(1.97 g, 6.90 mmol, 98%): mp 92 °C (lit.[15] mp 91-92 °C); IR (KBr) 3030, 2975, 2955, 2940, 2865, 1658, 1520-1490, 1460, 1422, 1375, 1302, 1166, 1130, 1117, 1025, 1003, 960, 941, 852, 821, 813, 728, 650, 615, 523 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.03 (s, 4 H), 2.88 (br s, 4 H), 2.30 (s, 3 H).

4,4'-Dimethyl-2,3,5,6-tetrafluorobibenzyl (5). To a solution of 2,3,4,5,6-pentafluoro-4'-methylbibenzyl (1.49 g, 5.21 mmol) in 25 mL of anhydrous ether under nitrogen was added methyllithium (3.8 mL, 1.39 M in ether) dropwise by syringe, and the mixture was refluxed for 3 h. Any remaining lithiate was carefully quenched with ammonium chloride solution (5 mL, 5%) at room temperature. The organic phase was separated and dried over anhydrous magnesium sulfate. Evaporation under reduced pressure afforded a yellow solid. Sublimation gave 4,4'-dimethyl-2,3,5,6-tetrafluorobibenzyl (1.33 g, 4.68 mmol, 90%) as white needles: mp 99 °C (lit.[15] mp 99 °C); IR (KBr) 3029, 2992, 2985, 2934, 2851, 1495, 1478, 1460, 1370, 1275, 1250, 1158, 1110, 1050, 1005, 932, 920, 877, 808, 632, 590, 510 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.06 (s, 4 H), 2.88 (br s, 4 H), 2.30 (s, 3 H), 2.21 (t, 3 h, J = 2.4 Hz); ^{13}C NMR ($CDCl_3$) δ 152.12-149.28 (m) and 139.82-137.01 (m) [J_{CF} = 245.6 Hz], 137.59 (s), 135.86 (s), 129.73-127.21 (m), and 118.06-115.21 (m) [J_{CF} = 236.6 Hz], 129.18 (s), 128.24 (s), 115.22-111.74 (m), 35.17 (s), 20.92 (s). Anal. Calcd for $C_{16}H_{10}F_4$: C, 68.08; H, 4.99; Found: C, 68.42; H, 5.36.

3'-Acetyl-4,4'-dimethyl-2,3,5,6-tetrafluorobibenzyl. Anhydrous aluminum chloride (948 mg, 7.10 mmol) was added to a solution of acetyl chloride (550 mg, 7.0 mmol) in 1,1,2,2-tetrachloroethane (15 mL) at ice-bath temperature, and 4,4'-dimethyl-2,3,5,6-tetrafluorobibenzyl (5) (1.01 g, 3.58 mmol) was added in one portion. After the mixture was stirred under nitrogen for 1 h, TLC (silica gel; hexanes/dichloromethane, 90:10) indicated a large amount of starting material remained along with product (R_f 0.38). The ice bath was removed. The reaction was quenched after 4 h, short of completion. The reaction mixture was hydrolyzed with dilute hydrochloric acid (2 ml) and washed with water (10 mL × 2) and sodium bicarbonate solution (5 mL × 2, 5%). The organic phase was dried over anhydrous magnesium sulfate and evaporated to dryness. The amorphous white solid was chromatographed on silica gel by gradient elution (hexanes/dichloromethane) and the remaining starting material (61 mg, 0.22 mmol, 6.1%) was eluted in hexanes. The acylated product was removed from the column by hexanes/dichloromethane (90:10). After evaporation of the solvents, the sample was sublimed [110 °C (0.1 mmHg)] as white needles (949 mg, 7.04 mmol, 85%): mp 75 °C (ethanol); IR (KBr) 3048, 2970, 2955, 2875, 1676, 1564, 1485, 1357, 1300, 1282, 1262, 1175, 1060, 938, 904, 885, 830, 596, 530 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.43 (br s, 1 H), 7.15 (m, 2 H), 2.93 (br s, 4 H), 2.53 (s, 3 H), 2.46 (s, 3 H), 2.22 (t, 3 H, J = 1.8 Hz); ^{19}F NMR ($CDCl_3$) 144.94-145.34 (m, 2 F), 146.73-147.14 (m, 2 F) ppm; ^{13}C NMR ($CDCl_3$) δ 201.74 (s), 138.14 (s), 137.96 (s), 136.26 (s), 132.23 (s), 131.42 (s), 129.06 (s), 34.83 (s), 29.55 (s), 24.57 (s), 21.03 (br s). (Note: fluoroaryl carbons not resolved.) Anal. Calcd for $C_{18}H_{16}F_4O$: C, 66.67; H, 4.97; F, 23.43. Found: C, 66.60; H, 5.06; F, 23.52.

The Protonated Cyclopropane Route to Bicyclic Cations

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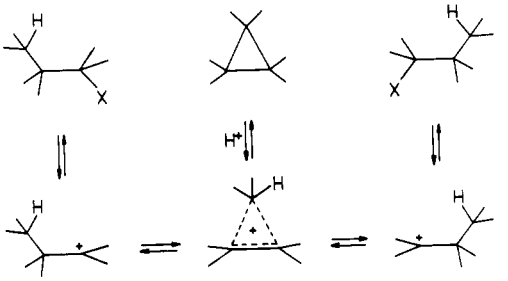
The protolytic cleavage of tricyclo[2.2.0.0^{2,6}]hexane (**3**), tricyclo[3.2.0.0^{2,7}]heptane (**10**), methyltricyclo[3.2.0.0^{2,7}]heptanes (**26**), tricyclo[3.3.0.0^{2,8}]octane (**53**), and tricyclo[3.2.1.0^{2,7}]octane (**58**) in acetic acid and in aqueous dioxane has been investigated. Protonation occurred at a specific site (**3**, **36b,d**, **58**) or competitively at two sites (**10**, **26c**, **53**), depending on the stability of the incipient carbocations. Product distributions and label redistributions, where applicable, were in good to excellent agreement with previous solvolytic studies. We conclude that the protonated cyclopropane and σ routes are equivalent in generating bridged carbocations. Edge-protonated cyclopropanes play a minor role, if any, in product formation. Stereoselectivity appears to be an intrinsic property of the cationic intermediates, largely independent of the specific orientation of their counterions.

Reactions in which carbocations undergo 1,2 alkyl shifts are common and have long been studied.[1] In considering possible intermediates and transition states for the Wagner-Meerwein rearrangement, one is virtually required to invoke structures containing three-membered rings with seven substituent atoms or groups (alkyl-bridged ions). Such cations might arise from the addition of a proton to a cyclopropane ring (Scheme I). Protonated cyclopropanes are well-established species, both experimentally and theoretically.[2,3] The stereochemistry and kinetics of the acid-induced ring opening of cyclopropanes have been

Scheme I



examined extensively.[3,4] The data indicate that proton transfer is rate determining and that the reaction proceeds toward the more stable carbocation. The products are formed in major extent by capture of the protonated

(1) Recent reviews include the following: (a) Shubin, V. G. *Top. Curr. Chem.* **1984**, *116*, 267. (b) Saunders, M.; Chandrasekhar, J.; Schleyer, P. v. R. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic: New York, 1980; Vol. 1, p 1. (c) Kirmse, W. *Top. Curr. Chem.* **1979**, *80*, 125.

