeuteride reduction of ketone **56**. Elimination with triflic anhydride in pyridine gave **41**-*4d*. The ^{13}C spectrum of **41**-*4d* showed only the C_3 olefinic signal at δ 124.9. (The unenhanced C_4 triplet does not appear under the spectral conditions.) The infrared spectrum of **41**-*4d* is also significantly different from that of the solvolysis product. Hence, the structure of the solvolysis product must be **41**-*3d*. Ester **41** therefore cannot arise by the Wagner–Meerwein rearrangement–fragmentation mechanism of Scheme VIII.

Solvolysis of triflate **30** gave, as expected, a product of Wagner–Meerwein rearrangement, ketal acetate **58**. The



58

similarity of this product with those observed in the solvolysis of 7,7-dimethoxy-*exo*-2-norbornyl tosylate[12] suggests a similar cationic intermediate. The chemistry of this intermediate has been discussed. The major effect of the dimethoxy grouping in **30** is a large inductive rate retardation with no resultant new or unusual processes.

Experimental Section

NMR spectra were recorded on a Varian A-60A or XL-100 spectrometer. Mass spectra were recorded on an AEI Scientific Apparatus MS902 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 455 or Infracord spectrometer.

2,2-Dimethoxycyclobutanol (1). Dry methanol (76 mL) was added to 50 g of 1,2-bis(trimethylsiloxy)cyclobutene, which was prepared by the procedure of Bloomfield.[1c] After refluxing under nitrogen for 6.5 h, 50 mL of solvent was removed at reduced pressure. More dry methanol (50 mL), 30.9 g of trimethyl orthoformate, and 50 mg of *p*-toluenesulfonic acid monohydrate were added, and the solution was stirred for 4 h. Acid was neutralized with 14 mg of sodium methoxide and the solvents were removed at 140 mm through a Vigreux column. The residue was distilled to give 22.5 g (79%) of **1**, previously prepared in a similar manner.[4c] Hydroxy ketal **1** had the following properties: bp 43–45 °C (1.4 mm); NMR (CCl_4) δ 3.8–4.2 (1 H, m), 2.9–3.4 (7 H, m with sharp s at 3.18 and 3.26, 1 H exchanges with D_2O), 1.0–2.3 (4 H, m).

2,2-Dimethoxycyclopentanol (2). 1,2-Bis(trimethylsiloxy)cyclopentene (107 g), prepared by the method of Ruhlmann,[16] was dissolved in 570 mL of dry methanol, and the solution was refluxed for 6 h. Solvents were removed under vacuum and the residue was distilled to give a mixture of acyloin and ketal (about 60% ketal). To complete ketalization, 5 g of this mixture was dissolved in 10 mL of dry methanol and 2.2 mL of trimethyl orthoformate and 4 mg of *p*-toluenesulfonic acid monohydrate was added. After stirring at 25 °C for 30 min, the acid was neutralized with sodium methoxide and the solvents were removed by vacuum distillation. The residue was distilled to give 5 g of **2**: bp 64–66 °C (4.5 mm); NMR (CCl_4) ν 3.7–4.0 (1 H, m), 3.28 (3 H, s), 3.19 (3 H, s), 2.21 (1 H, s exchanges with D_2O), 1.3–2.2 (6 H, m); mass spectroscopic molecular weight, 146.0908 (calcd for $C_7H_{14}O_3$, 146.0943).

2,2-Dimethoxycyclohexanol (3). 2-Hydroxycyclohexanone dimer (Aldrich Chemical Co.) (0.50 g) was heated to the melting point in a sealed tube and the liquid monomer was added to 0.58 g of trimethyl orthoformate and 5 mL of dry methanol. A small crystal of *p*-toluenesulfonic acid monohydrate was added and the solution was stirred for 2 h at 25 °C. Neutralization of the acid with sodium methoxide followed by distillation of solvents at 140 mm left a residue which distilled to give 0.51 g (73%) of **3**: bp 66–68 °C (2 mm); NMR (CCl_4) δ 3.57–3.82 (1 H, m), 3.16 (6 H, s), 1.0–2.1 (9 H, m, 1 H exchanges with D_2O); mass spectroscopic molecular weight, 160.1096 (calcd for $C_8H_{16}O_3$, 160.1099).

