Table II

Compd	Sample wt, mg	Pyrolysis temp, °C	Pressure, mm	Yield of products, mg (%)
1b	246	600–610	12	203 (100)[a]
1c	228	580–600	12	186 (100)[a]
2b	170	615	8–9	135 (97.5)[a]

[a] According to vpc analysis, these mixtures consisted chiefly (95%) of methylquinolines.

was added 675 mg of 3-hydroxyisoquinoline. The solution was stirred for 5 hr at −10 to −20° and was allowed to come to room temperature overnight. The solution was concentrated by directing a stream of air at its surface; dimethylformamide was removed *in vacuo*, and the residual oil was molecularly distilled. Pure **6** was isolated by preparative vpc; $\delta_{TMS}^{CDCl_3}$ 8.7 (singlet, 1 H), 7.36 (multiplet, 4 H), 6.78 (singlet, 1 H), and 3.90 (singlet, 3 H). Its picrate melted at 197–198°.

Anal. Calcd for $C_{16}H_{12}N_4O_8$: C, 49.47; H, 3.12; N, 14.43. Found: C, 49.54; H, 3.30; N, 14.48.

Product Characterization from the Pyrolysis of 1b, 1c, and 2b. 2-Methylquinoline picrate, mp 194–195°, was prepared from a commercial sample (lit.[24] mp 195°). 3-Methylquinoline was prepared from aniline and α-methylacrolein (Skraup) according to the procedure of Manske, *et al.*;[24] picrate mp 189° (lit.[24] mp 190°). 4- and 6-methylquinolines were commercially available. 5- and 7-methylquinolines were obtained from reaction of *m*-toluidine and glycerol under the conditions described by Palmer.[25] The isolated 8-methylquinoline afforded a picrate, mp 202–204° (lit.[26] mp 202–204°).

Some representative pyrolysis experiments are summarized in Table II (results and product ratios were consistently reproducible).

Partial Pyrolyses. The partial pyrolyses indicated in Table III were studied.

Table III

Compd	Temp, °C	Product ratio, %: 1	2	Aromatics
1a	500	75[b]	..	25[c]
1b	505	32[d]	..	68[e]
1c	580–600	3.5[f]	..	96.5[e]
2a	500	31[b]	67[g]	2[c]
2b	460	17.5[h]	52[i]	30.5[e]

[a] Percentage composition values were obtained directly from vpc analyses. [b] Exclusively **1a**. [c] A mixture of **3–6**. [d] Exclusively **1b**. [e] A mixture of methylquinolines. [f] Exclusively **1c**. [g] Exclusively **2a**. [h] A mixture of methylated derivatives. [i] Exclusively **2b**.

Acknowledgment. We wish especially to thank the Badische Anilin und Soda Fabrik for the generous gift of cyclooctatetraene which made this work possible.

(24) R. H. F. Manske, L. Marion, and F. Leger, *Can. J. Res.*, **20B**, 133 (1942).

(25) M. H. Palmer, *J. Chem. Soc.*, 3645 (1962).

(26) E. P. Adams, F. P. Doyle, and J. H. C. Naylor, *ibid.*, 3066 (1957).

The Involvement of Oxygenated Functions in the Acetolysis of 7-Oxygenated Norbornyl Tosylates

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Abstract: Acetolyses of *exo*- and *endo*-2-tosyloxybicyclo[2.2.1]heptan-7-one ethylene glycol ketal have been studied. Whereas the *exo*-tosylate gave *exo*-acetate as the major product, the predominant reaction path followed by the *endo* isomer was one of ring cleavage to yield substituted cyclohexenes. The *exo*-tosylate solvolyzed eleven times faster than the *endo* isomer. Although the rates of solvolysis were similar to *endo*-2-tosyloxybicyclo[2.2.1]heptane, the dramatic change in product ratios showed that more than one mechanism was involved.