(2) For reviews, see: (a) Saunders, M.; Vogel, P.; Hagen, E. L.; Rosenfeld, J. *Acc. Chem. Res.* **1973**, *6*, 53; (b) Lee, C. C. *Prog. Phys. Org. Chem.* **1974**, *7*, 129. (c) Fry, J. L.; Karabatsos, G. J. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1970; Vol. II, Chapter 14; (d) Collins, C. J. *Chem. Rev.* **1969**, *69*, 543.

(3) For a comprehensive list of references, see ref 4a.

(4) (a) Wiberg, K. B.; Kass, S. R. *J. Am. Chem. Soc.* **1985**, *107*, 988. (b) Wiberg, K. B.; Kass, S. R.; Bishop, K. C. *J. Am. Chem. Soc.* **1985**, *107*, 996. (c) Wiberg, K. B., Kass, S. R., de Meijere, A.; Bishop, K. C. *J. Am. Chem. Soc.* **1985**, *107*, 1003.

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species before it relaxes to an open carbocation.[4]

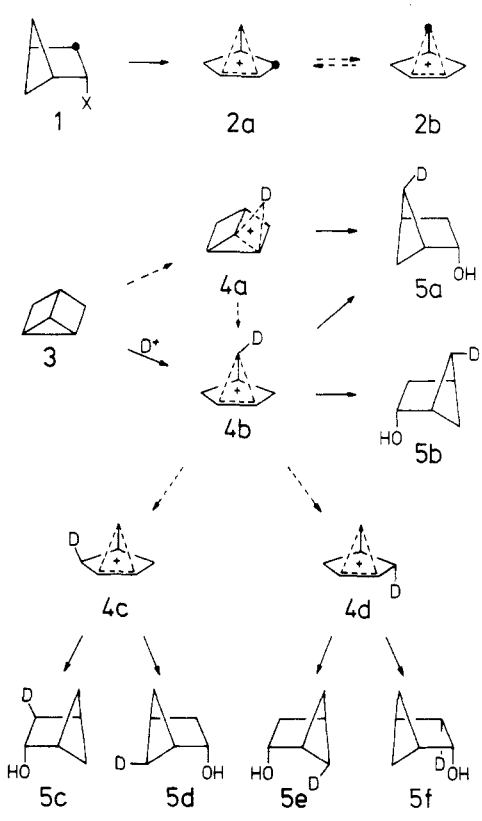
The impact of such studies on the "nonclassical ion problem" is obvious.[1c,5] The remarkable stereoselectivities of many bicyclic carbocations have been interpreted in terms of alkyl bridging (σ delocalization). Alternatively, stereochemical control by the counterion has been suggested.[6] Solvolyses of bicyclic substrates and protonation of tricycloalkanes lead to different orientations of the counterion relative to the carbocation. The product distributions from both reactions should reveal the importance of external directive effects as compared with intrinsic stereoselectivities. Relatively few investigations of the acidolysis of tricycloalkanes have been reported. The objective of the present study is to complement the well-known σ and π routes to bicyclic carbocations by the protonated cyclopropane route.

Results and Discussion

Tricyclo[2.2.0.0^{2,6}]hexane (3). Acidolysis of **3**[7] in aqueous dioxane and in acetic acid yielded 2-bicyclo[2.1.1]hexanol (**5**) and its acetate, respectively. Products known to arise from 2-bicyclo[2.2.0]hexyl[8] and 5-bicyclo[2.1.1]hexyl cations[8c,9] were not observed. The exclusive protonation at C-1 of **3** appears to be dictated by the relative stabilities of the incipient carbocations. Bicyclo[2.2.0]hexane is more strained than bicyclo[2.1.1]hexane (by 9 kcal/mol, MM 1 force field[10]), and the 5-bicyclo[2.1.1]hexyl cation suffers from the unfavorable bond angle at C-5 of bicyclo[2.1.1]hexane (electron diffraction,[11] 89.4°; force field calculation,[12] 81.2°).

The structure of the 2-bicyclo[2.1.1]hexyl cation (**2**) has been explored by NMR spectroscopy under stable ion conditions. The three methylene groups were found to be equivalent on the time scales of ^{1}H and ^{13}C NMR, even at −130 °C.[13,14] The small isotopic splitting in the ^{13}C NMR spectrum induced by ^{2}H indicates rapid equilibration of bridged ions (e.g., **2a** ⇄ **2b**).[15] Recently, we have shown that the degeneracy of **2** is lifted in nucleophilic media.[16] The solvolysis of [3-^{13}C]-2-bicyclo[2.1.1]hexyl brosylate (**1**-OBs) in aqueous acetone and the dediazoniation of the analogous diazonium ion (**1**-N_2^+) gave products derived predominantly from the bridged ion **2a**.

Scheme II



"Leakage" of **2a** to **2b** was a minor process (16% with 1-OBs at 80 °C and 8% with 1-N_2^+ at 20 °C) (Scheme II).

In order to probe the nature of the intermediate(s) en route from **3** to **5**, we treated **3** with 0.3 N D_2SO_4–dioxane (3:7, 20 °C, 0.5–3 h). The isotopomer distribution of [^{2}H]-**5** was estimated by ^{2}H NMR as follows: **5a**, 44%; **5b** + **5d**, 42%; **5c**, 3%; **5e**, 7%; and **5f**, 4%. Our analysis suffers somewhat from coincidence of the signals of anti-5-H and anti-6-H in the NMR spectra of **5**. However, the coupling patterns of syn-5-H set an upper limit of 3–4% for **5d**. Within experimental error (±2%), the deuterium distribution was independent of the conversion of **3** and remained unaffected by repeated acidolysis of [^{2}H]-**5** in 0.8 N D_2SO_4–dioxane.

Our data indicate that the major portion of [^{2}H]-**5** originates from the bridged ion (corner-protonated cyclopropane) **4b**. The edge-protonated species **4a** can at best make a minor contribution, judging from the excess of **5a** over **5b**. Rearrangement of **4b** to **4c** and **4d** leads to 17–18% of **5c–f** (assuming 3–4% of **5d**). This figure is in excellent agreement with previous results,[16] taking into account that the statistical chance of **4b** for "leakage" is twice that of **2a**. We conclude that virtually the same intermediates are generated by heterolysis of **1** and protonation of **3**.

The protonation of **3** compares well with that of the homologous tricyclo[2.1.1.0^{2,6}]heptane (nortricyclene). The corner-protonated nortricyclene dominates product formation in the parent system,[17,18] while electron-withdrawing groups at C-4 and C-3 lead to enhanced retention at the site of electrophilic attack (i.e., edge-protonation).[18,19] 6,2-Hydride shifts are a complicating factor, particularly

(5) Recent reviews include the following: (a) Barkhash, V. A. *Top. Curr. Chem.* **1984**, *116*, 1; (b) Grob, C. A. *Acc. Chem. Res.* **1983**, *16*, 426; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 87; (c) Brown, H. C. *Acc. Chem. Res.* **1983**, *16*, 432; *The Nonclassical Ion Problem* (with comments by Schleyer, P. v. R.); Plenum: New York, 1977; (d) Olah, G. A.; Prakash, G. K. S.; Saunders, M. *Acc. Chem. Res.* **1983**, *16*, 440. Olah, G. A. *Chem. Scr.* **1981**, *18*, 97; (e) Walling, C. *Acc. Chem. Res.* **1983**, *16*, 448; (f) Sargent, G. D. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1972; Vol. III, Chapter 24.