2,3-Bis(trimethylsiloxy)bicyclo[2.2.1]hept-2-ene. Sodium (29.0 g) was dispersed in 1.5 L of refluxing toluene and 137 g of chlorotrimethylsilane was added. *cis*-1,3-Dicarbomethoxycyclopentane (42.6

g), prepared by Fisher esterification of the acid,[21] dissolved in 500 mL of toluene was added dropwise over 10 h. Refluxing was continued for an additional 12 h and the mixture was cooled. After filtering through celite, the toluene was removed under reduced pressure and the residue was distilled to give 50.3 g (81%) of the bis(trimethylsilyl) ether: bp 60–65 °C (0.05 mm) lit.[22] bp 65–68 °C (0.1 mm).

***endo*-2,2-Dimethoxybicyclo[2.2.1]heptan-3-ol (4).** Hydroxy ketal **4** was prepared from 1,2-bis(trimethylsiloxy)bicyclo[2.2.1]-hept-2-ene as previously described.[22]

***exo*-2,2-Dimethoxybicyclo[2.2.1]heptan-3-ol (5).** Hydroxy ketal **5** was prepared from 2-oxo-*endo*-bicyclo[2.2.1]hept-3-yl triflate as previously described.[3]

Acid-Catalyzed Rearrangements of Hydroxy Ketals. General Procedure. A known amount of hydroxy ketal was placed in a glass tube. An HCl atmosphere (vapors from 12 N HCl) was introduced and the tube was sealed. After heating in an oil bath, the tube was broken open and the products were transferred to a distillation flask with a minimum amount of anhydrous ether. The residue was distilled to give the indicated products. Products **8**, **9**, and **10** contained traces of the corresponding ketal derivatives.

Rearrangement of 1. Hydroxy ketal **1** (0.45 g) gave 0.33 g of a 3 to 1 mixture of **6** and **7**. Ketone **6** had spectra consistent with those reported[4a] and **7** had the following properties: bp 50–52 °C (15 mm); NMR (CCl_4) δ 3.5–3.8 (1 H, m), 3.26 (3 H, s), 3.20 (3 H, s), 3.11 (3 H, s), 1.2–2.2 (4 H, m); mass spectrum exhibited no parent ion.

Rearrangement of 2. Hydroxy ketal **2** (0.46 g) gave 0.32 g (89%) of **8**: bp 67–70 °C (15 mm), lit.[23] bp 68–70 °C (15 mm). Ketone **8** had spectra identical to that previously reported for 2-methoxycyclopentanone.[23]

Rearrangement of 3. Hydroxy ketal **3** (0.179 g) gave 0.124 g (87%) of **9**: bp 72–75 °C (15 mm), lit.[10] bp 72–75 °C (14 mm); IR $\nu_{C=O}$ 5.78 μm; NMR (CCl_4) δ 3.2–3.7 (4 H, m with sharp singlet at 3.30), 1.1–2.7 (8 H, m).

Rearrangement of 4. Hydroxy ketal **4** (0.454 g) gave 0.329 g (89%) of **10**: bp 71–74 °C (3.5 mm). All spectra of ketone **10** were identical to those of independently synthesized *endo*-3-methoxybicyclo-[2.2.1]heptan-2-one.

Rearrangement of 5. Hydroxy ketal **5** (0.550 g) gave 0.425 g (95%) of **11**: bp 103–108 °C (0.15 mm); NMR (CCl_4) δ 3.11 (3 H, s), 3.03 (1 H, d, J = 2.3 Hz), 0.9–2.3 (8 H, m); mass spectroscopic molecular weight, 280.1597 (calcd for $C_{16}H_{24}O_4$, 280.1674).

2,2-Dimethoxycyclobutanone (12). Methylene chloride (200 mL) was added to 25 mL of dimethyl sulfoxide (Me_2SO) under dry nitrogen and the solution was cooled to −60 °C in a dry ice–chloroform bath. Trifluoroacetic anhydride (35.8 g) was slowly added dropwise and precipitation of a white complex was observed. Ketal–alcohol **1** (15.0 g) dissolved in 15 mL of Me_2SO and 15 mL of methylene chloride was slowly added dropwise. After stirring 10 min more, 34.5 of triethylamine was added dropwise and the solution was warmed to room temperature. Water was added and the aqueous phase was extracted with three portions of ether. The combined ether extracts were washed with a minimum of water to remove the Me_2SO, dilute sodium carbonate, and brine, and dried over sodium sulfate. The solvents were removed through a Vigreux column and the residue was distilled to give 12.47 g (83%) of the desired ketone: bp 55–60 °C (20 mm); IR (neat) $\nu_{C=O}$ 5.56 μm; NMR (CCl_4) δ 3.29 (6 H, s), 2.5–3.0 (2 H, m), 1.9–2.4 (2 H, m); mass spectroscopic molecular weight, 130.0588 (calcd for $C_6H_{10}O_3$, 130.0630).

