Pentacyclodecane Chemistry. IX. Acetolysis and Formolysis of Pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]dec-*6-d-syn*-6-yl *p*-Toluenesulfonate. Evidence for a Symmetrical Intermediate[1,2]

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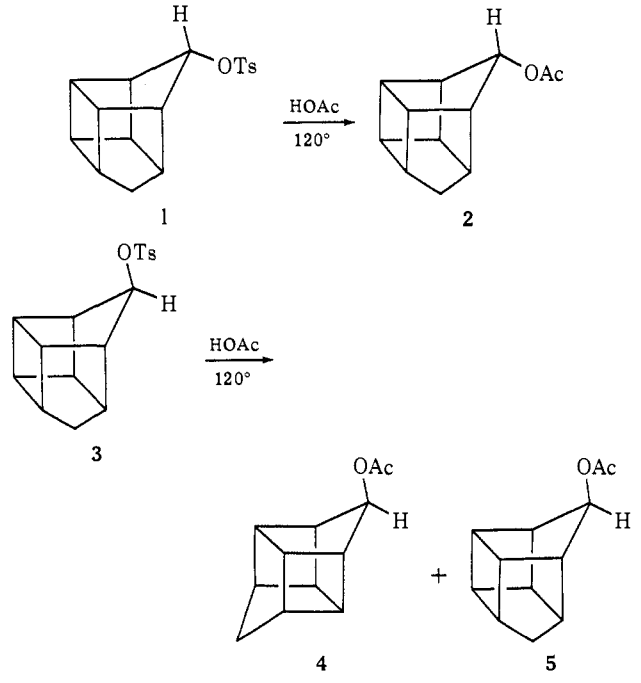
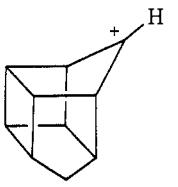
Abstract: Irradiation of *endo*-tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-*3-d-syn*-3-ol (**10**) in acetone gave pentacyclo-[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decan-*6-d-syn*-6-ol (**12**). Acetolysis and formolysis of the corresponding α-deuterated tosylate **14** gave acetate and formate esters of *syn*-pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decan-6-ol (**20**), respectively, in which the deuterium was distributed equally between the α (6) position (**15**, **16**) and a tertiary (presumably 5) position (**23**, **24**). Extensive scrambling of the deuterium in the tosylate occurred on acetolysis, and moderate scrambling occurred on formolysis. Approximate rate constants for internal return in both solvents were determined. The ratio of rate constants for internal return to solvolysis was ~3.9 in acetic acid at 110° and ~1.5 in formic acid at 55°. The deuterium scrambling results are best interpreted in terms of a symmetrical bridged carbonium ion intermediate **25**, although a pair of equilibrating classical ion pairs **26** and **27** cannot be excluded. Acetolysis of *anti*-pentacyclo-[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]dec-6-yl tosylate (**3**) in the presence of sodium acetate gave essentially the same product distribution as reported previously for the unbuffered acetolysis. The mass spectra of *syn*- (**20**) and *anti*-pentacyclo-[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decan-6-ol (**30**) are reported, and their relation to the solvolysis reactions of the corresponding tosylates is discussed.

Acetolysis of *syn*-pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]dec-6-yl tosylate (**1**) (a 1,3-bishomocubyl system[3]) gave almost exclusively the unrearranged acetate **2** with retention of configuration at the methylene bridge.[3] A small amount of the symmetrical acetate **4** (a 1,4-bishomocubyl system[3]) may have been formed.[3] On the other hand, acetolysis of the *anti*-tosylate **3** gave mainly rearranged acetate **4** (85%) along with a smaller amount of the unrearranged acetate **5** (15%), again with retention of configuration.[3] The sharp distinction in product distributions from the isomeric tosylates **1** and **3** ruled out any significant amount of the cationic intermediate **6** which was symmetrically solvated about the cation center, since such an intermediate





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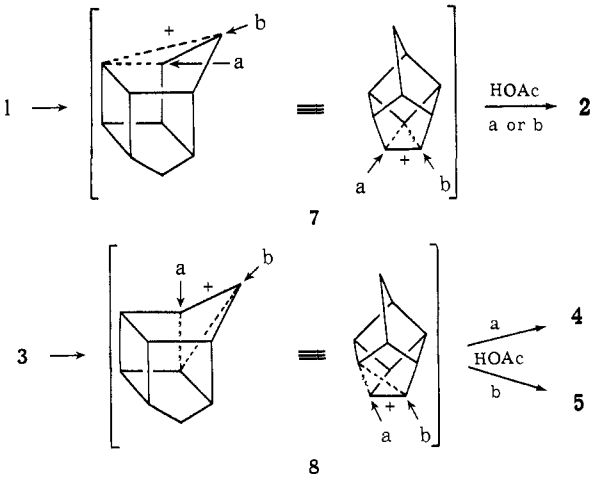
should lead to identical product distributions from either precursor. On the basis of these data and a probable rate acceleration it was suggested that bridged intermediates similar to **7** and **8** could account for the observed products.[3] In view of the recent nmr data



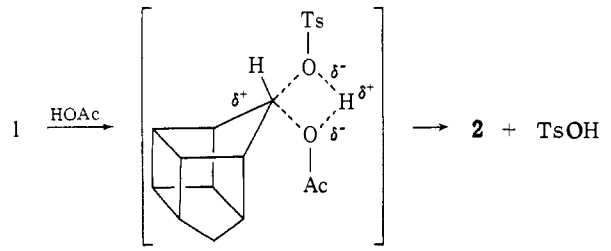
(1) (a) Part VIII: W. L. Dilling and C. E. Reineke, *Org. Photochem. Syn.*, **1**, 85 (1971); (b) part VII: W. L. Dilling and J. A. Alford, *Tetrahedron Lett.*, 761 (1971).

(2) A preliminary account of this work was reported in part VI: W. L. Dilling, R. A. Plepys, and R. D. Kroening, *J. Amer. Chem. Soc.*, **91**, 3404 (1969); **92**, 3522 (1970).

(3) W. L. Dilling, C. E. Reineke, and R. A. Plepys, *J. Org. Chem.*, 34, 2605 (1969).

of Olah and coworkers[4] concerning the structure of the stable 2-norbornyl cation, it is probably more accurate to draw the bridged ions as hybrids of two σ-bonded resonance forms as in **7** and **8**, eliminating the olefinic resonance forms originally proposed as contributors to the hybrids.[3,5] No products are formed which correspond to the olefinic resonance form analogs of ions **7** and **8**.[3]

The products resulting from solvent attack at the two positions of intermediate **7** are the same except that one is the enantiomer of the other.[6] Alternatively, the retention of the carbon skeleton and stereochemistry in the acetolysis of the *syn*-tosylate **1** could be explained by some type of front-side displacement, perhaps with assistance by the leaving tosylate anion (see **9**),[7] as has been proposed for several acyclic systems.[8] The reaction scheme involving intermediate **7** predicts equal attack by acetic acid at two different carbon atoms while the front-side displacement mechanism predicts attack by solvent only at the carbon which was originally attached to the tosylate group. The differentiation of these processes is the major subject of this paper. The formolysis of the *syn*-tosylate **1** was also examined.



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Solvolysis of the *anti*-tosylate **3** in unbuffered acetic acid gave the acetates **4** and **5** in 75% total yield in addition to some black carbonaceous material.[3] It was of interest to examine this reaction in the presence of sodium acetate, which would neutralize the toluenesulfonic acid liberated. The carbonaceous material could have resulted from some strong acid-sensitive product (olefin possibly) which might be stable in the presence of sodium acetate.