(6) Review: Collins, C. J. *Chem. Soc. Rev.* **1975**, *4*, 251.

(7) Roth, R. J.; Katz, T. J. *J. Am. Chem. Soc.* **1972**, *94*, 4770.

(8) (a) McDonald, R. N.; Reineke, C. E. *J. Org. Chem.* **1967**, *32*, 1878. (b) McDonald, R. N.; Curi, C. A. *J. Am. Chem. Soc.* **1979**, *101*, 7116. (c) McDonald, R. N.; Curi, C. A. *J. Am. Chem. Soc.* **1979**, *101*, 7118.

(9) (a) Wiberg, K. B.; Fenoglio, R. A. *Tetrahedron Lett.* **1963**, 1273. (b) Wiberg, K. B.; Fenoglio, R. A.; Williams, V. Z.; Ubersax, R. W. *J. Am. Chem. Soc.* **1970**, *92*, 568.

(10) (a) Engler, E. M.; Andose, J. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 8005. (b) Maier, W. F.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 1891.

(11) Chiang, J. F. *J. Am. Chem. Soc.* **1971**, *93*, 5004.

(12) Allinger, N. L.; Tribble, M. T.; Miller, M. A.; Wertz, D. H. *J. Am. Chem. Soc.* **1971**, *93*, 1637.

(13) Seybold, G.; Vogel, P.; Saunders, M.; Wiberg, K. B. *J. Am. Chem. Soc.* **1973**, *95*, 2045.

(14) Olah, G. A.; Liang, G.; Jindal, S. P. *J. Am. Chem. Soc.* **1976**, *98*, 2508.

(15) Saunders, M.; Kates, M. R.; Wiberg, K. B.; Pratt, W. *J. Am. Chem. Soc.* **1977**, *99*, 8072.

(16) Kirmse, W.; Zellmer, V.; Goer, B. *J. Am. Chem. Soc.* **1986**, *108*, 4912.

(17) Nickon, A.; Hammons, J. H. *J. Am. Chem. Soc.* **1964**, *86*, 3322.

(18) Werstiuk, N. H.; Dhanoa, D.; Timmins, G. *Can. J. Chem.* **1979**, *57*, 2885.

(19) (a) Werstiuk, N. H.; Timmins, G.; Cappelli, F. P. *Can. J. Chem.* **1980**, *58*, 1709. (b) Werstiuk, N. H.; Cappelli, F. P. *Can. J. Chem.* **1980**, *58*, 1725.

Table I. Acidolyses of Tricyclo[3.2.0.0^{2,7}]heptane (10)

entry	solvent	acid	temp, °C	products, % 12	13	16	20	endo/exo
1	AcOH	0.08 N H_2SO_4	20	1.3	18.9	20.2	59.6	0.34
2	AcOH	0.11 N H_2SO_4	20	1.3	18.5	21.0	59.2	0.35
3	AcOH	0.39 N H_2SO_4	20	1.3	18.9	18.6	61.2	0.30
4	AcOH	0.07 N $HClO_4$	20	0.9	20.2	16.4	62.5	0.26
5	H_2O–sulfolane (3:7)	1.4 N H_2SO_4	20	1.2	19.3	33.3	46.2	0.72
6	H_2O–dioxane (3:7)	0.4 N H_2SO_4	20	1.1	19.0	47.6	32.3	1.47
7	H_2O–dioxane (3:7)	1.5 N H_2SO_4	20	1.2	21.3	45.6	31.9	1.43
8	H_2O–dioxane (3:7)	1.5 N H_2SO_4	70	0.9	16.1	31.7	51.3	0.62
9	H_2O–dioxane (3:7)	1.5 N H_2SO_4	100	0.7	11.6	24.1	63.6	0.38
10	EtOH	0.2 N H_2SO_4	20	nd[a]	15.5	59.8	24.6	2.43

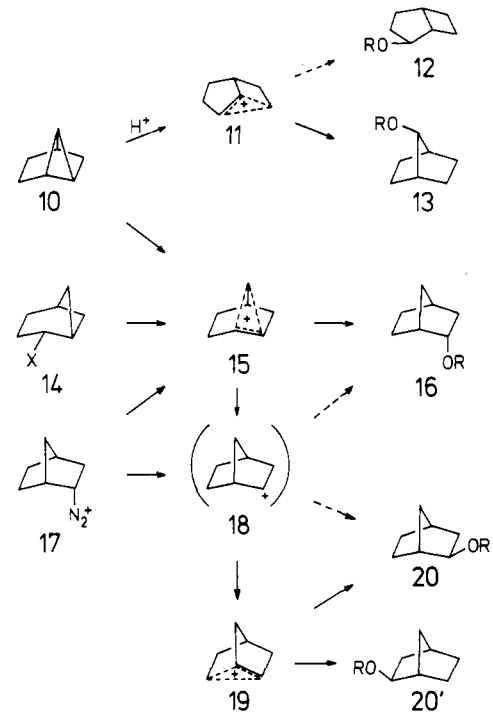
[a] Not determined.

in strong acids.[20] We should recall that nearly equal quantities of exo- and endo-6-D (observed ratio: 1.08–1.09[17,18]) in products derived from deuteriated nortricyclene may also be interpreted in terms of rapidly equilibrating, exo-selective classical 2-norbornyl cations. An analogous mechanism cannot apply in the case of **3** since the open 2-bicyclo[2.1.1]hexyl cation lacks intrinsic stereoselectivity. Rapid equilibration of such ions would distribute the deuterium equally between all methylene positions.

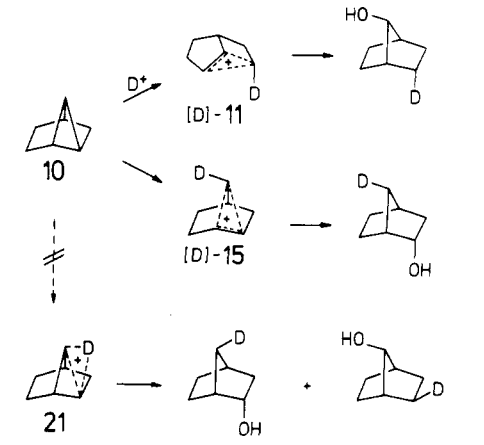
Tricyclo[3.2.0.0^{2,7}]heptane (10). Several syntheses of **10** are available,[21-24] sodium borohydride reduction of 2-norbornen-*anti*-7-yl tosylate being the most efficient approach.[21] Protolytic cleavage of the 1,7 bond in **10** gives rise to norbornyl cations while other modes of cleavage generate less favorable bicyclo[3.1.1]heptyl and bicyclo[3.2.0]heptyl structures. The acetolysis data for *exo*-2-norbornyl tosylate ($k_{25°}$ = 2.33 × 10^{-5} s^{-1}, $\Delta H^{\ddagger}$ = 21.6 kcal/mol, $\Delta S^{\ddagger}$ = −7.2 eu)[25] and 7-norbornyl tosylate ($k_{25°}$ = 6.36 × 10^{-15} s^{-1}, $\Delta H^{\ddagger}$ = 35.7 kcal/mol, $\Delta S^{\ddagger}$ = −3.5 eu)[26] reveal substantial differences in energy of the analogous carbocations. In view of the relative stability and notorious exo selectivity of the 2-norbornyl cation,[5] we were surprised to read that protolytic cleavage of **10** in acetic acid gives nearly equal amounts of *exo*-2-, *endo*-2-, and 7-norbornyl acetates.[24]