Few intermediates in the history of chemistry have received more attention than the norbornyl cation. In attempts to define the nature of this unusual cation, investigators have pursued a remarkably singular mode of attack. This commonly accepted approach has been to functionalize generously the norbornyl skeleton with groups which could stabilize an incipient cation (relative to stabilization by hydrogen) by either their electron-donating ability or through resonance. In view of the interest in this problem it is surprising that only a few examples of norbornyl systems bearing electron-withdrawing substituents have been studied.[2–5] Unfortunately even among these few cases there is no clear-cut example which allows a rigorous comparison of the behavior of *exo*- and *endo*-arenesulfonates. Roberts and coworkers[2,6] and Wilt and Wagner[5] studied only *exo*-tosylates. The investigations of Gassman and Marshall on derivatives of 7-ketonorbornane were complicated by the change in hybridization at C-7 and by the possibility that the carbonyl group might be exerting an unprecedented influence on the developing carbonium ion center. In the solvolysis of the 7,7-dimethoxy-2-tosyloxynorbornanes, the interpretation of the results was complicated by the fact that the *endo*-tosylate **1** solvolyzed with MeO-4 neighboring group participation,[3] while the *exo*-tosylate **2** appeared to solvolyze without participation of the neighboring methoxyl func-

(1) Alfred P. Sloan Research Fellow, 1967–1969.

(2) W. G. Woods, R. A. Carboni, and J. D. Roberts, *J. Am. Chem. Soc.*, 78, 5653 (1956).

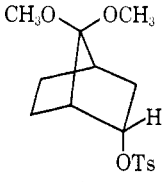
(3) P. G. Gassman and J. L. Marshall, *ibid.*, **88**, 2822 (1966).

(4) P. G. Gassman and J. L. Marshall, *Tetrahedron Letters*, 2429, 2433 (1968).

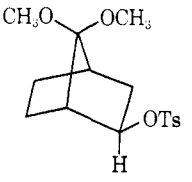
(5) J. W. Wilt and W. J. Wagner, *J. Am. Chem. Soc.*, **90**, 6135 (1968).

(6) For a detailed reinvestigation of the acetolyses of the 7-chloro, norbornyl tosylates, see P. G. Gassman and J. M. Hornback, *ibid.*, **9-1** 4280 (1969).

tion. In order to bypass the MeO-4 participation in the case of **1**, we have prepared the epimeric tosylates **3** and **4** in which the heterotoms at C-7 are "tied back" by incorporation into a dioxolane ring. We wish to report at this time on the anomalous solvolytic behavior of **3** and **4**.