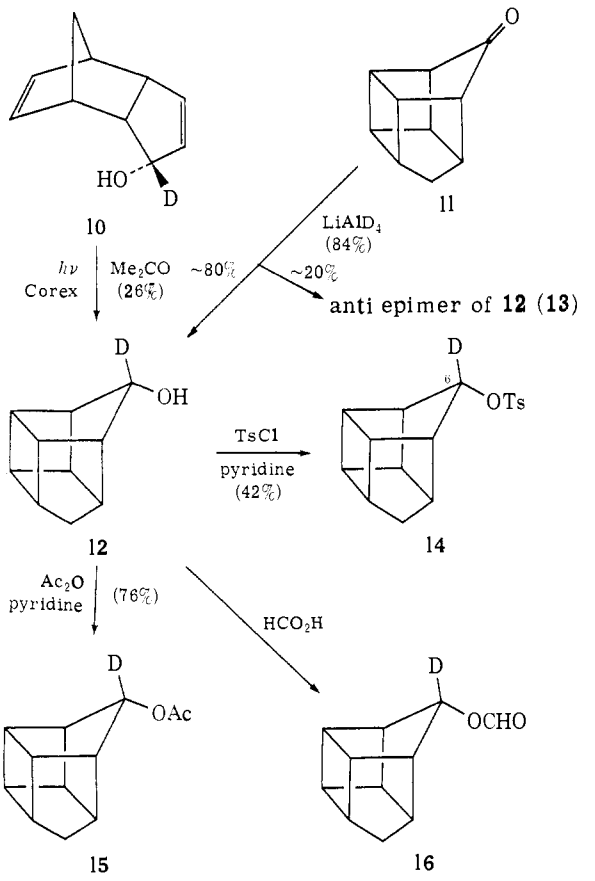
Several systems closely related to **1** and **3** have been studied recently. 7-Norbornyl tosylate and brosylate have been shown to undergo solvolysis with 80–90% retention of configuration.[9] No skeletal rearrangement occurs in these reactions which lead to 7-norbornyl products. In the case of acetolysis of 7-norbornyl tosylate in the presence of sodium acetate, it was established that the retention of configuration was not due to sulfur–oxygen bond cleavage; only carbon–oxygen cleavage occurred.[10] *anti,endo*-Tricyclo[4.2.1.0^{2,5}]non-9-yl tosylate undergoes acetolysis 18,000 times faster than the syn isomer, but no skeletally unrearranged products were formed.[11] Although these fused cyclobutyl-7-norbornyl systems are contained within tosylates **1** and **3**, they appear to have little in common with the latter as regards products or relative rates; the rate difference between **1** and **3** is a factor of only 3–6.[3] Several other related systems, such as the homocubyl which involved multiple degeneracy, have been reviewed recently.[12,13]

Results

Of the several possible methods available for detecting skeletal rearrangement of the *syn*-tosylate **1** upon conversion to the acetate **2**, we chose to label the anti 6 position of the tosylate with deuterium and look for the presence of hydrogen at the 6 position of the acetate.

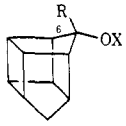
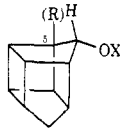
The synthesis of the required deuterated esters starting from the known deuterated dienol **10**[14] is outlined in Scheme I. Spectral data corroborating the structures of the deuterated compounds are presented in the Experimental Section. No hydrogen could be detected by nmr spectroscopy at the deuterium position of any of the deuterated compounds shown in

Scheme I



(4) G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras, and C. Y. Lui, *J. Amer. Chem. Soc.*, 92, 4627 (1970).
(5) W. L. Dilling and C. E. Reineke, *Tetrahedron Lett.*, 2547 (1967).
(6) All structures shown in this paper represent racemic mixtures although only one enantiomer is shown.
(7) Six-membered-ring transition states may also be drawn.
(8) (a) H. L. Goering and S. Chang, *Tetrahedron Lett.*, 3607 (1965); (b) H. L. Goering, R. G. Briody, and J. F. Levy, *J. Amer. Chem. Soc.*, 85, 3059 (1963); (c) H. L. Goering and H. Hopf, *ibid.*, 93, 1224 (1971); (d) H. Hart and H. S. Eleuterio, *ibid.*, 76, 1379 (1954).
(9) (a) P. G. Gassman and J. M. Hornback, *ibid.*, 89, 2487 (1967); (b) F. B. Miles, *ibid.*, 89, 2488 (1967); (c) F. B. Miles, *ibid.*, 90, 1265 (1968); (d) P. G. Gassman, J. M. Hornback, and J. L. Marshall, *ibid.*, 90, 6238 (1968).
(10) P. G. Gassman, J. M. Hornback, and J. M. Pascone, *Tetrahedron Lett.*, 1425 (1971).
(11) (a) M. Sakai, A. Diaz, and S. Winstein, *J. Amer. Chem. Soc.*, 92, 4452 (1970); (b) for a related system, see M. A. Battiste and J. W. Nebzydoski, *ibid.*, 92, 4450 (1970).
(12) R. E. Leone and P. v. R. Schleyer, *Angew. Chem.*, 82, 889 (1970); *Angew. Chem., Int. Ed. Engl.*, 9, 860 (1970).
(13) For recent results on the solvolysis of other bishomocubyl systems, see W. G. Dauben and D. L. Whalen, *J. Amer. Chem. Soc.*, 93, 7244 (1971).
(14) W. L. Dilling and R. A. Plepys, *J. Org. Chem.*, 35, 2971 (1970).

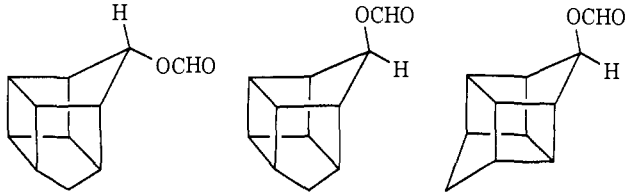
Table I. Deuterium and Proton Chemical Shifts of *syn*-1,3-Bishomocubyl Derivatives[a]

Compound	X	Chemical shift of atom R[b] R = D[c]	Chemical shift of atom R[b] R = H[d]
	H	3.92 (**12**)[e]	3.92 (**20**)[e]
	Ts	4.40 (**14**)	4.50 (**1**)
	Ac	4.70 (**15**)	4.70 (**2**)
	CHO	4.77 (**16**)	4.86 (**17**)
	H	~2.6 (**21**)	2.2–3.1[f] (**20**)
	Ts	2.54 (**22**)	2.3–3.1[f] (**1**)
	Ac	2.67 (**23**)	2.3–3.1[f] (**2**)
	CHO	~2.6 (**24**)	2.4–3.1[f] (**17**)

[a] All spectra taken in CCl_4 solution. [b] Chemical shifts (δ) in ppm from internal Me_4Si. Chemical shifts downfield from the reference are positive; those upfield from the reference are negative. [c] $CDCl_3$ used as an internal reference related to Me_4Si by $\delta_{Me_4Si} = \delta_{CHCl_3} + 7.25$ (F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1969, p 251). [d] Me_4Si used as an internal reference. [e] Compound number. [f] Actual chemical shift is somewhere within stated range.

Scheme I. The lower limit of detectability by this method was probably 5% or less.

The nondeuterated formate esters **17**, **18**, and **19** were prepared from the known alcohols[3] with formic acid by the method of Vogel.[15]

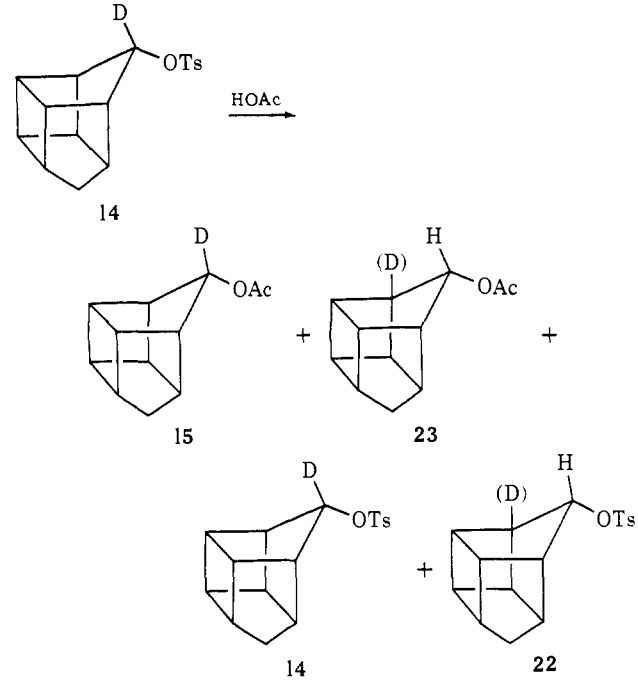


17 18 19

The solvolysis reactions were carried out in unbuffered acetic acid as described previously[3] or in unbuffered formic acid. The acetate **15** and formate **16** were completely stable to the reaction medium which contained 1 equiv of *p*-toluenesulfonic acid.