The results of our more extensive studies (Table I) indicate that the concentration of strong acid (entries 1–3, 6, 7) and the counterion (entries 1, 4) have little effect on the product distribution. The ratios of 7-norbornyl (**13**) to 2-bicyclo[3.2.0]heptyl (**12**) products are within the range observed in solvolyses and deaminations of appropriate precursors.[27,28] Impressive evidence supports the bridged ion **11** as the precursor of **12** and **13**.[28] In contrast, the *endo*/*exo* (**16**/**20**) ratio of the 2-norbornyl products is found to increase with increasing nucleophilicity of the solvent (entries, 1, 5, 6, 10) and to decrease with increasing temperature (entries 7–9). The data suggest initial formation of an *endo*-selective intermediate, which is captured by solvent competitively with its rearrangement to the "conventional" 2-norbornyl cation (Scheme III). We invoke the 7-bridged norbornyl cation (**15**) as the endo-selective intermediate.[29] A similar response of endo/exo product ratios to solvent nucleophilicity has been observed in the rearrangement of 2-bicyclo[3.1.1]heptyl substrates **14**, the σ route to **15**.[30] Dediazoniation of norbornane-

Scheme III



Scheme IV



(20) Liu, K. T. *Tetrahedron Lett.* **1978**, 1129.
(21) (a) Brown, H. C.; Bell, H. M. *J. Am. Chem. Soc.* **1963**, *85*, 2324. (b) Winstein, S.; Lewin, A. H.; Pande, K. C. *J. Am. Chem. Soc.* **1963**, *85*, 2325.
(22) Moss, R. A.; Whittle, J. R. *J. Chem. Soc. D* **1969**, 341.
(23) Adam, W.; DeLucchi, O. *Angew. Chem.* **1980**, *92*, 815; *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 762.
(24) Davis, D. D.; Johnson, H. T. *J. Am. Chem. Soc.* **1974**, *96*, 7576.
(25) Schleyer, P. v. R.; Donaldson, M. M.; Watts, W. E. *J. Am. Chem. Soc.* **1965**, *87*, 375.
(26) Winstein, S.; Shatavsky, M.; Norton, C.; Woodward, R. B. *J. Am. Chem. Soc.* **1955**, *77*, 4183.
(27) Winstein, S.; Gadient, F.; Stafford, E. T.; Klinedinst, P. E. *J. Am. Chem. Soc.* **1958**, *80*, 5895.
(28) Kirmse, W.; Streu, J. *J. Org. Chem.* **1985**, *50*, 4187.
(29) For a review, see: Kirmse, W. *Acc. Chem. Res.* **1986**, *19*, 36.

Table II. Acidolyses of 2-Methyltricyclo[3.2.0.0^{2,7}]heptane (26c) and Related Reactions

entry	precursor	conditions[a]	products, % 31	32	33	41	42	43	45
1	**26c**	HOAc	0.2	7.4	0.4	42.2	32.5	0.8	16.3
2	**26c**	0.2 N H_2SO_4–dioxane (3:7)	0.6	29.2		28.6	26.0	1.4	14.2
3	**26c**	0.3 N H_2SO_4–dioxane (3:7)	1.9	32.3	0.6	31.9	20.5	0.9	11.9
4	**26c**	0.6 N H_2SO_4–dioxane (3:7)	5.0	37.8	0.6	39.6	5.3	0.6	11.1
5	**42**-OAc	HOAc				14.7	81.7		3.6
6	**42**-OH	0.3 N H_2SO_4–dioxane (3:7)				46.5	42.0	0.5	10.0
7	**32**	HOAc	tr[b]	99.7	tr				
8	**32**	0.3 N H_2SO_4–dioxane (3:7)	7.2	92.6	0.2				
9	**32**	1.0 N H_2SO_4–dioxane (3:7)	11.2	88.7	0.1				
10	**32**-OPNB[c]	acetone–H_2O (1:1), reflux[28]	1.7	96.6	1.7				
11	**36**	0.3 N H_2SO_4–dioxane (3:7)[28]	5.1	91.1	3.8				
12	**39**	HNO_2, H_2O, pH 3.5[40]				41	47		12
13	**42**-OPNB	acetone–H_2O (1:1), reflux[40]				39.2	48.8	0.1	12.3

[a] Unless otherwise specified, 18–20 h at 20 °C. [b] tr = trace. [c] PNB = p-$O_2NC_6H_4CO$.

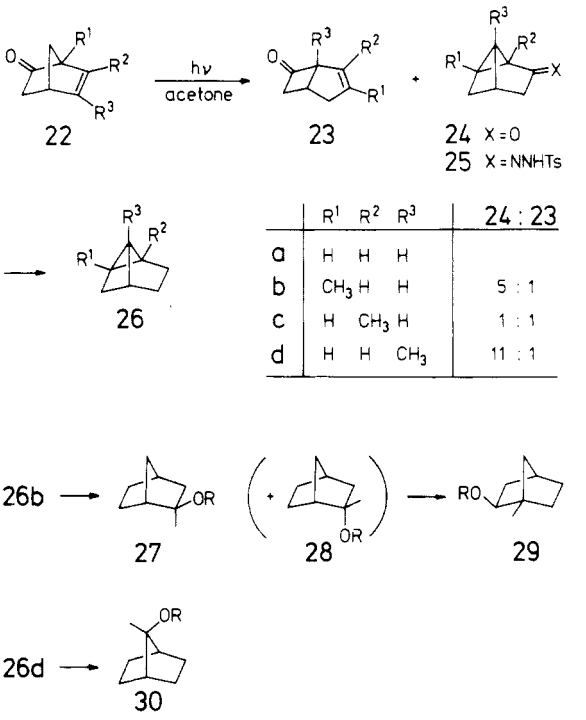
endo-2-diazonium ions (**17**) also proceeds (in part) via **15**.[31]

When the acidolysis of **10** was performed in 1.5 N D_2SO_4–dioxane (3:7, 70 °C), the 7-norbornanol thus obtained was deuteriated in the endo,anti position (^{2}H NMR, δ 1.12). The syn-7-H and anti-7-H resonances of *endo*-2-norbornanol (**16**-OH) were not sufficiently resolved, but the coupling pattern of endo-3-H (the signal at highest field, δ 0.85, $J_{3x,3n}$ = 13.2, $J_{2x,3n}$ = 3.3, $J_{3n,7a}$ = 3.3 Hz) permitted an assignment. The absence of one of the small couplings (3.3 Hz) in the ^{1}H NMR spectrum of [^{2}H]-**16**-OH is consistent with the anti-7-position (but not with the syn-7-position) of the deuterium. We conclude that protolysis of the C-1–C-7 bond occurs with inversion at the site of electrophilic attack, thus excluding the edge-protonated cyclopropane **21** as a significant source of **16** (Scheme IV).