Preparation of 12-d_2. A small piece of sodium (1 mm^3) was dissolved in 12 mL of methanol-d_1. Ketone **12** (2 g) was added and the solution was heated (sealed tube) for 14 min at 87 °C. The tube was opened and the solvent was removed at 140 mm. The residue distilled only at a high pot temperature (130–150 °C) to give 1 g of partially deuterated ketone, bp 55–65 °C (14 mm). This ketone was recycled with another piece of sodium dissolved in 6 mL of methanol-d_1. After heating at 83 °C for 30 min, workup gave 0.69 g of the fully deuterated ketone. The deuterated ketone had the following spectral properties: NMR (CCl_4) δ 3.33 (3 H, s), 2.15 (1 H, br s).

Preparation of 1-d_2. Lithium aluminum hydride (0.4 g) was suspended in 4 mL of anhydrous ether, and 0.65 g of 12-d_2 dissolved in 3 mL of anhydrous ether was slowly added dropwise. After stirring at an ambient temperature for 10 min, 0.4 mL of water, 0.4 mL of 15% aqueous sodium hydroxide, and 1.2 mL of water were added in that order. The mixture was filtered and the ether phase was dried over sodium sulfate. Solvents were removed through a Vigreux column and the residue was distilled to give 0.54 g (82%) of 1-d_2: bp 65–68 °C (14 mm); NMR (CCl_4) δ 4.04 (1 H, br s), 3.28 (3 H, s), 3.20 (3 H, s), 2.7–3.1 (1 H, m, exchanges with D_2O), 1.85–2.20 (1 H, m), 1.30–1.70 (1 H, m).

Rearrangement of 1-d_2. The deuterated hydroxy ketal 1-d_2 (0.239 g) was sealed in a glass tube containing HCl vapors as previously described. After heating at 110 °C for 15 min, the residue was distilled giving 0.128 g of a mixture of deuterated **6** and **7** which were separated by preparative gas chromatography on 6 ft, 5% SE 30 on chromosorb G (column A). Deuterated **6** showed equal integrations for protons at C-3 and C-4 by using 100-MHz NMR which cleanly separated the two methylene multiplets: 100-MHz NMR (CCl_4) δ 1.3–2.0 (2 H, m, C-3), 2.0–2.5 (2 H, m, C-4), 3.21 (3 H, s), 4.0–4.25 (1 H, m).

Preparation of 4-*d*. 2,3-Bis(trimethylsiloxy)bicyclo[2.2.1]hept-2-ene (1.88 g) was refluxed in 8 mL of methanol-d_1 for 2.5 h. The solvent was removed by aspirator and the residue was dissolved in 5 mL of methanol-d_1 and 4 mL of trimethyl orthoformate, and 3 mg of *p*-toluenesulfonic acid monohydrate was added. After stirring at room temperature for 35 min, the acid was neutralized with sodium methoxide and the solvents were removed at reduced pressure. The residue was dissolved in 7 mL of methanol and after 5 min the solvent was again removed. After repeating the same procedure with another 7 mL of methanol, the residue was distilled to give 1.13 g (94%) of 4-*d*: bp 64 °C (1.1 mm); NMR (CCl_4) δ 3.25 (3 H, s), 3.10 (3 H, s), 2.1–2.5 (3 H, m, 1 H exchanges with D_2O), 0.9–1.9 (6 H, m).