1

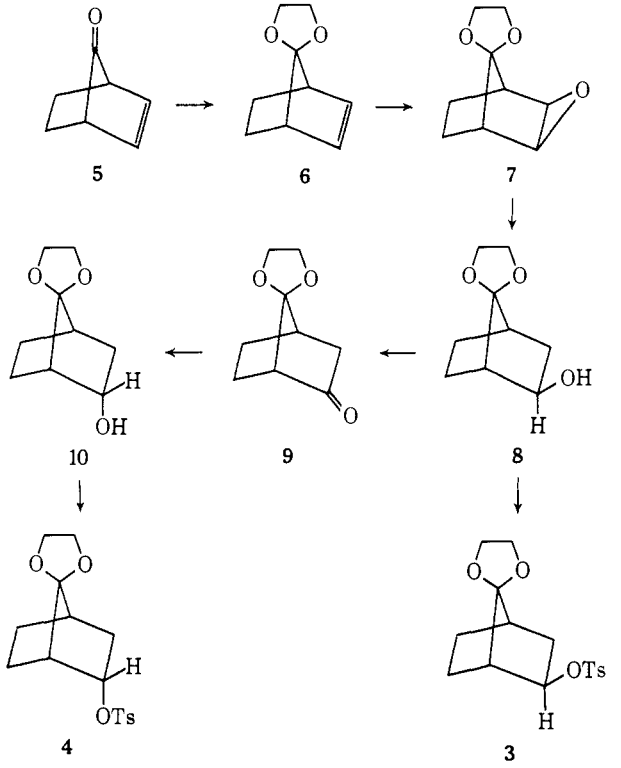


2

Synthesis and Solvolysis

The synthesis of **3** and **4** is outlined in Chart I. Bi-

Chart I

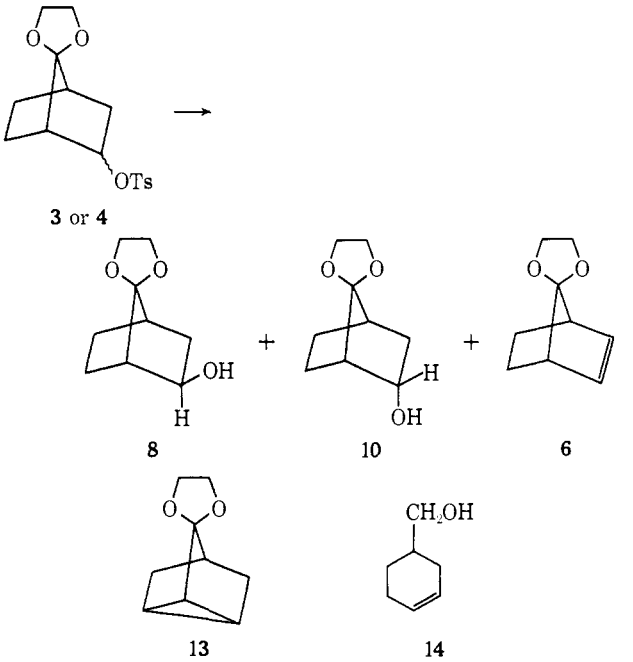


5 6 7 10 9 8 4 3

cyclo[2.2.1]hept-2-en-7-one (**5**)[7] was converted into the ketal **6** with ethylene glycol in an acid-catalyzed reaction. Epoxidation of **6** with *m*-chloroperbenzoic acid gave **7**. Reduction of **7** to **8** with lithium aluminum hydride required 12 days in refluxing tetrahydrofuran. High-dilution near-infrared studies showed that **8** was intramolecularly hydrogen bonded, thus establishing the *exo* nature of the hydroxyl group of **8** and the epoxide function of **7**. Oxidation of **8** with chromium trioxide–pyridine gave **9**. Reduction of **9** with aluminum isopropoxide in isopropyl alcohol gave **10** in 90% yield. Both **8** and **10** were readily converted into the epimeric tosylates **3** and **4**, respectively, *via* reaction with *p*-toluenesulfonyl chloride in pyridine.

Table I lists the rate constants for **3** and **4** and the corresponding data for the norbornyl tosylates (**11** and **12**),[8] for solvolysis in anhydrous acetic acid buffered with sodium acetate. As noted, relatively little difference exists between the rates of **3**, **4**, and **12** whereas it might have been anticipated that the inductive effect of the ethylene glycol bridge would make **3** and **4** considerably slower than **12**. From the rate data alone it is clear that the ethylene glycol bridge is playing more than a simple inductive role.

Product studies showed that solvolysis of **3** and **4** in buffered acetic acid gave the same five products in combined yield of 76 and 77%, respectively. Ether extraction of the neutralized solvolysis mixture from **3**, followed by lithium aluminum hydride reduction, gave a mixture of **8**, **10**, **6**, **13**, and **14** in 53, 9, 3, 20, and 15% yields, respectively. Under similar work-up conditions **4** gave the same products in 18, 5, 1, 19, and 57% yield, respectively.[9] Products **6**, **13**, and the acetates of **8** and **10** (**15** and **16**, respectively) were subjected separately to

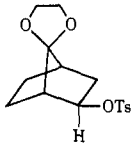
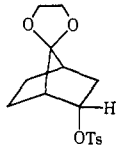
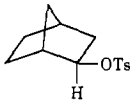
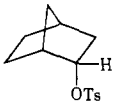


the reaction conditions for greater than ten half-lives. In each case the material was recovered unchanged in greater than 90% yield and 95% purity showing that **6**, **13**, **15**, and **16** were not interconverting or producing **14** (or its precursor) under the reaction conditions.

The most obvious change in the products derived from the acetolysis of **3** and **4** was the enhanced tendency of **4** to give ring cleavage. This cleavage was probably concerted with the separation of the ion pair derived from **4**[10] to yield **17** directly as shown in Chart II. The carbonium ion **17** would be expected to react with acetic acid to yield the ethylene glycol diester **18** which should give **14** on reduction with lithium aluminum hydride. In confirmation of this hypothesis, we found that **18** could be isolated from the reaction mix-

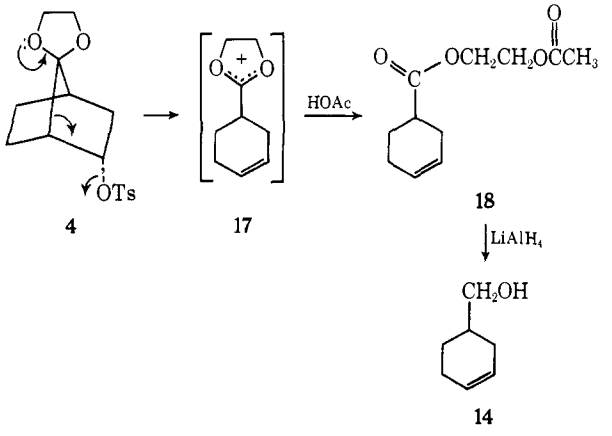
(7) P. G. Gassman and J. L. Marshall, *Org. Syn.*, 48, 25 (1968).
(8) P. von R. Schleyer, M. M. Donaldson, and W. E. Watts, *J. Am. Chem. Soc.*, 87, 375 (1965).
(9) Yields were determined *via* vpc *vs.* an internal standard. Compounds **8**, **10**, **6**, **13**, and **14** were shown to have the assigned structures through a comparison of vpc retention times and by isolation by preparative vpc and comparison of infrared spectra with those of authentic samples. For details of the synthesis of **13** and **14**, see Experimental Section.
(10) It is interesting to note that careful examination of the products from the acetolysis of **1** showed no indication of any products arising from cleavage of the C_1–C_7 bond. Thus MeO-4 neighboring group participation must have been sufficiently strong to overcome any tendency toward ring opening (ref 4).