Methyltricyclo[3.2.0.0^{2,7}]heptanes (26). We examined the effect of charge-stabilizing groups on the protolytic cleavage of **10** with the aid of 1-, 2-, and 7-methyltricyclo[3.2.0.0^{2,7}]heptanes (**26b–d**). The route leading to **10**[21] is not applicable to the synthesis of isomerically pure methyl derivatives. Therefore, we resorted to the oxa-di-π-methane rearrangement[32,33] of appropriate methyl-5-norbornen-2-ones (**22b–d**)[34] (Scheme V). Irradiation of **22b,d** in acetone yielded predominantly **24b,d** while **22c** gave an equimolar mixture of **24c** and **23c**, the latter arising via 1,3 acyl shift.[32] Similar methyl effects have been reported for bicyclo[2.2.2]oct-5-en-2-ones.[35] The isomeric ketones **23** and **24** were separated by GC. Wolff–Kishner reduction of **24** failed, but reductive cleavage of the analogous tosylhydrazones **25** with lithium aluminum hydride[36] afforded the hydrocarbons **26** in moderate yields.

Acidolyses of **26b** in acetic acid and in 0.4 N aqueous H_2SO_4–dioxane (20 °C) produced >98% of 2-methyl-*exo*-2-norbornyl products (**27**), along with <2% of the endo isomers **28** (Scheme V). More forcing conditions (e.g., 0.6 N H_2SO_4 in acetic acid, 20 °C) converted **26b**, as well as **27**, into 1-methyl-*exo*-2-norbornyl acetate (**29**-OAc), the thermodynamically more stable isomer.[37] Protolytic

Scheme V



cleavage of **26d** gave exclusively 7-methyl-7-norbornyl products (**30**), regardless of the reaction conditions. D_2SO_4–D_2O–dioxane (1 N) led to incorporation of deuterium in the endo position of **30**-OH, but a detailed stereochemical analysis was precluded by the insufficient resolution of endo-2,3-H from endo-5,6-H in the NMR spectrum.

The methyl effect leads to unidirectional cleavage of **26b** and **26d**. Formation of the stable 2-methyl-2-norbornyl cation is unquestionably the most attractive reaction path for **26b** whereas the behavior of **26d** is less predictable. The acetolysis of 7-methyl-7-norbornyl tosylate ($k_{25°}$ = 2.8 × 10^{-6} s^{-1})[38] proceeds more slowly than that of *exo*-2-norbornyl tosylate ($k_{25°}$ = 2.33 × 10^{-5} s^{-1}),[25] albeit faster than that of *endo*-2-norbornyl tosylate ($k_{25°}$ = 8.33 × 10^{-8} s^{-1}).[25] Owing to the unfavorable bond angle at C-7, the energy of the tertiary 7-methyl-7-norbornyl cation is comparable to that of the secondary 2-norbornyl cation.

(30) Kirmse, W.; Siegfried, R.; Wroblowsky, H. J. *Chem. Ber.* **1983**, *116*, 1880.
(31) Kirmse, W.; Siegfried, R. *J. Am. Chem. Soc.* **1983**, *105*, 950.
(32) For reviews, see: (a) Dauben, W. G.; Lodder, G.; Ipaktschi, J. *Top. Curr. Chem.* **1975**, *54*, 73; (b) Schuster, D. I In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic: New York, 1980; Vol. 3, pp 232–268.
(33) **22a** → **24a**: Ipaktschi, J. *Tetrahedron Lett.* **1969**, 2153.
(34) Goering, H. L.; Chang, C. S. *J. Org. Chem.* **1975**, *40*, 2565.
(35) Demuth, M.; Schaffner, K. *Angew. Chem.* **1982**, *94*, 809; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 820.
(36) Fischer, M.; Pelah, Z.; Williams, D. H.; Djerassi, C. *Chem. Ber.* **1965**, *98*, 3236.
(37) Berson, J. A.; Walia, J. S.; Remanick, A.; Suzuki, S.; Reynolds-Warnhoff, P.; Willner, D. *J. Am. Chem. Soc.* **1961**, *83*, 3986. For the equilibration of **27**-OH, **28**-OH, and **29**-OH, see: Rei, M. H.; Brown, H. C. *J. Am. Chem. Soc.* **1966**, *88*, 5335.
(38) Gassman, P. G.; Pascone, J. M. *J. Am. Chem. Soc.* **1973**, *95*, 7801.

Table III. Acidolyses of Tricyclooctanes 53 and 58 and Related Reactions

entry	precursor	conditions	products, % 46	49	50	52	55	57	60
1	**53**	0.1 N H_2SO_4–HOAc, 20 °C, 47 h	6.3	0.2	20.2	6.5	64.9	1.0	0.1
2	**53**	0.4 N H_2SO_4–HOAc, 20 °C, 44 h	5.7	0.4	20.0	6.9	63.8	0.9	0.2
3	**53**	0.5 N H_2SO_4–dioxane, 20 °C, 160 h	3.4	0.2	18.6	5.9	70.7	0.5	0.2
4	**50**-OTs[44]	HOAc	30.6	–	51.3	16.5			
5	**52**-OTs[45]	HOAc	21	–	46	29			
6	**58**	0.2 N H_2SO_4–HOAc, 20 °C, 40 h					0.2	52.9	47.1
7	**58**	0.6 N H_2SO_4–HOAc, 20 °C, 40 h					0.1	52.1	47.8
8	**58**	1.0 N H_2SO_4–dioxane, 20 °C, 60 h					–	49.9	50.1
9	**55**-OTs[43]	HOAc					89.4	6.6	4.0
10	**55**-OTs[43]	80% aq acetone					94.9	4.1	1.0
11	**57**-OTs[43]	HOAc					0.6	45.5	53.9
12	**57**-OTs[43]	80% aq acetone					–	43.3	56.7
13	**60**-OTs[43]	HOAc					0.4	46.2	53.4
14	**60**-OTs[43]	80% aq acetone					–	42.8	57.2

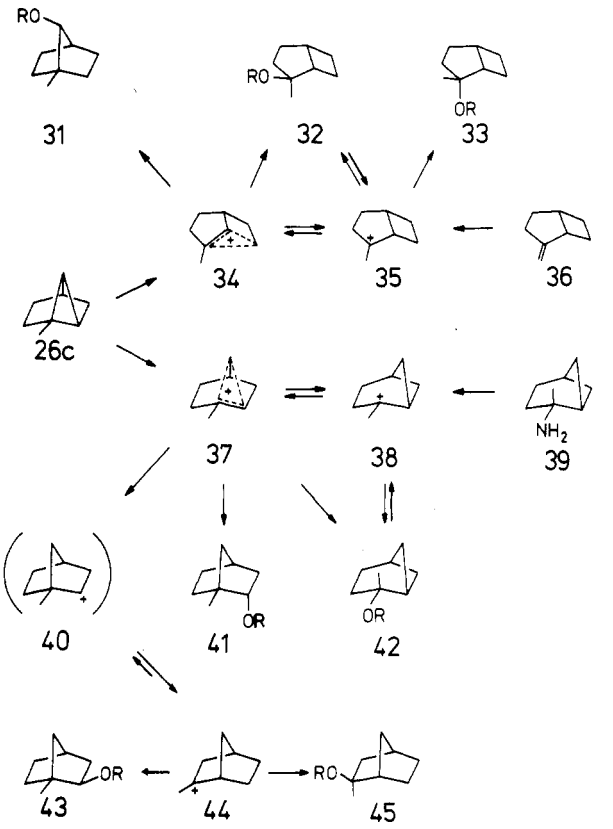
Consequently, competitive processes might have been expected in the protolytic cleavage of **26d**. As we have seen above, however, protonation of **10** does not proceed immediately to the 2-norbornyl cation but produces initially the less stable 7-bridged ion **15**. On the basis of Scheme IV, the directive effect of the methyl group in **26d** is eminently reasonable.