Kinetics of Acid-Catalyzed Rearrangement of 4 and 4-*d*. Di-*n*-propyl ether was dried by distillation from lithium aluminum hydride. Dry hydrochloric acid gas was bubbled through the solvent and the resulting solution was diluted to approximately 0.05 M in hydrochloric acid. The exact concentration of hydrochloric acid was determined by pipetting 1 mL of the solution into 2 mL of water and titrating the aqueous phase to pH 7 with standard sodium hydroxide while vigorously stirring the system. The rate of disappearance of **4** (or 4-*d*) was monitored by gas chromatography using naphthalene as internal standard. In a typical run, 48.4 mg of **4** and 8.1 mg of naphthalene were diluted to 1 mL with 0.057 M hydrochloric acid in di-*n*-propyl ether. Nine aliquots were sealed in glass tubes and withdrawn at appropriate times. Analysis consisted of breaking open the tubes, addition of 20 μL of triethylamine followed by vigorous shaking, and addition of 100 μL of 0.3 M sodium carbonate. The organic phase was separated and dried over anhydrous sodium sulfate and immediately analyzed on 5 ft, 5% SE 30 on chromosorb G (column B).

3,3-Dimethoxybicyclo[2.2.1]heptan-2-one. This ketone was prepared by Sarett oxidation of **4** as previously reported.[22]

Preparation of 17. 3,3-Dimethoxybicyclo[2.2.1]heptan-2-one (1.5 g) was dissolved in 10 mL of anhydrous ether and cooled to 0 °C under dry nitrogen. Methyl lithium (6.3 mL of 1.84 M) was slowly added dropwise. After warming to 25 °C, water was carefully added and the phases were separated. The ether phase was washed with brine and dried over sodium sulfate. Removal of solvents and distillation of the residue gave 1.58 g (96%) of **17**: bp 75–80 °C (1.6 mm); NMR ($CDCl_3$) δ 3.32 (3 H, s), 3.28 (3 H, s), 1.0–2.5 (11 H, m with sharp s at 1.31); mass spectroscopic molecular weight, 186.1268 (calcd for $C_{10}H_{18}O_3$, 186.1256).

Preparation of 18. 3,3-Dimethoxybicyclo[2.2.1]heptan-2-one (0.54 g) was dissolved in 2 mL of anhydrous ether, and phenyllithium (5.3 mL of 1.8 M) was added dropwise at 0 °C. After stirring at 25 °C for 10 min, a workup procedure identical to that used for the preparation of **17** gave 0.69 g (86%) of **18**: bp 105–110 °C (0.1 mm); NMR (CCl_4) δ 7.0–7.8 (5 H, m), 3.23–3.40 (4 H, overlapping singlets at 3.29 (3 H) and 3.33, 1H (at 3.33) exchanges with D_2O), 0.7–2.7 (11H, m with sharp s at 2.56); mass spectroscopic molecular weight, 248.1413 (calcd for $C_{15}H_{20}O_3$, 248.1412).

Preparation of 23. Pyridine (10 mL) was cooled to 0 °C and 1.5 g of **1** was added. *p*-Toluenesulfonyl chloride (2.6 g) was dissolved with stirring and the solution was stored at −5 °C for 48 h. Ether (40 mL) and ice-cold water (20 mL) were added, and the phases were separated. The ether extract was washed consecutively with cold water, cold dilute hydrochloric acid until acidic to litmus, and brine, and dried over sodium sulfate. Solvent was removed on a rotary evaporator leaving a white solid (3.09 g) (95%) of **23**. A pure sample was obtained by recrystallization from hexane: mp 61.5–62.5 °C; NMR ($CDCl_3$) δ 7.2–8.1 (4 H, m), 4.6–5.0 (1 H, m), 3.27 (3 H, s), 3.15 (3 H, s), 1.4–2.6 (7 H, m with sharp s at 2.48).

Preparation of 25. The preparation of **25** was analogous to the preparation of **23**. Ten milliliters of pyridine, 1.57 g of *p*-toluenesulfonyl chloride, and 1.0 g of **2** were used. After storing at −5 °C for 12 h, workup gave a clear viscous oil which crystallized after several days at −5 °C but was unstable neat at 25 °C. Yield of crude **25** was 1.23 g (60%): NMR ($CDCl_3$) δ 7.2–8.0 (4 H, m), 4.4–4.6 (1 H, m), 3.16 (6 H, s), 2.43 (3 H, s), 1.3–2.1 (6 H, m).