Table I. Acetolysis Rates of 2-Norbornyl Tosylates

Compound	Temp, °C	k, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, eu	k_{rel}
 3	100.0 ± 0.02	(2.56 ± 0.05) × 10^{-3}	28.5	+5.6	11
	90.0 ± 0.02	(8.05 ± 0.30) × 10^{-4}			
	80.0 ± 0.02	(2.71 ± 0.04) × 10^{-4}			
	(25)[a]	1.29 × 10^{-7}			
 4	100.0 ± 0.02	(3.22 ± 0.07) × 10^{-4}	29.5	+4.1	1
	90.0 ± 0.02	(1.13 ± 0.01) × 10^{-4}			
	80.0 ± 0.02	(3.32 ± 0.05) × 10^{-5}			
	(25)[a]	1.20 × 10^{-8}			
 11	(25)	2.33 × 10^{-5}	21.6	−7.2	1940
 12	(25)	8.28 × 10^{-8}	25.8	−4.4	7

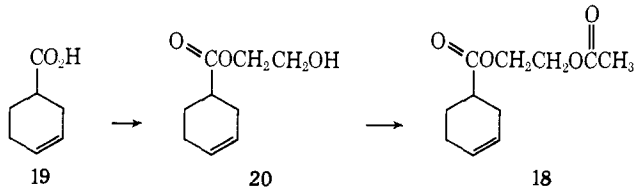
[a] Extrapolated from higher temperatures.

Chart II



4 17 18 14

ture prior to hydride reduction. The synthesis of **18** originated from **19**, which on reaction with thionyl chloride followed by ethylene glycol gave **20**. Acetylation of **20** with acetic anhydride in pyridine gave **18**.



19 20 18

Since the product mixtures from **3** and **4** differ considerably in their relative per cent composition, it is clear that **3** and **4** were not undergoing acetolysis to yield the same norbornyl cation. In addition, since no ketonic products were formed, MeO-4 neighboring group participation, as observed for **1**, should not be a complicating factor. We picture the solvolyses of **3** and **4** as involving two discrete reaction paths, one involving the formation of the acetates of **8** and **10**, and **6** and **13**, while the other involved concerted ring cleavage and ionization. We feel that the first step in both solvolyses involved the formation of an ion pair which could partition itself between the formation of **6**, **13**, **15**, and **16** and bond cleavage. Since **3** and **4** should undergo initial ionization to give stereochemically different ion pairs, it was to be expected that some variation in the ratio of **6**, **13**, **15**, and **16** should occur.

The dramatic difference in behavior between the epimeric pairs of tosylates derived from 2-hydroxybicyclo[2.2.1]heptan-7-one[3] and 7,7-dimethoxybicyclo[2.2.1]heptan-2-ol,[4] and the epimeric pair **3** and **4**, clearly demonstrates the problems involved in using oxygenated substituents on the norbornyl skeleton to investigate the classical–nonclassical nature of the norbornyl cation. We feel that none of the three systems listed above can be used as models for the formation of a classical norbornyl cation. Although we do not know the precise nature of the involvement in each of the cases, it is evident that in each epimeric pair of tosylates discussed above the oxygenated function is interacting in a different and unique manner with one of the epimers.[11]

Experimental Section[12]

Bicyclo[2.2.1]hept-2-en-7-one Ethylene Glycol Ketal (6). A solution of 11.82 g (0.109 mole) of bicyclo[2.2.1]hept-2-en-7-one (**5**)[6] and 10.0 g of ethylene glycol in 150 ml of benzene containing 0.1 g of *p*-toluenesulfonic acid was heated at reflux for 9 hr after which 2.5 ml of water was azeotropically separated using a Dean–Stark water trap. Upon cooling the benzene solution was poured into 100 ml of saturated aqueous sodium bicarbonate and the resulting mixture was extracted three times with 50-ml portions of ether. The combined ether extracts were dried over anhydrous magnesium sulfate and filtered, and the solvent removed by distillation

(11) For a further discussion of this point, see P. G. Gassman, J. L. Marshall, J. G. Macmillan, and J. M. Hornback, *J. Am. Chem. Soc.*, **91**, 4282 (1969).