The protolytic cleavage of **26c** is more complex than that of **26b,d**, owing in part to the instability of some products. Our data (Table II) reveal that 2-methyl-2-bicyclo[3.1.1]heptyl derivatives (**42**) isomerize slowly in acetic acid, and more rapidly in H_2SO_4–dioxane, to give 1-methyl-*endo*-2-norbornyl (**41**) and, in smaller amount, 2-methyl-*exo*-2-norbornyl (**45**) products (entries 5, 6). 2-Methyl-*exo*-2-bicyclo[3.2.0]heptyl derivatives (**32**) are stable in acetic acid but are slowly converted into 1-methyl-7-norbornyl (**31**) products by H_2SO_4–dioxane (entries 7–9; complete conversion has been achieved under more forcing conditions[39]). Thus, the **42**/**41** and **32**/**31** ratios reported in Table II are probably lower than they would be in the absence of acid-induced rearrangements.

With these caveats in mind, the acidolysis of **26c** (entries 1–4) may now be analyzed. We suggest that the products originate from 2-methyl-2-bicyclo[3.2.0]heptyl/1-methyl-7-norbornyl cations (**34**)[28] and from 2-methyl-2-bicyclo[3.1.1]heptyl/1-methyl-2-norbornyl cations (**37**)[40] (Scheme VI). Increasing acidity appears to enhance the **34**/**37** ratio. Both intermediates have been generated previously from a variety of precursors,[28,29,40] some relevant data being included in Table II (entries 10–13). Since no interconversion of **34** and **37** has been observed, formation of the isomeric ions from **26c** must proceed in parallel, rather than consecutive, reactions. Studies with labeled and optically active materials[28,40] support the notion that the bridged ions **34** and **37** equilibrate with the classical structures **35** and **38**, respectively, but nevertheless give rise to most of the tertiary (**32**, **42**) and all of the secondary alcohols (**31**, **41**). The product ratios indicate that virtually the same intermediates are generated from all precursors, including **26c**.

Tricyclo[3.3.0.$0^{2,8}$]octane (53) and Tricyclo[3.2.1.$0^{2,7}$]octane (58). The protolytic cleavage of **53**[41] and **58**[42] showed little variation with the solvent and with the concentration of acid (Table III, entries 1–3, 6–8). All products proved to be stable under our reaction conditions. Our results with **58** differ from those of a previous study.

Scheme VI

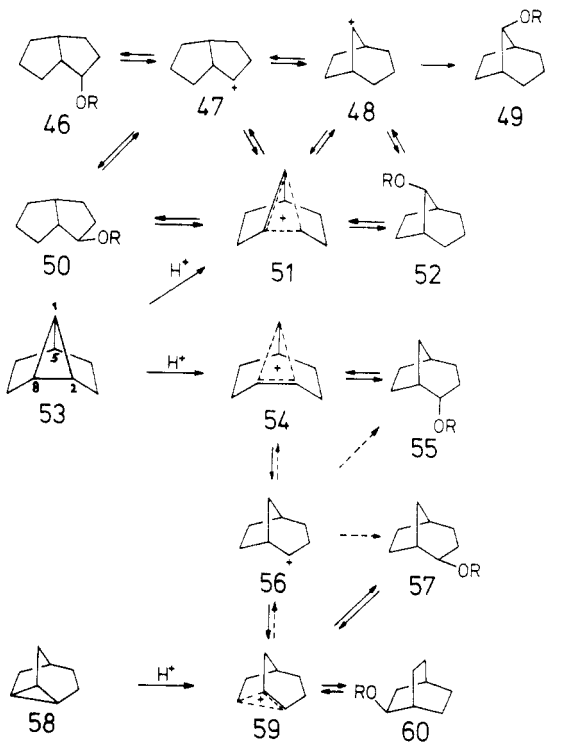


In refluxing acetic acid–toluenesulfonic acid, Appleton et al. obtained a complex mixture of products, including 3- and 6-bicyclo[3.2.1]octyl derivatives.[42] In our hands, the acidolysis of **58** proceeded cleanly, yielding **57** and **60** in a 1:1 ratio (entries 6–8). Analogous results, derived from solvolyses of **57**-OTs and **60**-OTs (entries 10–14) have been interpreted in terms of the bridged intermediate **59**.[43] We conclude that the protonation of **58** occurs exclusively at C-7.

The product distributions obtained from the protolytic cleavage of **53** (entries 1–3) indicate competitive electrophilic attack at C-1 and at C-2,8 (Scheme VII). The latter process yields **55** and very minor amounts of **57** and **60**. In their solvolytic studies, Goering and Fickes observed more "leakage" from the endo-selective bridged ion **54** to the exo-selective intermediate **59** than in the reverse direction (entries 9–14).[43] The carbocations generated from

(39) Kirmse, W.; Streu, J. *Synthesis* **1983**, 994.
(40) Banert, K.; Kirmse, W.; Wroblowsky, H. J. *Chem. Ber.* **1983**, *116*, 2474.
(41) Fickes, G. N.; Rose, C. B. *J. Org. Chem.* **1972**, *37*, 2898.
(42) Appleton, R. A.; Fairlie, J. C.; McCrindle, R.; Parker, W. *J. Chem. Soc. C* **1968**, 1716.
(43) Goering, H. L.; Fickes, G. N. *J. Am. Chem. Soc.* **1968**, *90*, 2848, 2856, 2862.

Scheme VII



53 and **58** behave analogously, the rate of "leakage" being even smaller (probably due to the lower temperature). Protonation of **53** at C-2 (to give **51**) induces less stereoselective reactions; in particular, the low **50**/**46** (exo/endo) ratio suggests ready interconversion of **51** with the open 2-bicyclo[3.3.0]octyl cation (**47**). Our results fully corroborate previous studies with **50**-OBs[44] and **52**-OTs[45] (entries 4, 5). The high **52**/**49** (anti/syn) ratio (**49** went unnoticed in the solvolytic work[44,45]) may be attributed to predominance of the bridged ion **51** or to steric effects favoring the anti approach of nucleophiles to the open ion **48**.

Conclusion

In a representative number of examples, the protolytic cleavage of tricycloalkanes and the heterolysis of bicyclic substrates give virtually identical intermediates. When detectable, inversion at the site of electrophilic attack prevails; i.e., edge-protonated cyclopropanes play a minor role, if any. Our results strongly support the notion that stereoselectivity may be an intrinsic property of (bridged) carbocations. With the compounds studied here, and under our experimental conditions, specific orientation of the counterion makes small or even negligible contributions. Structural factors (strain, flexibility, charge-stabilizing substituents) are of major importance in defining the limitations of bridging.