The extent of deuterium scrambling in the acetate and formate products and in the recovered tosylate was determined by integration of the peak areas in both the proton and deuterium nmr spectra. The appearance of a C-6 proton signal indicated that rearrangement had occurred. A corresponding decrease in the area of the tertiary proton's multiplet indicated the appearance of deuterium at one of the tertiary positions. The acetoxy methyl protons, formate proton, and tosylate aromatic protons were used as internal standards in the proton nmr analyses. Deuterium nmr analyses, in general, confirmed the results obtained from the proton nmr analyses. A comparison of the pertinent deuterium and proton chemical shifts for the deuterated and nondeuterated compounds is shown in Table I. In general, the agreement between the deuterium and proton shifts for those atoms on the carbon atom which bore the functional group (C-6) was satisfactory. The line shape for the deuterium atom on the tertiary carbon atom(s) for compounds **21**–**24** indicated that the deuterium atom was probably all at one position (presumably C-5). The resonance lines for the deuterium atoms on the tertiary carbon atoms were nearly the same width (or slightly wider) than those for the deuterium atom on C-6. The C-5 deuterium resonance line is expected to be slightly broader than the C-6 deuterium line due to a larger total coupling with the three vicinal protons, two of which have smaller dihedral angles than the C-5–C-6 dihedral angle.[16] The C-6 proton resonance lines for all of the *syn*-1,3-bishomocubyl derivatives examined to date[3] are rather narrow with widths at half-height of only *ca.* 3–4 Hz presumably due to dihedral angles which are near 90°.[16]

The results of acetolysis of the deuterated tosylate **14** under various conditions are presented in Table II.



14 15 23 14 22

The accuracy of the ratios of unrearranged to rearranged esters is *ca.* ±3–4% for both the proton and deuterium nmr analyses.

Formolysis of the *syn*-tosylate **1** gave the *syn*-formate **17** as the only detectable product with a rate constant of $3.8 \pm 0.4 \times 10^{-4}$ sec^{-1} at 55°. Neither the *anti*-formate **18** nor the symmetrical 1,4-bishomocubyl formate **19** could be detected by nmr analysis.

The results of formolysis of the deuterated tosylate **14** under various conditions are presented in Table

(15) A. I. Vogel, *J. Chem. Soc.*, 624 (1948).

(16) (a) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); (b) H. Conroy, *Advan. Org. Chem.*, **2**, 308 (1960).

Table II. Acetolysis of α-Deuterated *syn*-1,3-Bishomocubyl Tosylate **14**

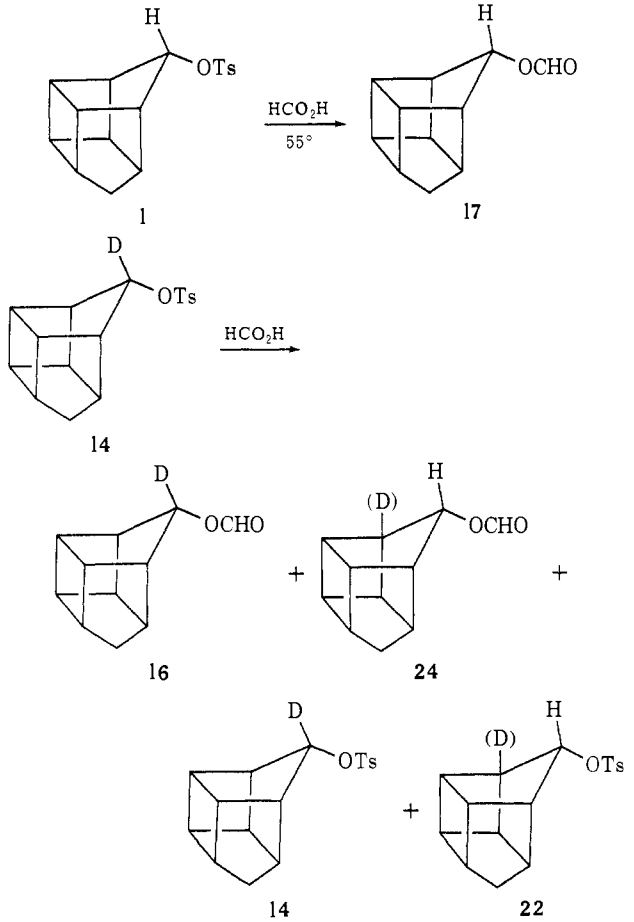
Temp, °C	Time, hr	Per cent acetolysis[a]	Ratio **15**:**23**[b] By H nmr	Ratio **15**:**23**[b] By D nmr	Ratio **14**:**22**[b] By H nmr	Ratio **14**:**22**[b] By D nmr
120 ± 2	7	~100[c]	52:48	50:50		
120 ± 1	0.67	52[d]	51:49		51:49	
100 ± 1	4.75	48[e]	53:47		56:44	
110 ± 1	0.75	26[f]	48:52	*g*	59:41	*g*
68 ± 1	4.75	8[h]	*i*		92:8	

[a] Based on unrecovered tosylate. [b] Accuracy of nmr analyses *ca.* ±3–4%. [c] Material balance 79%. [d] Material balance 92%. [e] Material balance 88%. [f] Per cent calculated based on known rate constant for nondeuterated tosylate **1**.[3] Value of 36% obtained from ratio of total acetates:total tosylates. Material balance 56% assuming 26% acetolysis. [g] Ratio of **14** + **15**:**22** + **23** = 56:44; H nmr gave ratio of 55:45. [h] Material balance 96%. [i] Amount of acetate too small to analyze.

Table III. Formolysis of α-Deuterated *syn*-1,3-Bishomocubyl Tosylate **14**

Temp, °C	Time, hr	Per cent formolysis[a]	Ratio **16**:**24**[b] By H nmr	Ratio **16**:**24**[b] By D nmr	Ratio **14**:**22**[b] By H nmr	Ratio **14**:**22**[b] By D nmr
55–60	5	~100	49:51	48:52		
55 ± 1	0.5	44	50:50	*c*	79:21	*c*

[a] Based on ratio of total formates to total tosylates in isolated product. [b] Accuracy of nmr analyses *ca.* ±3–4%. [c] Ratio of **14** to **16** was *ca.* 2:1; H nmr gives a ratio of 2:1. Ratio of **14** + **16**:**22** + **24** = 64:36; H nmr gives 66:34.

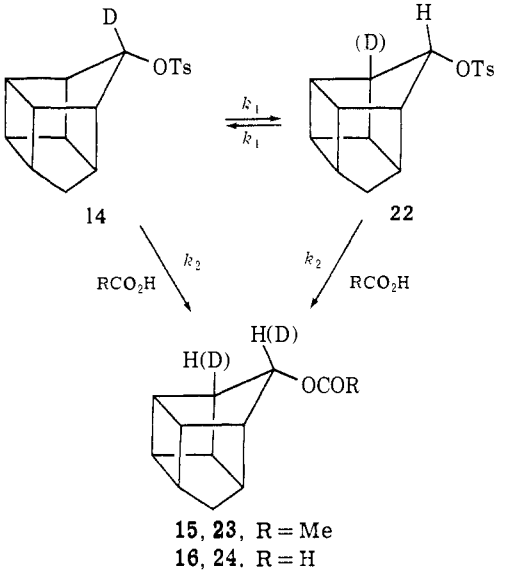


III. The 44% formolysis of tosylate **14** in 30 min corresponds to a first-order rate constant of 3.2 ± 0.4 × 10^{-4} sec^{-1}.

The rate of internal return (scrambling, k_1 in Scheme II) was determined from eq 1 where k_2 is the solvolytic rate constant, x is the concentration difference between the tosylates **14** and **22** expressed as mole fractions of the total reaction products (excluding toluenesulfonic acid), and t is the time.

$$k_1 = {}^1/_2\left(k_2 - \frac{\ln x}{t}\right) \quad (1)$$

Scheme II



15, **23**, R = Me
16, **24**, R = H

Secondary deuterium isotope effects were assumed to be negligible within our experimental error. Therefore the forward (**14** → **22**) and the reverse (**22** → **14**) reaction rate constants (k_1) are assumed to be equal. The solvolytic rate constants (k_2) for both **14** and **22** are also assumed to be equal. Approximate rate constants for solvolysis and internal return are presented in Table IV.