Preparation of Triflates. General Procedure. A given amount of pyridine was cooled to 0 °C and 1.5–2.0 equiv of trifluoromethanesulfonic (triflic) anhydride was added slowly dropwise with stir-

ring. A white solid precipitate formed and was dissolved by warming the mixture to near 20 °C. After recooling the solution to 0 °C, 1 equiv of the alcohol was added slowly dropwise with stirring and the resulting solution was stored at −5 °C for the noted times. Workup consisted of a threefold dilution with ether, extraction with ice-cold water, ice-cold dilute hydrochloric acid until the aqueous phase was acidic, and brine, and drying over sodium sulfate. After removal of the solvent, distillation under high vacuum gave the triflate products, which were unstable at room temperature in air.

Attempted Preparation of 2,2-Dimethoxycyclobut-1-yl Triflate. Nine grams of pyridine, 2.8 g of triflic anhydride, and 1.09 g of **1** gave, after 12 h at −5 °C, no triflate, and the only product present was identified as methylcyclopropane carboxylate by comparison of its infrared spectrum with an authentic sample.

Preparation of 26. Ten milliliters of pyridine, 2.24 g of triflic anhydride, and 0.6 g of **2**, after 1.5 h at −5 °C, rapid workup and rotary evaporation of the solvent gave 0.84 g of **26** which was stable at 0 °C only for about 1 day: NMR (CCl_4) δ 4.9–5.1 (1 H, m), 3.32 (3 H, s), 3.23 (3 H, s), 1.4–2.6 (6 H, m).

Preparation of 28. Eleven milliliters of pyridine, 2.6 g of triflic anhydride, and 1.0 g of **4** after reaction for 1 h and distillation give 1.54 g (87%) of **28:** bp 67–69 °C (0.15 mm); NMR (CCl_4) δ 4.78 (1 H, d, J = 5 Hz), 3.25 (3 H, s), 3.19 (3 H, s), 2.3–2.8 (3 H, m), 1.1–2.0 (6 H, m).

Preparation of 30. Ten milliliters of pyridine, 1.7 g of triflic anhydride, and 0.71 g of **5** gave after distillation at less than 0.07 mm 1.16 g (92%) of **30:** NMR (CCl_4) δ 4.47 (1 H, d, J = 2.5 Hz), 3.31 (3 H, s), 3.23 (3 H, s), 2.3–2.6 (2 H, m), 1.1–2.25 (6 H, m).

Kinetics Procedure. The kinetics procedure for runs in acetic acid is described elsewhere,[24] as is the kinetics procedure in 70% aqueous acetone.[25]

Solvolysis of 23. Product Analysis. Tosylate **23** (0.497 g) and 0.43 g of triethylamine were dissolved in 12 mL of 70% aqueous acetone and heated (sealed tube) at 100 °C for 18 h. A standard workup and distillation gave one product homogeneous by gas chromatographic analysis at 60 °C on 6 ft, 10% XE 60 on Chromosorb P which was identical by infrared and NMR spectral comparison to methylcyclopropane carboxylate. An authentic sample was prepared by esterification of the acid by standard techniques. The yield of methylcyclopropane carboxylate was 86% as determined in a separate run by gas chromatography, using di-*n*-butyl ether as an internal standard.

Solvolysis of 26 in Methanol-d_4. Product Analysis. Crude triflate **26** (0.2 g) and 0.15 g of triethylamine were dissolved in 2 mL of methanol-d_4 and the solution was heated (sealed tube) at 30 °C for 50 min. A standard workup and distillation gave 0.03 g of **36** and **37:** bp 60–70 °C (14 mm); NMR (CCl_4) δ 3.1–3.5 (7 H, m with 3 sharp s at 3.14, 3.21, 3.29; relative areas 0.61:0.39:1), 1.2–2.1 (6 H, m).

Solvolysis of 26 in Acetic Acid. Product Analysis. Crude triflate **26** (0.29 g) and 0.14 g of sodium acetate were dissolved in 7 mL of acetic acid and the solution was heated (sealed tube) at 55 °C for 30 min. Workup consisted of dilution with ether and extraction with water, dilute sodium carbonate until basic, and brine, and drying over sodium sulfate. Solvents were distilled through a Vigreux column and the residue was distilled and analyzed by gas chromatography which showed one major (~80%) product and two minor unidentified products. For the major product **38:** IR (neat) $\nu_{C=C}$ 6.04 μm; NMR (CCl_4) δ 4.5–4.7 (1 H, m), 3.95–4.25 (1 H, m), 3.59 (3 H, s), 3.30 (3 H, s), 1.4–2.5 (4 H, m); mass spectroscopic molecular weight, 128.0853 (calcd for $C_7H_{12}O_2$, 128.0837).