Experimental Section

General Methods. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. ^{1}H NMR spectra were determined in $CDCl_3$ solution on Bruker WP-80, WM-250, and AM-400 instruments. ^{2}H NMR spectra were determined in CCl_4 solution on the Bruker AM-400 (61.42 MHz) spectrometer. Gas chromatography (GC) was performed by the use of a Siemens Sichromat equipped with glass capillary columns. Varian Aerograph 920 instruments, equipped with packed glass columns, were used for preparative gas chromatography (PGC).

Protolytic Cleavage of Tricycloalkanes. General Procedures. The hydrocarbon (20–50 mg) was stirred with 2–5 mL of aqueous sulfuric (perchloric) acid–dioxane (sulfolane) (3:7), as specified in Tables I–III. The mixture was neutralized with sodium carbonate and extracted with ether. The extracts were washed with water, dried over magnesium sulfate, concentrated, and analyzed by GC. Analogous workup of the acetolyses was followed, in many cases, by lithium aluminum hydride reduction of the acetates and GC analysis of the alcohols. For the preparation of authentic samples of the alcohols, the literature referring to previous solvolytic work should be consulted.

Deuterolysis of Tricyclo[2.2.0.0^{2,6}]hexane (3). Samples of **3** (60 mg) were treated with a 3:7 mixture of 0.3 N D_2SO_4–D_2O and dioxane for 0.5–3 h. Bicyclo[2.1.1]hexan-2-ol (**5**) was the only product (99.7% by GC). Since **5** is rather volatile, residual solvent was removed by PGC to give 32 mg (45%) of pure [^{2}H]-**5**. The ^{2}H NMR spectrum of [^{2}H]-**5** has been assigned.[46] ^{1}H NMR ($CDCl_3$, 400 MHz) of **5**: δ 0.97 (dd, 6s-H, $J_{6s,5s}$ = 9.8, $J_{6s,5a}$ = 7.0), 1.28 (dddd, 3s-H, $J_{3s,3a}$ = 11.5, $J_{3s,6a}$ = 3.6, $J_{3s,2}$ = 2.0, $J_{3s,4}$ = 1.4), 1.42 (dd, 5s-H, $J_{5s,6s}$ = 9.8, $J_{5s,5a}$ = 7.0), 1.60 (br s, OH), 1.67 (m, 5a-H, 6a-H), 2.07 (dddd, 3a-H, $J_{3s,3a}$ = 11.5, $J_{3a,2}$ = 7.2, $J_{3a,5a}$ = 2.5, $J_{3a,4}$ = 1.4), 2.42 (m, 4-H, $J_{4,5a}$ = $J_{4,6a}$ = 2.9, $J_{4,3a}$ = $J_{4,3s}$ = 1.4), 2.46 (m, 1-H, $J_{1,4}$ = 6.6, $J_{1,5a}$ = $J_{1,6a}$ = 2.8), 4.41 (dddd, 2-H, $J_{2,3a}$ = 7.2, $J_{2,3s}$ = 2.0, $J_{2,1}$ = 1.8, $J_{2,5}$ = 1.2 Hz). The ^{1}H NMR spectrum of [^{2}H]-**5** deviated as follows: 6s-H, intensity 0.52 H, overlapping dt ($J_{6s,5s}$ = 9.8, $J_{6s,6a\text{-}D}$ = 1.2, **5b**) and dd (small, $J_{6s,5s}$ = 9.8, $J_{6s,6a}$ = 7.0, **5c**,**d**,**f**); 5s-H, intensity 0.87 H, overlapping dt ($J_{5s,5a}$ = 7.0, $J_{5s,6s\text{-}D}$ = 1.5, **5a**) and dd ($J_{5s,6s}$ = 9.8, $J_{5s,5a}$ = 7.0, **5b**,**c**,**f**); a signal attributable to **5d** (lacking $J_{5s,5a}$) was not detected; 5a-H and 6a-H, intensity 1.55 H (intensities referring to 2-H = 1.00).

Deuterolysis of Tricyclo[3.2.0.0^{2,7}]heptane (10). Samples of **10** (0.25 g) were treated with a 3:7 mixture of 1.5 N D_2SO_4–D_2O and dioxane for 2 days at 70 °C and 100 °C. The products were separated by PGC (4-m Carbowax–KOH, 110 °C). [^{2}H]-7-Norbornanol: ^{2}H NMR δ 1.12. The assignment of the signal rests on the spectra of [*exo*,*exo*-5,6-$^2H_2$]-**13**[47] (^{2}H NMR: δ 1.50) and [*exo*,*exo*-2,3-$^2H_2$]-**13**[47] (^{2}H NMR: δ 1.82). The endo-5,6 protons of [*exo*,*exo*-5,6-$^2H_2$]-**13** (^{1}H NMR: δ 1.12) and the endo-2,3 protons of [*exo*,*exo*-2,3-$^2H_2$]-**13** (^{1}H NMR: δ 1.21) are readily identified by their small geminal coupling. [^{2}H]-*endo*-2-Norbornanol: The high-field signal (δ 0.85) assigned to *endo*-3-H[48] is dd (J = 13.2 and 3.3 Hz) in the ^{1}H NMR spectrum of [^{2}H]-**16** whereas the coupling is dt ($J_{3x,3n}$ = 13.2, $J_{2x,3n}$ = $J_{3n,7a}$ = 3.3 Hz) in the ^{1}H NMR spectrum of **16**.

Synthesis of Methyltricyclo[3.2.0.0^{2,7}]heptanes (26). The appropriate methylbicyclo[2.2.1]hept-5-en-2-one (**22**)[34] (1.0 g) in 250 mL of acetone was irradiated through Pyrex with a medium-pressure mercury arc (125 W). The reaction was monitored by GC and carried to complete conversion of **22** (48 h for **22b**,**d**, 18 h for **22c**). The products **23** and **24** were separated by PGC (4.5-m Carbowax-KOH, 150 °C), **23** eluting first. The yields of pure (>99%) material were as follows: **24b**, 50%; **24c**, 27%; **24d**, 38%. The ^{1}H NMR data of **24a–d** (Table IV) reveal a consistent pattern of chemical shifts and coupling constants.

Solutions of 1.60 g (8.6 mmol) of tosylhydrazine in 10 mL of methanol and 1.00 g (8.2 mmol) of **24** in 4 mL of methanol were mixed and heated to reflux for 30 min. After cooling slowly to room temperature, the mixture was kept at −20 °C for 12 h. The crystals of **25** were filtered with suction and recrystallized from ethanol: **25b** (73%), mp 163 °C; **25c** (70%), mp 199 °C; **25d** (68%), mp 161 °C. Compound **25** (1.0 g, 3.4 mmol) and 1.9 g (50 mmol) of lithium aluminum hydride, dissolved in 50 mL of anhydrous dioxane, were slowly heated (a vigorous reaction ensued at 60–70 °C). After the mixture was refluxed for 2 h, hydrolysis was effected by dropwise addition of water. The mixture was filtered, and most of the dioxane was removed by extracting several times with water. The organic phase was dried over magnesium sulfate and concentrated by fractional distillation (15-cm Vigreux column). PGC (4.5-m Carbowax–KOH, 60 °C) of the residue

(44) Closson, W. D.; Kwiatkowski, G. T. *Tetrahedron Lett.* **1966**, 6435.
(45) Foote, C. S.; Woodward, R. B. *Tetrahedron* **1964**, *20*, 687.
(46) Wesener, J. R.; Günther, H. *J. Am. Chem. Soc.* **1985**, *107*, 1537.
(47) Sunko, D. E.; Vancik, H.; Deljac, V.; Milun, M. *J. Am. Chem. Soc.* **1983**, *105*, 5364.
(48) Liu, K. T. *J. Chin. Chem. Soc. (Taipei)* **1976**, *23*, 1.