Acetolysis of the *anti*-tosylate[3] for 10 half-lives at 120° in the presence of excess sodium acetate gave primarily (87% of isolated product) the rearranged 1,4-bishomocubyl acetate **4**, a smaller amount (12%) of unrearranged *anti*-1,3-bishomocubyl acetate **5**, and a trace (1%) of inverted *syn*-1,3-bishomocubyl acetate **2** in 77% overall yield. In addition, a black carbonaceous precipitate formed, analogous to that formed in the absence of sodium acetate.[3]

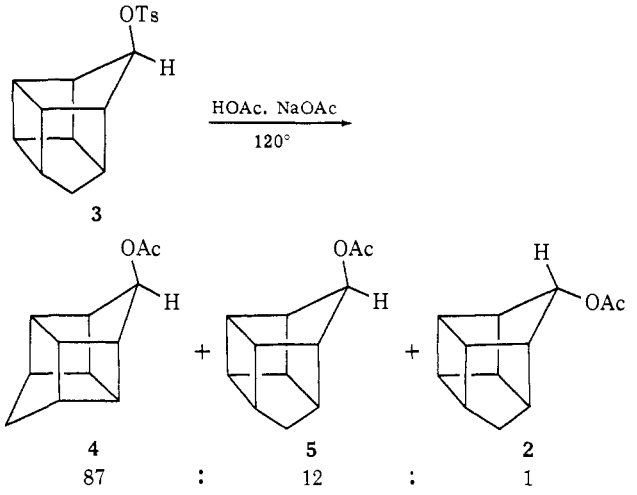
Discussion

In the acetolysis and formolysis of the tosylate **14** skeletal rearrangement occurred, and the deuterium atoms in the product were, within experimental error,

Table IV. Rates of Solvolysis and Internal Return for α-Deuterated *syn*-1,3-Bishomocubyl Tosylate **14**

Solvent	Temp, °C	k_2, sec^{-1}	k_1, sec^{-1}	k_1/k_2
HOAc	120	$2.82 \pm 0.04 \times 10^{-4}$ [a-c]	$>7.7 \times 10^{-4}$ [d]	>2.7[d]
	110	$1.10 \pm 0.02 \times 10^{-4}$ [a-c]	$4.3 \pm 0.9 \times 10^{-4}$ [e]	3.9 ± 0.8[e]
	68	$2.8 \pm 1.6 \times 10^{-6}$ [f]	$8.0 \pm 2.8 \times 10^{-6}$ [g]	2.9 ± 1.0[h]
	55	2.3×10^{-7} [b,i]		
HCO_2H	55	$3.5 \pm 0.7 \times 10^{-4}$ [j]	$4.7 \pm 0.5 \times 10^{-4}$ [k]	1.5 ± 0.2[h,k]

[a] Data from ref 3. [b] For nondeuterated tosylate **1**. [c] Standard deviation given.[3] [d] Lower limit assuming maximum error, 4%, in nmr analysis. Assuming the 51:49 ratio in Table II, k_1 is 1.1×10^{-3} sec^{-1} and k_1/k_2 is 3.9. [e] Average error given, assuming maximum and minimum rate constants (±4% of nmr analysis). [f] Error limits estimated from difference between experimental value (see Experimental Section) for **14** and calculated value for **1** based on data at higher temperatures.[3] [g] Error limits based on ±4% maximum error in nmr analysis for ratio of **14**:**22** and a k_2 value of 2.8×10^{-6} sec^{-1}. [h] Error limits based on error in k_1 only. [i] Calculated from data at higher temperatures.[3] [j] Average of rate constants for **1** and **14**. Error limits based on ±4% maximum error in nmr analysis. [k] Error limits based on ±4% maximum error in nmr analysis for ratio of **14**:**22** and a k_2 value of 3.2×10^{-4} sec^{-1} (value for **14**).



equally distributed between the 6 position and one of the tertiary carbon atoms (presumably the 5 position). These observations are consistent with, and are demanded by, the proposed bridged intermediate **25**. Although the results presented in this and previous papers[3] are consistent with, and most economically explained by, a bridged intermediate, such an intermediate is not mandatory. An alternate explanation which involves a pair of rapidly equilibrating ion pairs **26** and **27**, and their solvent-separated counterparts **28** and **29**, is shown in Scheme III.

After 1 half-life for acetolysis, the recovered tosylate **14** was essentially completely scrambled (especially at 120° and nearly so at 100°, Table II). The *anti*-tosylate **3** was shown previously to undergo internal return to the 1,4-bishomocubyl tosylate.[3] Partial acetolysis of the tosylate **14** at 110° (Table II) in which the acetate products, **15** and **23**, were completely scrambled within experimental error under conditions where the recovered tosylate was not completely scrambled served to prove that there must be a symmetrical intermediate **25** (or pair of intermediates which taken together are symmetrical, such as **26** and **27**) in the acetolysis as well as the formolysis (Scheme III).

Arguments concerning the relative merits of the bridged ion **25** or the equilibrating ion pairs **26** and **27** as the intermediate(s) in this solvolysis reaction have been discussed previously.[3] That the solvent-separated ion pairs **28** and **29** are responsible for the high degree of stereochemical retention remains a possibility, albeit rather unlikely, in light of recent work by Goering and Hopf.[8c] These authors found a slight predominance of retention of configuration in the solvolysis of several acyclic benzylic *p*-nitrobenzoates and "presume that retention results from favored capture (probably of a solvent-separated ion pair) by solvent molecules that are hydrogen bonded to the anion and as a result are more nucleophilic than the rest of the solvating molecule(s)." However, the stereospecificity was much lower in these reactions than that which we observed with the tosylate **1** (and **3**), even though the *p*-nitrobenzoate anion is a stronger base than the tosylate anion. On the other hand, angle strain at the cation center of ions **28** and **29** could lead to a nonplanar cation[9c,d,17] which would render rear-side displacement by solvent less facile.

The relative rates of formolysis and acetolysis (1500 ± 300) for the *syn*-tosylate **1** (**14**) at 55° are of the same order of magnitude or slightly larger than those reported for related compounds,[18] *e.g.*, 340 for *endo*-2-norbornyl brosylate[18a] and 1230 for 3,3-dimethyl-2-butyl brosylate.[18b] The ratio of rate constants for internal return (k_1) and solvolysis (k_2) of tosylate **14** in acetic acid (3.9 ± 0.8 at 110°) and formic acid (1.5 ± 0.2 at 55°) is also comparable to those for related compounds,[18e,19] *e.g.*, 3.48 for *exo*-2-norbornyl brosylate in acetic acid,[19a] 4.59 for *threo*-2-phenylethyl tosylate in acetic acid,[19b] and 1.16 for the latter compound in formic acid.[19b]

The results of acetolysis of the *anti*-1,3-bishomocubyl tosylate **3** in the presence of excess sodium acetate were essentially the same as those observed in the absence of sodium acetate.[3] The total yield of acetates in the absence (75%) and presence (77%) of sodium acetate was nearly the same. A black precipitate was formed in both reactions. Thus, the presence of sodium acetate did not prevent extensive decomposition [to carbon and (or) polymer] of about a quarter of the tosylate **3** or product derived thereform. The finding of a small amount (*ca.* 1%) of the *syn*-1,3-bishomocubyl acetate **2** in this study and not in the previous one,[3] where sodium acetate was absent, was probably due to the use of a more sensitive analytical technique (see Exper-

(17) See for example (a) J. E. Williams, Jr., R. Sustmann, L. C. Allen, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 91, 1037 (1969); (b) J. E. Williams, Jr., V. Buss, L. C. Allen, P. v. R. Schleyer, W. A. Lathan, W. J. Hehre, and J. A. Pople, *ibid.*, 92, 2141 (1970); (c) G. V. Pfeiffer and J. G. Jewett, *ibid.*, 92, 2143 (1970).

(18) (a) S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan, and H. Marshall, *ibid.*, 74, 1127 (1952); (b) S. Winstein and H. Marshall, *ibid.*, 74, 1120 (1952); (c) S. Winstein, C. R. Lindegren, H. Marshall, and L. L. Ingraham, *ibid.*, 75, 147 (1953); (d) S. Winstein, M. Brown, K. C. Schreiber, and A. H. Schlesinger, *ibid.*, 74, 1140 (1952); (e) S. Winstein and G. C. Robinson, *ibid.*, 80, 169 (1958).