Hydrolysis of 38. Enol ether **38** (30 mg) was dissolved in 0.5 mL of dilute hydrochloric acid, and methanol was added to cause complete solution. After heating at 50 °C for 5 min, the solution was saturated with salt and extracted with ether. The ether extract was dried over sodium sulfate and solvents were removed by aspirator. The infrared spectrum of the residue indicated methanol and **8** to be present.

Solvolysis of 28. Product Analysis. The procedure was identical to that used for **26.** Acetic acid (31 mL), 0.71 g of **28,** 0.31 mL of acetic anhydride, and 0.28 g of sodium acetate, after heating at 120 °C for 1.75 h and distillation, gave 270 mg of a mixture of **22, 41, 42,** and **43** which were separated by preparative gas chromatography on column A. Structural assignments of **22, 41,** and **43** were confirmed by independent syntheses. Product **43** showed a carbonyl band at 5.57 μm, but did not exhibit other spectral properties consistent with authentic *exo*-2-acetoxybicyclo[2.2.1]heptan-7-one and was assigned the endo structure **43.** Cyclohex-3-enecarboxaldehyde was oxidized to cyclohex-3-enecarboxylic acid as previously described.[26] An acid-catalyzed esterification gave authentic **41.** Yields of **22, 41, 42,** and **43** were 18, 23, 31, and 18%, respectively, as determined in a separate run by gas chromatography using column B and naphthalene as an internal standard.

Methylation of 5. Sodium hydride (0.1 g) was suspended in 5 mL of tetrahydrofuran and 0.5 g of **5** was added at 25 °C. The mixture was refluxed under nitrogen for 15 min. After cooling, an excess of methyl iodide was added and the mixture was refluxed for 1 h. The mixture was again cooled and 3 mL of water was added slowly. Ether was added and the phases were separated. The ether layer was washed with brine and dried over sodium sulfate. The solvent was removed through a Vigreux column, with the last traces by aspirator. The residue was distilled to give 0.44 g of 2,2,3-trimethoxybicyclo[2.2.1]heptane: bp 63 °C (1.7 mm); NMR (CCl_4) δ 3.30 (3 H, s), 3.24 (3 H, s), 3.13 (3 H, s), 2.90 (1 H, d, J = 2.5 Hz), 0.9–2.4 (8 H, m).

Preparation of 22. Three milliliters of 5% aqueous sulfuric acid was added to 0.32 g of 2,2,3-trimethoxybicyclo[2.2.1]heptane. The heterogeneous mixture was stirred at 25 °C for 12 h. Ether was added and the phases were separated. The ether phase was washed with saturated sodium carbonate and brine, and dried over sodium sulfate. Solvent was removed through a Vigreux column and the residue was distilled to give 170 mg (71%) of **22:** bp 53–55 °C (4.7 mm); IR (neat) $\nu_{C=O}$ 5.69 μm; NMR (CCl_4) δ 3.41 (3 H, s), 2.89 (1 H, d, J = 2.5 Hz), 1.1–2.6 (8 H, m); mass spectroscopic molecular weight, 140.0815 (calcd for $C_8H_{12}O_2$, 140.0837).

Preparation of 45. A solution of 0.48 g of **5** in 7 mL of pyridine was cooled to 0 °C and 0.42 g of acetyl chloride was added slowly dropwise. After stirring at 25 °C for 35 min, the solution was diluted with ether and extracted with water, dilute hydrochloric acid until acidic, and brine, and dried over sodium sulfate. Removal of solvents and distillation of the residue gave 0.48 g (84%) of **45:** bp 79–81 °C (1.9 mm); IR (neat) $\nu_{C=O}$ 5.74 μm; NMR (CCl_4) δ 4.40 (1 H, d, J = 2.5 Hz), 3.18 (6 H, s), 0.9–2.5 (11 H, m with sharp s at 1.99).