Table IV. ^{1}H NMR Spectra of Tricyclo[3.2.0.0^{2,7}]heptan-3-ones 24[a]

compd	CH_3	1-H	2-H	4x-H	4n-H	5-H	6x-H	6n-H	7-H
				Chemical Shifts, δ					
24a		3.00	1.98	2.33	1.87	2.83	2.69	1.23	2.11
24b	1.16	2.76	1.66	2.08	1.72	2.66	2.30	1.23	–
24c	1.12	2.74	–	2.25	1.85	2.67	2.54	1.18	1.81
24d	1.37	–	1.62	2.27	1.79	2.45	2.45	1.03	1.97

compd	1,2	1,5	1,6n	1,7	2,7	4x,4n	4x,5
			Coupling Constants:[b] J, Hz				
24a	3.6	3.6	3.6	3.6	6.8	16.4	5.5
24b	3.6	3.6	3.6	–	–	16.2	5.7
24c	–	3.0	3.0	3.0	–	16.8	5.3
24d	–	–	–	–	6.7	17.5	

compd	4x,6	5,4x	5,6x	5,7	6x,6n	6x,7
			Coupling Constants:[b] J, Hz			
24a	0.9	5.5	8.2	3.6	9.0	3.6
24b		5.7	7.4	–	9.3	–
24c		5.3	8.5	3.0	9.5	3.0
24d					9.2	3.0

[a] $CDCl_3$, 250 MHz. [b] Blanks indicate that coupling constants could not be obtained from first-order analysis of the spectra.

provided pure (96–99%) **26** (isolated yield 12–19%). All new compounds gave satisfactory elemental analyses.

The mass spectra of the isomers were virtually identical, e.g., **26d**: *m/e* 108 (M^+, 1), 93 (14), 91 (24), 81 (8), 80 (100), 79 (53), 77 (26), 53 (12). The ^{1}H NMR spectra consisted of unresolved multiplets, except for the methyl signal. **26b**: δ 1.17 (s, CH_3), 1.0–2.2 (m, 8 H), 2.3–2.6 (m, 1 H). **26c**: δ 1.10 (s + m, CH_3 + 1 H), 1.2–1.3 (m, 1 H), 1.35–2.5 (m, 7 H). **26d**: δ 1.10 (s, CH_3), 1.0–1.2 (m, 1 H), 1.2–1.55 (m, 1 H), 1.6–2.1 (m, 5 H), 2.25 (m, 1 H). Anal. Calcd for C_8H_{12}: C, 88.82; H, 11.18. Found, **26b**: C, 88.75; H, 11.27. Found, **26c**: C, 88.92; H, 11.16. Found, **26d**: C, 88.92; H, 11.18.

Conformational Studies of Annulated 2,2′-Bipyridinium Salts

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The synthesis of several 4,4′-disubstituted 2,2′-bipyridinium bridged diquaternary salts, by reaction of the corresponding 2,2′-bipyridines with several dibromide substrates, is reported. Further sulfonation of two of these salts gives rise to bridged 2,2′-bipyridines with zwitterionic character, **4a,b**. The twist angle between the two pyridine rings can be estimated from spectroscopic data of these salts. In a propane-bridged salt, **9b**, a barrier to conformational mobility of 16.5 kcal mol^{-1} has been obtained by a variable-temperature NMR experiment.

Interest in the chemistry of 2,2′-bipyridine and its derivatives has grown rapidly during recent years due to their applicability in a variety of fields. Derivatives of this biaryl molecule have been extensively used as effective ligands to coordinate a large diversity of metals. The corresponding ruthenium complexes are important photosensitizers in water decomposition studies.[1] Ruthenium complexes of bipyridine have also been attached to a polymer support and used as hydrogenation catalysts.[2] The ruthenium complex of 4-vinyl-4′-methyl-2,2′-bipyridine has been employed in electroactive polymer films, allowing the study of chemically modified electrodes.[3] Moreover, bridged diquaternary 2,2′-bipyridines have potent herbicide properties,[4] and similar or modified diquaternized 2,2′-bipyridinium molecules are being used as mediators or relays for photochemical hydrogen evolution from water.[5]

Ruthenium complexes of bipyridine have been covalently anchored to insoluble polymers, and these photosensitizers have been tried in sacrificial photoreduction of water.[6] Also, we have introduced several relay compounds

(1) (a) Kirch, M.; Lehn, J. M.; Sauvage, J. P. *Helv. Chim. Acta* **1979**, *62*, 1345. (b) Kiwi, J.; Borgarello, E.; Pelizzetti, E.; Visca, M.; Grätzel, M. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 646. (c) Sutin, N.; Creutz, C. *Pure Appl. Chem.* **1980**, *52*, 2717. (d) Keller, P.; Moradpour, A.; Amouyal, E.; Kagan, H. B. *Nouv. J. Chim.* **1980**, *4*, 377. (e) Degani, Y.; Willner, I. *J. Am. Chem. Soc.* **1983**, *105*, 6228. (f) Grätzel, M.; Kalyanasundaran, K.; Kiwi, J. *Solar Energy Materials*; Springer Verlag: Berlin, 1982; pp 37–126.

(2) Drago, R. S.; Nyberg, E. D.; El A'mma, A. G. *Inorg. Chem.* **1981**, *20*, 2461.

(3) (a) Gosh, P. K.; Spiro, T. G. *J. Am. Chem. Soc.* **1980**, *102*, 5543. (b) Abruña, H. D.; Denisevich, P.; Umaña, M.; Meyer, T. J.; Murray, R. W. *J. Am. Chem. Soc.* **1981**, *103*, 1. (c) Abruña, H. D.; Breiks, A. I.; Collum, D. B. *Inorg. Chem.* **1985**, *24*, 988.

(4) Summers, L. A. *The Bipyridinium Herbicides*; Academic: New York, 1980.

(5) (a) Amouyal, E.; Zidler, B.; Keller, P.; Moradpour, A. *Chem. Phys. Lett.* **1980**, *74*, 314. (b) Keller, P.; Moradpour, A.; Amouyal, E.; Zidler, B. *J. Mol. Catal.* **1981**, *12*, 261. (c) Bourdelande, J. L.; Camps, J.; Font, J.; de March, P.; Brillas, E. *J. Photochem.* **1985**, *30*, 437.

(6) Bosch, P.; Campá, C.; Camps, J.; Font, J.; de March, P.; Virgili, A. *An. Quim., Ser. C* **1985**, *81*, 162.

0022-3263/87/1952-0521$01.50/0