(19) (a) S. Winstein and D. Trifan, *ibid.*, 74, 1154 (1952); (b) S. Winstein and K. C. Schreiber, *ibid.*, 74, 2165 (1952).

Scheme III

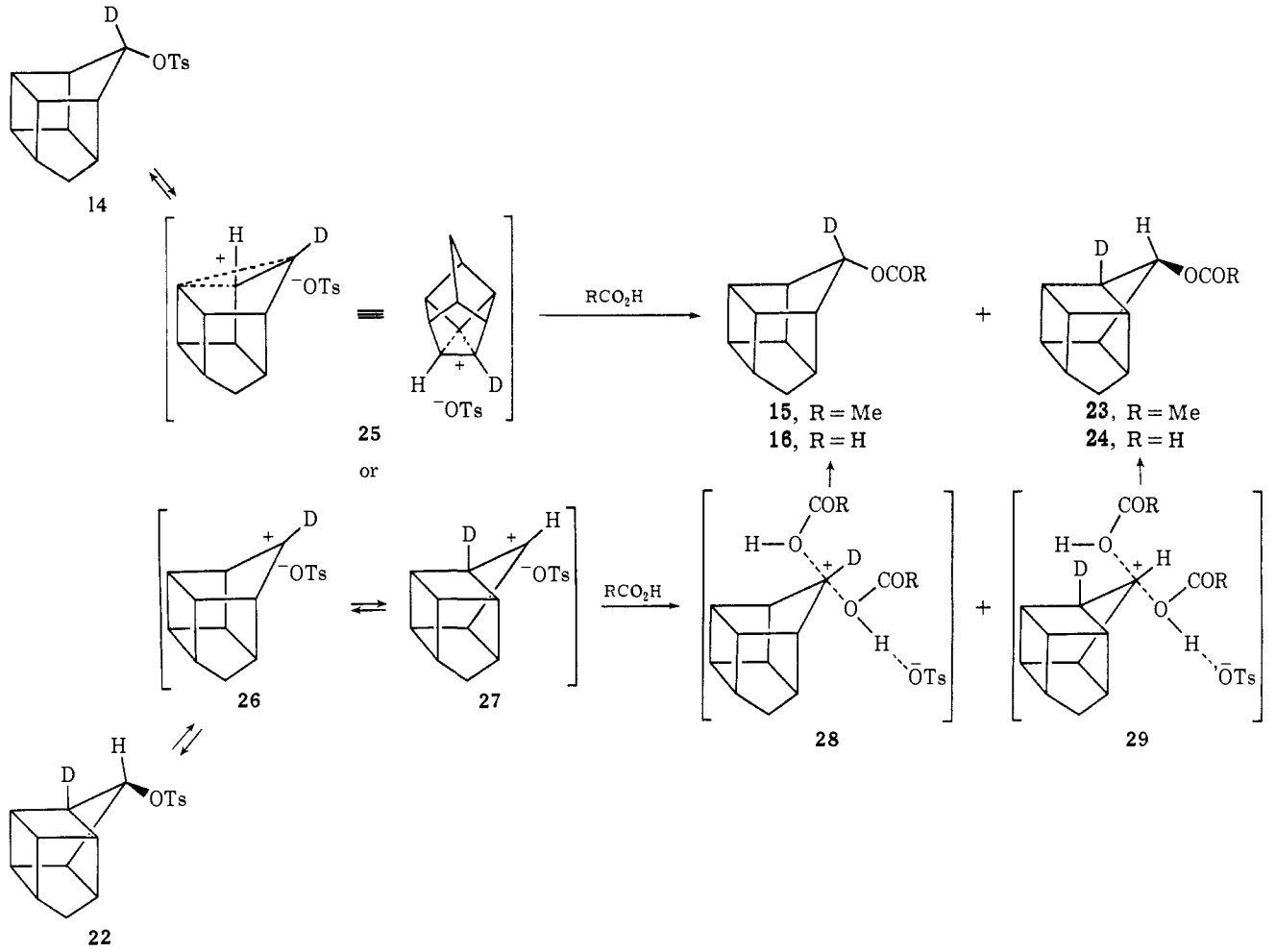


Table V. Major Fragment Ions in Mass Spectra of *syn*-1,3-Bishomocubyl Alcohols **12** and **20**

Nondeuterated **20**			Deuterated **12**		
m/e	Rel intensity[a]	Assignment	*m/e*	Rel intensity[a]	Assignment[b]
66	1	$C_5H_6^+$	66	1	$C_5H_6^+$
82	3	$C_5H_6O^+$	83	3	$C_5H_5DO^+$
117	5	$M^+ - CH_3O$	117	5	$M^+ - CH_2DO$
129	4	$M^+ - H_3O$	130	4	$M^+ - H_3O$
130	2	$M^+ - H_2O$	131	2	$M^+ - H_2O$

[a] Numbers 1–5 refer to five most intense ion peaks in spectrum, 1 most intense, etc. [b] These assignments are for the major contributors to the indicated ion peaks. Minor amounts of other ions may contribute; *e.g.*, a small fraction of *m/e* 130 may be due to $M^+ - HDO$.

imental Section). There may have been a small amount of this isomer produced in the absence of sodium acetate.

The mass spectral fragmentation patterns of the alcohols **20** and **30** were of interest with respect to a possible correlation with the solvolytic reactivity of their corresponding tosylates. Such correlations have been made previously in other systems.[20] The spectra of the alcohols **20** and **30** are shown in Figures 1 and 2, respectively. Some aspects of the mass spectrum of the mixed isomers **20** and **30** have been discussed previously.[21] With the *syn*-6-deuterio derivative **12** in hand we were in a position to make more definite assignments of some of the fragmentation mechanisms. In Table V are listed the most prominent ion peaks occurring in the mass spectrum of the nondeuterated alcohol **20** and the deuterated alcohol **12**.

The fragment ions at *m/e* 66, 82, and 83 are consistent with our previous proposal of cleavage of the carbon skeleton in half.[21] These results also indicate that H–D scrambling is not extensive in the molecular ion before fragmentation.

The identical masses, *m/e* 117 $(C_9H_9)^+$, for the fifth most intense ion peak in each spectrum show that in the loss of CH_3O (not necessarily in one step) from the molecular ion of **20**, one of the hydrogen atoms comes from C-6. It is tempting to postulate that $C_9H_9^+$ is the homocubyl cation[22] although no evidence is available on this point.

(20) (a) D. C. DeJongh and S. R. Shrader, *J. Amer. Chem. Soc.*, **88**, 3881 (1966); (b) T. W. Bentley and R. A. W. Johnstone, *Advan. Phys. Org. Chem.*, **8**, 223 (1970).

(21) W. L. Dilling and M. L. Dilling, *Tetrahedron*, **23**, 1225 (1967).

(22) (a) P. v. R. Schleyer, J. J. Harper, G. L. Dunn, V. J. DiPasquo, and J. R. E. Hoover, *J. Amer. Chem. Soc.*, **89**, 698, 2242 (1967); (b) J. C. Barborak and R. Pettit, *ibid.*, **89**, 3080 (1967).

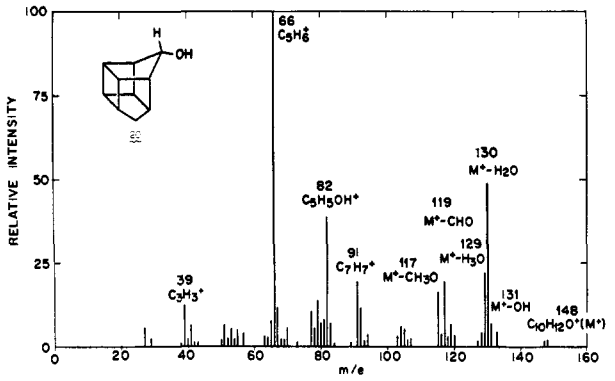


Figure 1. Mass spectrum of *syn*-pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]-decan-6-ol (**20**).