Acetolysis of 45. Eleven milliliters of 0.1 M sodium acetate–acetic acid was added to 0.364 g of **45** and after heating (sealed tube) at 100 °C for 15.75 h the contents were diluted with ether, and water was added. The aqueous phase was extracted with another portion of ether and the combined ether extracts were washed with dilute sodium carbonate and brine and dried over sodium sulfate. Removal of solvent afforded a residue which was distilled to give **42,** 0.253 g (88%): bp 57–59 °C (0.08 mm); IR (neat) $\nu_{C=O}$ 5.65 and 5.74 μm; NMR (CCl_4) δ 4.44 (1 H, d, J = 2.5 Hz), 2.4–2.7 (2 H, m), 1.2–2.3 (9 H, m with sharp s at 2.04); mass spectroscopic molecular weight, 168.0818 (calcd for $C_9H_{12}O_3$, 168.0786).

Solvolysis of 30. Product Analysis. The procedure was identical to that used for **26** and **28.** Triflate **30** (0.0776 g), 0.03 mL of acetic anhydride (0.03 mL), and 0.2 M sodium acetate–acetic acid (3 mL) at 100 °C for 10 min gave 28.3 mg (52%) of the previously reported **58.**[12] Longer reaction times (15 h) lead to formation of nortricyclanone and *exo*-2-acetoxybicyclo[2.2.1]heptan-7-one.

Solvolysis of 28-*d*. Deuterated **28**-*d* (prepared in a manner analogous to **28** from 4-d) was solvolyzed in acetic acid using the procedure for product analysis of **28.** Preparative gas chromatographic separation of the products gave pure **41**-*3d*: ^{13}C NMR ($CDCl_3$) δ 176.0, 126.4 (C-4), 51.5, 39.2, 27.4, 25.1, 24.3, C-3 was not observable; IR (neat) $\nu_{C=O}$ 5.73 μm, $\nu_{C=C}$ 16.9 μm, ν_{C-D} 4.41 μm; mass spectroscopic molecular weight, 141.0895 (calcd for $C_8H_{11}DO_2$ 141.0900).

Preparation of 57. Methyl 4-cyclohexanonecarboxylate (**56**) (0.897 g) was dissolved in 5 mL of dry methanol containing one drop of triethylamine. Sodium borodeuteride (0.124 g) was added slowly to the solution at 5 °C and the reaction was allowed to warm to 25 °C. After stirring for 2 h, the solution was added to 0.8 g of acetic acid in 3 mL of water cooled in an ice bath. After 2 min, the aqueous phase was extracted with 2–10-mL portions of ether, and the combined ether extracts were washed with dilute sodium carbonate and brine and dried over sodium sulfate. The solvent was removed through a Vigreux column and the residue was distilled to give 0.710 g (78%) of **57:** bp 71–76 °C (0.08 mm); IR (neat) ν_{OH} 2.85 μm, $\nu_{C=O}$ 5.75 μm; NMR (CCl_4) δ 3.58–3.75 (3 H, overlapping sharp s at 3.29 and 3.31), 2.75 (1 H, s, exchanges with D_2O), 0.9–2.6 (9 H, m); mass spectroscopic molecular weight, 159.1032 (calcd for $C_8H_{13}DO_3$, 159.1004).

Preparation of 41-*4d*. Deuterated alcohol **57** (0.600 g) was dissolved in 6 mL of pyridine and the solution was cooled to 0 °C in an ice–water bath. Triflic anhydride (1.27 g) was added slowly dropwise, the reaction was stored, at −5 °C for 35 min. The solution was diluted with 10 mL of ether and extracted with water. The water extract was extracted with one more portion of ether and the combined ether extracts were washed with dilute hydrochloric acid until acidic and brine, and dried over sodium sulfate. The solvent was removed through a Vigreux column, and the residue was distilled to give 0.300 g (56%) of **41**-*4d*: bp 72–73 °C (12 mm); IR (neat) $\nu_{C=O}$ 5.73 μm, ν_{C-D} 4.41 μm, $\nu_{C=C}$ 17.0 μm; NMR ($CDCl_3$) δ 5.6–5.9 (1 H, m), 3.70 (3 H, s), 1.4–2.8 (7 H, m); fully decoupled ^{13}C NMR ($CDCl_3$) δ 176.0, 124.9

(C-3), 51.5, 39.2, 27.4, 25.1, 24.3; C-4 was not observable; mass spectroscopic molecular weight, 141.0891 (calcd for $C_8H_{11}DO_2$, 141.0900). Ester **41** showed ^{13}C NMR ($CDCl_3$) δ 176.0, 126.4 (C-4), 124.9 (C-3), 51.5, 39.2, 27.4, 25.1, 24.3; IR (neat) $\nu_{C=O}$ 5.73 μm, $\nu_{C=C}$ 15.1 μm.