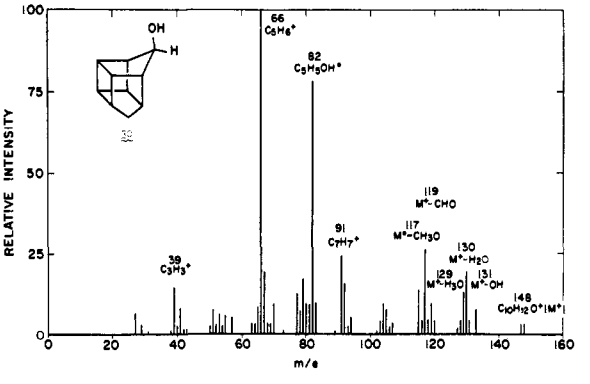
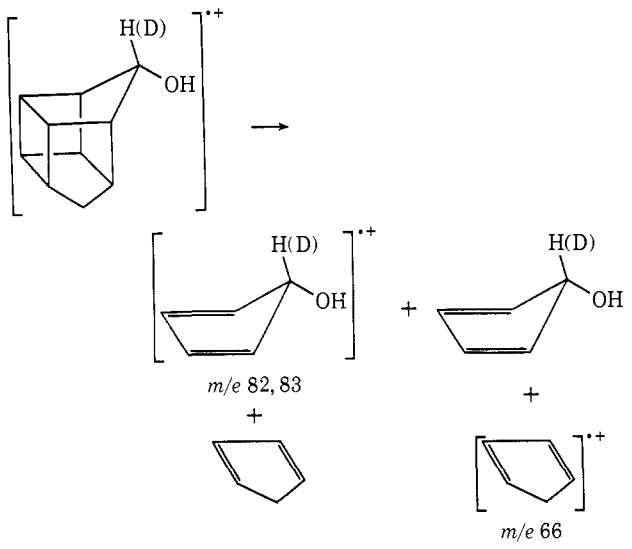


Figure 2. Mass spectrum of *anti*-pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]-decan-6-ol (**30**).



Comparison of the ion peaks at *m/e* 129, 130, and 131 indicates that for the most part the loss of H_2O and H_3O from the molecular ion of **20** does not involve loss of the hydrogen atom on C-6. Based on previous work in acyclic systems[23] one does not expect the hydrogen atom on the hydroxyl-bearing carbon atom to be lost in these fragmentations.

A comparison of the intensity of some of the more significant ion peaks in the spectra of the syn and anti alcohols **20** and **30** is given in Table VI. It is particularly interesting to note the greater intensity for the ions at *m/e* 129 and 130, which represent loss of the functional group plus one or two additional hydrogen atoms, for the syn isomer **20**. These results parallel the solvolytic reactivity of the corresponding tosylates. The *syn*-tosylate **1** undergoes acetolysis 3–6 times as fast as the anti isomer **3**.[3] The loss of one or two hydrogen atoms in addition to the hydroxyl group, on electron impact, renders the analogy with the solvolysis less direct than desirable. Due to the low intensity of the ion peaks at *m/e* 131 (see Figures 1 and 2) and the isotopic contribution from *m/e* 130, a comparison of the $M^+ - OH$ ion-peak intensities is probably unreliable. The lower intensity of the molecular ion from the *syn*-alcohol **20** was also consistent with the solvolytic reactivity. Often the more sterically hindered isomer of a pair of epimeric alcohols exhibits the lower intensity molecular ion peak and the greater intensity ion peaks for the loss of the functional group.[24] This explanation cannot be valid for the epimers **20** and **30** since they are of equal thermodynamic stability.[3]

Table VI. Per Cent Total Ionization in Mass Spectra of *syn*- and *anti*-1,3-Bishomocubyl Alcohols **20** and **30**

	—Per cent total ionization[a]—		
m/e	*syn*-**20**	*anti*-**30**	Assignment
66	19.5	16.9	$C_5H_6^+$
82	7.6	13.3	$C_5H_5OH^+$
129	4.3	2.2	$M^+ - H_3O$
130	9.5 (9.0)	3.3 (3.1)	$M^+ - H_2O$
148	0.39	0.51	M^+

[a] Σ_{15}. The numbers in parentheses are the per cent total ionization due to the ions designated in the assignment column. The remainder is due to the ^{13}C isotope peak from the (*m/e*) − 1 ion peak.

(23) F. W. McLafferty, "Interpretation of Mass Spectra," W. A. Benjamin, New York, N. Y., 1966, p 131.

Experimental Section

General. Melting points were taken in capillary tubes and were uncorrected. Infrared spectra were obtained by Mr. F. L. Beman and coworkers with a Perkin-Elmer 337 grating infrared spectrophotometer. Unless otherwise specified, proton nmr spectra were obtained by Mr. Beman and coworkers with a Varian A-60 analytical spectrometer operating at 60 MHz. Spectra obtained at 60 MHz with a computer averager were obtained by Dr. J. P. Heeschen and coworkers with a Varian A-56/60A spectrometer equipped with a Varian C-1024 time-averaging computer. The 100-MHz spectra were obtained by Dr. Heeschen and coworkers with a Varian HA-100 high-resolution spectrometer. All proton chemical shifts (δ) are relative to internal tetramethylsilane (positive when downfield from the reference). Deuterium nmr spectra were obtained by Dr. L. M. Huber with a spectrometer designed and built by Baker and Burd.[25] The operating frequency was 9.212 MHz. Chloroform-*d* was used as an internal reference. Chemical shifts in parts per million relative to chloroform-*d* (negative when upfield from the reference) were related to shifts from tetramethylsilane-d_{12} by the relationship $\delta_{(CD_3)_4Si} = \delta_{CDCl_3} + 7.25$ which was assumed to be equivalent to $\delta_{Me_4Si} = \delta_{CHCl_3} + 7.25$.[26] The deuterium chemical shifts are reported relative to tetramethylsilane-d_{12}. All nmr area measurements were made by electronic integration and are accurate to *ca.* ±3–4%. In some cases integrations were checked by planimeter measurements and weights of peaks cut from paper. Mass spectral analyses were carried out by Dr. L. A. Shadoff, Mrs. M. L. Dilling, and their coworkers with a magnetically scanning 90° sector spectrometer using an electron ionizing voltage of 75 eV. The sample inlet temperature was 200° unless

(24) (a) K. Biemann and J. Seibl, *J. Amer. Chem. Soc.*, **81**, 3149 (1959); (b) K. Biemann, "Mass Spectrometry, Organic Chemical Applications," McGraw-Hill, New York, N. Y., 1962, pp 145–148.

(25) E. B. Baker and L. W. Burd, *Rev. Sci. Instrum.*, 34, 238 (1963).

(26) See reference in footnote *c*, Table I.

otherwise specified. High-resolution mass spectra were obtained with a CEC 21-110B spectrometer employing a variable temperature direct probe sample introduction system. Gas chromatographic analyses and preparative separations were carried out with an F & M 500 temperature programmed gas chromatograph. Microanalyses were determined by Mr. L. E. Swim and coworkers.

Pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decan-6-*d*-*syn*-6-ol (12). (a) Irradiation of *endo*-Tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-*d*-*syn*-3-ol (10). According to the procedure described previously[3] for the preparation of the nondeuterated analog, the deuterated dienol **10**[14] (13.55 g) in 140 ml of acetone was converted to 3.47 g (26%) of deuterated alcohol **12**, mp 149–158°, which was used in the preparation of the tosylate **14** and acetate **15**. Further recrystallization from hexane and sublimation gave a sample of alcohol **12**: mp 176.5–178° (lit. mp of nondeuterated analog, 175–176°,[3] 180–181°[27]); $\nu_{max}^{CCl_4}$ 2160 (w) and 2140 cm^{-1} (w) (C–D).[28]

Anal. Calcd for $C_{10}H_{11}DO$: C, 80.50; H(D), 8.78; mol wt, 149. Found: C, 80.6, 80.7; H(D), 8.47, 8.78; mol wt, 149 (mass spectrometry).

(b) Lithium Aluminum Deuteride Reduction of Pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decan-6-one (11). By the method described[21] for the lithium aluminum hydride reduction, 0.75 g of the ketone **11**[27] and 0.16 g of lithium aluminum deuteride gave 0.63 g (84%) of alcohols (presumably 80% **12**, 20% **13** based on the lithium aluminum hydride reduction[21]), mp 168–173° (lit.[21] mp 173–174° for 80:20 mixture of alcohols **20** and **30**). The nmr spectrum in the 1.8–1.1-ppm region was in approximate agreement with this composition although a reliable quantitative analysis could not be made.

Pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]dec-6-*d*-*syn*-6-yl-*p*-Toluenesulfonate (14). According to the procedure described previously,[3] 2.15 g of the alcohol **12** and 3.0 g of *p*-toluenesulfonyl chloride in pyridine gave 1.85 g (42%) of deuterated tosylate **14**: mp 64–66° (lit.[3] mp of nondeuterated analog, 64.5–65.5°); $\nu_{max}^{CCl_4}$ 2210 cm^{-1} (w, C–D); mass spectrum *m/e* 131 ($C_{10}H_9D^+$, $M^+ - CH_3C_6H_4SO_3H_2$), 148 ($C_{10}H_{11}DO^+$, $M^+ - CH_3C_6H_4SO_2$), 155 ($CH_3C_6H_4SO_2^+$, $M^+ - C_{10}H_{11}DO$), 238 ($C_5H_4DOSO_2C_6H_4CH_3^+ + H$, $M^+ - C_5H_5$), 303 (M^+).[28]

Anal. Calcd for $C_{17}H_{17}DO_3S$: C, 67.30; H(D), 6.31; mol wt, 303. Found: C, 67.3; H(D), 5.89; mol wt, 303 (mass spectrometry).

Pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]dec-6-*d*-*syn*-6-yl Acetate (15). According to the method described[3] for the nondeuterated acetate, 0.38 g of the deuterated alcohol **12** and 1.6 ml of acetic anhydride in pyridine gave 0.37 g (76%) of the deuterated acetate **15** as a light yellow oil: $\nu_{max}^{CCl_4}$ 2215 (w) and 2165 cm^{-1} (w) (C–D); mass spectrum *m/e* 43 (third most intense ion peak, CH_3CO^+), 66 (second most intense, $C_5H_6^+$), 83 (base peak, $C_5H_5DO^+$, $M^- - C_5H_6$, C_2H_2O), 126 (sixth most intense, $C_5H_4DOCOCH_3^+ + H$, $M^+ - C_5H_5$), 131 (fifth most intense, $C_{10}H_9D^+$, $M^+ - CH_3CO_2H$), 132 (fourth most intense, $C_{10}H_{10}D^+$, $M^+ - CH_3CO_2$).[28] Gc analysis (10 ft × 0.25 in. column packed with 20% Apiezon L on 60–80 mesh Chromosorb WAW, 175°, 43 ml of He/min) showed one major component, t_R 47.6 min (99.4% of the total area), and an impurity, t_R 33.5 min.

***syn*-Pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]dec-6-yl Formate (17).** According to the general procedure of Vogel,[15] a mixture of the *syn*-alcohol **20**[3] (0.2 g, 1.3 mmol) and 0.5 ml of 98–100% formic acid was allowed to stand at ~25° for 3 hr. The mixture was diluted with 10 ml of water and extracted with 10 ml of pentane. The organic layer was washed with 5 ml of 10% aqueous sodium carbonate solution and then water and dried. Evaporation of the solvent afforded ~0.2 g (~84%) of **17** as a slightly yellow oil: ν_{max}^{neat} 2980 (s) and 2865 (m) (CH), 1725 (s, C=O), 1175 cm^{-1} (s, CO); nmr spectrum (CCl_4) a singlet at 7.97 (1.0 H, OCHO), a slightly broadened singlet at 4.86 (1.0 H, -CH(OCHO)-), a multiplet at 3.1–2.4 with maximum intensity at 2.72 (7.9 H, >CH), two unsymmetrical doublets centered at 1.69 and 1.41 ppm with further ill-defined splitting (2.1 H, CH_2, J_{gem} = 11.2 Hz). A sample was purified for analysis by preparative gc (Apiezon L column, 150°, 150 ml of He/min).

Anal. Calcd for $C_{11}H_{12}O_2$: nuclidic mass, 176.0837. Found: nuclidic mass, 176.0819.

The *syn*-alcohol **20** (0.1 g) in 0.3 ml of 98–100% formic acid at 0° was converted to the formate **17** to the extent of 82% in ~0.5 hr and 100% in 1.5 hr as determined by integration of the α-proton resonances at 4.18 (**20**) and 4.97 ppm (**17**).

***anti*-Pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]dec-6-yl Formate (18).** The *anti*-alcohol **30**[3] (0.1 g) in 0.3 ml of 98–100% formic acid was converted to the formate **18** to the extent of 85% in less than 0.5 hr and 100% in 3 hr as determined by integration of the α-proton resonances at 4.46 (**30**) and 5.22 ppm (**18**). The *anti*-formate **18** was isolated by preparative gc (Apiezon L column, 150°, 150 ml of He/min): ν_{max}^{neat} 2980 (s) and 2865 (m) (CH), 1725 (s, C=O), ~1175 cm^{-1} (s, CO); nmr spectrum (CCl_4) a singlet at 7.86 (1.0 H, OCHO), a slightly broadened singlet at 5.12 (1.0 H, -CH(OCHO)-), a multiplet at 3.0–2.4 with maxima at 2.77 and 2.70 (8.0 H, >CH), two unsymmetrical doublets centered at 1.67 and 1.25 ppm (2.0 H, CH_2, J_{gem} = 10.9 Hz).

Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 75.0; H, 6.88.

Pentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]dec-5-yl Formate (19). Pentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decan-5-ol[3] (**31**) (0.1 g, 90% pure, contained 10% *anti*-alcohol **30**[3]) in 0.3 ml of 98–100% formic acid was converted to the formate **19** to the extent of 82% in less than 0.5 hr and 100% in 3 hr as determined by integration of the α-proton resonances at 4.25 (**31**) and 5.03 ppm (**19**). The 10% of *anti*-formate **18** was also observed (5.22 ppm). The 90:10 mixture of formates **19** and **18** was isolated by preparative gc (Apiezon L column, 150°, 150 ml of He/min): ν_{max}^{neat} 2980 (s) and 2850 (m) (CH), 1725 (s, C=O), 1172 cm^{-1} (CO); nmr spectrum (CCl_4) a singlet at 7.89 (1.0 H, OCHO), a broad singlet at 5.12 (0.1 H, -CH(OCHO)- of **18**), a slightly broadened singlet at 4.93 (0.8 H, -CH(OCHO)- of **19**), a multiplet at 3.1–2.3 with a maximum at 2.85 (8.0 H, >CH), and a slightly broadened singlet at 1.44 ppm (1.7 H, CH_2 of **19**) superimposed on the low-intensity AB quartet of **18** (0.3 H).

Pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]dec-6-*d*-*syn*- (16) and -*anti*- (32) 6-yl Formates. The approximate 80:20 mixture of α-deuterated alcohols **12** and **13** (0.15 g, 1.0 mmol), prepared by the lithium aluminum deuteride reduction of ketone **11**, was heated at 60° for 30 min in 0.3 ml of 98–100% formic acid to give the corresponding mixture of α-deuterated formates **16** and **32**: nmr spectrum (HCO_2H) a multiplet at 3.2–2.4 (7.9 H, >CH) and two unsymmetrical doublets with further ill-defined splitting centered at 1.69 and 1.41 ppm (2.1 H, CH_2 of **16**, J_{gem} = 11.0 Hz) superimposed on weak absorption due to the methylene group of the anti isomer **32**. The formate proton absorptions were obscured by solvent absorption.

Acetolysis of Pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]dec-6-*d*-*syn*-6-yl *p*-Toluenesulfonate (14). (a) At 120° for 7 Hr. According to the previously described method[3] a solution (0.058 *M*) of the deuterated tosylate **14** (0.400 g) in acetic acid was heated for 10 half-lives[3] and worked up to give 0.224 g (89%) of light yellow liquid acetate. Gc analysis (Apiezon L column, 225°, 41 ml of He/min) showed only trace amounts of impurities (<0.5% of area) in addition to one major acetate component, t_R 12.6 min. The D nmr spectrum showed singlets for -CDOAc- [$W_{h/2}$ (width at half-height) = 1.3 Hz] and >CD ($W_{h/2}$ = 2.1 Hz); $CDCl_3$ (internal reference) had $W_{h/2}$ = 1.1 Hz. Addition of benzene to the H nmr solution as an internal standard indicated the acetate to be ~89% pure (weight per cent). The acetate was purified by preparative gc (10 ft × 0.25 in. 20% 410 silicone gum rubber on 60–80 mesh Chromosorb WAW, column temperature 235°, 42 ml of He/min, t_R 8.4 min). Addition of benzene to the H nmr solution as an internal standard indicated a purity of 102% for the acetate. The nmr analyses are shown in Table II. The mass spectrum showed significant ion peaks at *m/e* 131 ($C_{10}H_9D^-$, $M^+ - HOAc$), 149 ($C_{10}H_{11}DO^+$, $M^+ - C_2H_2O$), and 191 (M^+).

(b) At 120° for 0.67 Hr. The same quantities of reactants as in the preceding experiment were heated for 1.0 half-life[3] to give 0.329 g of yellow liquid and white crystals. Addition of trichloroethylene to the nmr solution as an internal standard indicated the presence of 0.186 g of recovered tosylate (92% of the theoretical amount calculated for 1.0 half-life) and 0.115 g of acetate (92%). The mixture of tosylate and acetate was heated at 50° and 0.2-mm pressure to remove the acetate and other volatile components. A red liquid remained which would not crystallize. The D nmr spectrum showed singlets for -CDOTs- (0.6 D, $W_{h/2}$ = 3.2 Hz) and >CD (0.4 D, $W_{h/2}$ = 4.5 Hz). This result was not used in the calculation of k_1 in Table IV. The nmr analyses are shown in Table II.

(c) At 100° for 4.75 Hr. The same quantities of reactants as in

(27) R. C. Cookson, J. Hudec, and R. O. Williams, *J. Chem. Soc. C*, 1382 (1967).

(28) The spectral data for the deuterated compounds were the same as those reported[3] for the nondeuterated analogs except as noted. The infrared spectra in the fingerprint region (1400–400 cm^{-1}) were different.

part a were heated for 1.0 calcd half-life[3] to give 0.318 g of a tosylate–acetate mixture. Addition of trichloroethylene to the H nmr solution as an internal standard indicated the presence of 0.210 g (52%) of recovered tosylate and 0.092 g (36%) of acetate. The nmr analyses are shown in Table II.

(d) **At 110° for 0.75 Hr.** The α-deuterated *syn*-tosylate **14** (83.1 mg) in glacial acetic acid (0.069 *M*) was heated for 45 min to give 42.4 mg of an oil. The nmr analyses are shown in Table II.

(e) **At 68° for 4.75 Hr.** The same quantities of reactants as in part a above were heated for 0.029 calcd half-life[3] to give 0.389 g of oil. On cooling the crude reaction mixture, 0.218 g of crystals were obtained. Recrystallization from ether–hexane gave 0.140 g of light yellow crystals, mp 62.5–65°. The nmr analyses are shown in Table II.

Stability of Acetate 15 in Acetic Acid Which Contained Toluenesulfonic Acid. A solution of *p*-toluenesulfonic acid hydrate (0.1004 g, 0.523 mmol) and acetic anhydride (60 μl, 0.64 mmol) in 9 ml of purified acetic acid (0.058 *M* in toluenesulfonic acid) was heated at 120° for 16 hr to dehydrate the toluenesulfonic acid. The deuterated acetate **15** (0.10 g, 0.52 mmol, 0.058 *M*) was added, and the resulting solution was heated at 120 ± 2° for 7 hr. The reaction mixture was worked up as in the acetolysis reactions above to give 0.09 g (90%) of yellow liquid. The infrared spectrum was identical with that of the starting acetate with the exception of several weak maxima (estimated impurity level <5%). No absorption could be detected in the H nmr spectrum below 3.2 ppm for –CHOAc–. The H nmr spectrum was identical with that of the starting acetate with the exception of several minor impurity absorptions. Addition of a known amount of the nondeuterated acetate **2**[3] demonstrated that 8% hydrogen at C-6 could be detected. It was estimated that 4% hydrogen at C-6 would have been easily detected.

Formolysis of *syn*-Pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]dec-6-yl *p*-Toluenesulfonate (1). A solution (~0.57 *M*) of the *syn*-tosylate **1**[3] (60 mg, 0.20 mmol) in 0.35 ml of 98–100% formic acid was heated at 54.5° for 30 min. The nmr spectrum of the solution indicated a 51:49 ratio of tosylate **1** to formate **17**. This 49% reaction in 30 min corresponds to a first-order rate constant of 3.8×10^{-4} sec^{-1}. After the solution was heated at 54.5° for 2.5 hr the reaction was complete. The H nmr spectrum of the solution showed only the *syn*-formate **17** (in addition to *p*-toluenesulfonic acid); none of the *anti*-**18** or symmetrical **19** formates were detected.

Formolysis of Pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]dec-*6-d-syn*-6-yl *p*-Toluenesulfonate (14). (a) **At 55–60° for 5 Hr.** A solution (0.33 *M*) of deuterated tosylate **14** (0.20 g, 0.66 mmol) in 2 ml of 98–100% formic acid was heated for ~10 half-lives. The reaction mixture was poured into 75 ml of cold water, and the products were extracted with two 30-ml portions of ether. The combined ether extracts were washed with water, 10% sodium carbonate, and water and dried over anhydrous magnesium sulfate. Evaporation afforded a light yellow oil. The nmr analyses are shown in Table III. There was no indication of any isomeric formate. The D nmr spectrum (CCl_4) (taken 27 months after the H nmr spectrum) showed singlets at 4.77 ($W_{h/2}$ = 2.0 Hz), 3.92 ($W_{h/2}$ = 2.8 Hz), and 2.55 ppm. Infrared and proton nmr spectroscopic examination of this sample confirmed the supposition that the original formate ester had largely hydrolyzed to the alcohol during storage.

(b) **At 55° for 0.5 Hr.** The same quantities of reactants as in the preceding experiment were heated for 1 half-life and worked up as described in part a. The nmr analyses are shown in Table III.

Stability of Formate 16 in Formic Acid Which Contained Toluenesulfonic Acid. A solution of the approximately 80:20 mixture of deuterated formates **16** and **32** (from 0.15 g of alcohols **12** and **13**, 1.0 mmol) and *p*-toluenesulfonic acid monohydrate (0.19 g, 1.0 mmol) in 0.3 ml of 98–100% formic acid (3.3 *M* in formate ester and in toluenesulfonic acid) was heated at 60° for 45 min. The H nmr spectrum of this solution showed no absorption between 6.0 and 3.1 ppm which indicated the absence of rearranged formate **24** (or rearranged formates corresponding to **18** or **19**). The limit of detectability was ~2%.

Acetolysis of *anti*-Pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]dec-6-yl *p*-Toluenesulfonate (3) with Added Sodium Acetate. A solution of the *anti*-tosylate **3** (185.5 mg, 0.61 mmol) and anhydrous (reagent grade material dried at 160° for 2 days) sodium acetate (201.1 mg, 2.45 mmol) in 10.0 ml of glacial acetic acid (0.0614 *M* in tosylate and 0.245 *M* in acetate ion) was heated at 120 ± 1° for 38 hr (10 half-lives[3]). The reaction was worked up as described previously[3] to give 89.4 mg (77%) of a pale yellow liquid acetate mixture: ν_{max}^{neat} 2970 (s) and 2850 (m) (CH), 1735 (s, C=O), 1240 (s, CO), 1032 (s) cm^{-1}; nmr spectrum (CCl_4, 60 MHz) a broad singlet centered at 4.96 (0.11 H, -CHOAc- of **5**), a triplet at 4.76 [0.80 H, $(>CH^B)_2CH^AOAc$ of **4**, J_{AB} = 1.6 Hz], a multiplet at 3.1–2.4 (8.0 H, $\geqslant$CH), three singlets at 1.97 ($COCH_3$ of **2**), 1.90 ($COCH_3$ of **4**), 1.88 ($COCH_3$ of **5**) (3.1 H total, area ratio 1.3:86.9:11.8, respectively by planimeter measurement on a 50-Hz sweep width scan run on a 100-MHz spectrometer), and an unsymmetrical triplet at 1.48 [$(>CH^C)_2CH_2^D$ of **4**, J_{CD} = 1.6 Hz] overlapping a multiplet at 1.8–1.1 ppm (CH_2 of **2** and **5**) (2.0 H total).

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