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Registry No.—**1**-d_2, 63703-42-4; **4**-*d*, 63703-43-5; **6a**, 63703-44-6; **6b**, 63703-45-7; **7**, 63703-46-8; **9**, 7429-44-9; **11**, 63703-47-9; **12**, 63703-48-0; **12**-d_2, 63703-49-1; **17**, 63703-50-4; **18**, 63703-51-5; **22**, 63329-06-9; **28**-*d*, 63703-52-6; **36**, 63703-53-7; **37**, 63703-54-8; **38**, 61860-73-9; **41**, 6493-77-2; **41**-*3d*, 63703-55-9; **41**-*4d*, 63703-56-0; **42**, 63703-57-1; **45**, 63703-58-2; **56**, 6297-22-9; **57**, 63703-59-3; 1,2-bis(trimethylsiloxy)cyclobutene, 17082-61-0; 1,2-bis(trimethylsiloxy)cyclopentene, 6838-66-0; 2-hydroxycyclohexanone dimer, 30282-14-5; 2-hydroxycyclohexanone, 533-60-8; 2,3-bis(trimethylsiloxy)bicyclo[2.2.1]hept-2-ene, 63715-72-0; 3,3-dimethoxybicyclo[2.2.1]heptan-2-one, 35611-45-1; *p*-toluenesulfonyl chloride, 98-59-9; triflic anhydride, 358-23-6; 2,2,3-trimethoxybicyclo[2.2.1]heptane, 63703-60-6.

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Photochemical Cycloadditions of Benzonitrile to Alkenes. Factors Controlling the Site of Addition

Thomas S. Cantrell

Department of Chemistry, The American University, Washington, D.C. 20016

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The photochemical cycloaddition of benzonitrile to a diverse array of alkenes has been studied in order to determine the factors controlling the site of addition to the nitrile. The reaction course depends critically on the number and type of electron-donating groups on the alkene. Alkenes having four alkyl substituents, or two alkoxyls, or two alkyl and one alkoxyl, undergo addition to the C≡N triple bond, furnishing mainly 2-azabutadienes, together with varying amounts of their azetine precursors. With less electron-rich alkenes, i.e., those containing two or three alkyl groups, addition occurs at the 1,2 positions of the ring, furnishing 1-cyanobicyclo[4.2.0]octadienes. Both types of alkenes strongly quench benzonitrile fluorescence, indicating intermediacy of excited nitrile singlets. It is speculated that the difference in reaction sites for the two classes is the result of different sites of complexation at benzonitrile in singlet exciplexes.

Much of the vast amount of research performed during the past 15 years on the photochemical behavior of organic molecules has centered on carbonyl compounds, particularly ketones.[1] A wide array of interesting transformations have been observed, the reaction course depending on the exact structure of the ketone and upon the presence or absence of substrates or reactive solvents. In contrast, there have been very few reports on the photochemistry of nitriles and other carboxylic acid derivatives. In an early study, Buchi and colleagues showed that benzonitrile undergoes a [2 + 2] cycloaddition at the 1,2 positions of the benzene ring to certain alkenes, including 2-methyl-2-butene and ethoxyethylene, to yield 1-cyanobicyclo[4.2.0]octadienes.[2] Certain α,β-unsaturated nitriles, such as acrylonitrile,[3a] 2-cyanobutadiene,[3b] and 1-cyanocyclohexene,[3c] are reported to add alkenes across the C=C double bond and/or dimerize. Naphthonitriles have been observed to add certain alkenes at the 1,2 positions,[4a] as does naphthalene itself to acrylonitrile,[4b-d] via intermediate exciplexes. Two groups have observed [2 + 2] cycloaddition of 9-phenanthronitrile to alkenes at the 9,10 positions.[5] Since the publication of some of the present results, Yang and coworkers have very recently reported both 2-azabutadienes and azetines to be formed from benzonitrile and naphthonitriles with 2,3-dimethyl-2-butene.[6]

In a preliminary communication, it was reported that photochemically excited benzonitrile adds to certain electron-rich alkenes, such as 2,3-dimethyl-2-butene and 1,1-dimethoxy-2,2-dimethylethylene, across the cyano group to