(12) Melting points and boiling points are uncorrected.

through a 12-in. Vigreux column. Distillation *in vacuo* of the crude product yielded 14.86 g (89%), bp 122–125° (76 mm), of the desired ketal olefin, **6**, n_D 1.4952.

Anal. Calcd for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 71.28; H, 8.06.

***exo*-2,3-Epoxybicyclo[2.2.1]heptan-7-one Ethylene Glycol Ketal (7).** To a solution of 28.93 g (0.190 mole) of **6** in 1 l. of chloroform was added with stirring 60.0 g of *m*-chloroperbenzoic acid in 1 l. of chloroform over 2 hr. The solution was stirred an additional 12 hr at room temperature after which it was extracted twice with 250-ml portions of 10% aqueous potassium hydroxide. Two additional extractions of the chloroform solution with 250-ml portions of water were followed by drying of the chloroform solution over anhydrous magnesium sulfate. The solution was filtered and the solvent removed by distillation through a 12-in. Vigreux column. The resulting crude product was distilled *in vacuo* to yield 28.35 g (89%), bp 77° (0.1 mm), of the desired ketal epoxide, **7**, $n^{26}D$ 1.5080.

Anal. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.36; H, 7.23.

***exo*-2-Hydroxybicyclo[2.2.1]heptan-7-one Ethylene Glycol Ketal (8).** A solution of 23.35 g (0.169 mole) of epoxy ketal **7** and 8.0 g of lithium aluminum hydride in 400 ml of dry tetrahydrofuran was stirred at reflux for 12 days. After the reaction mixture was cooled, 35 ml of water in 100 ml of tetrahydrofuran was added dropwise (with caution) followed by stirring until the precipitate was completely white. Filtration of the slurry followed by distillation of the solvent through a 12-in. Vigreux column yielded a crude product which was distilled *in vacuo* to yield 24.41 g (85%) of **8**, bp 70–75° (0.3 mm), $n^{26}D$ 1.4863.

Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.60; H, 8.29.

***exo*-2-Acetoxybicyclo[2.2.1]heptan-7-one Ethylene Glycol Ketal (15).** A solution of 1.00 g of ketal alcohol **8** and 0.65 g of acetic anhydride in 15 ml of dry pyridine was stirred at room temperature for 18 hr. The solution was poured into 50 ml of saturated aqueous sodium bicarbonate followed by three extractions with 25-ml portions of ether. The combined ether extracts were washed with two 25-ml portions of water and two 25-ml portions of dilute hydrochloric acid. After drying the ethereal solution over anhydrous magnesium sulfate the solution was filtered and the solvent removed on a rotary evaporator. The product was distilled *in vacuo* to yield 0.59 g (51%) of acetate **15**, bp 75–77° (0.25 mm). Preparative vpc yielded an analytical sample, $n^{26.3}D$ 1.4764.

Anal. Calcd for $C_{11}H_{16}O_4$: C, 78.23; H, 7.88. Found: C, 78.14; H, 7.81.

***exo*-2-Tosyloxybicyclo[2.2.1]heptan-7-one Ethylene Glycol Ketal (3).** To a solution of 0.506 g (0.0298 mole) of ketal alcohol **8** in 10 ml of dry pyridine cooled to 0° was added 0.571 g of *p*-toluenesulfonyl chloride. The mixture was allowed to stand at 5° for 24 hr after which it was poured onto 50 ml of water. The aqueous solution was extracted three times with 25-ml portions of chloroform. The combined chloroform extracts were dried over anhydrous magnesium sulfate and filtered, and the solvent removed on a rotary evaporator to yield a clear oil which slowly crystallized. Recrystallization from hexane yielded 0.518 g (54%) of a white crystalline product, mp 62–64° A second recrystallization from the same solvent yielded an analytical sample, mp 64.5–65.5°.

Anal. Calcd for $C_{16}H_{20}SO_5$: C, 59.25; H, 6.22; S, 9.87. Found: C, 59.43; H, 6.25; S, 10.06.

Oxidation of 8 to 9. To a solution of pyridine cooled to 0° was added 30.0 g (0.3 mole) of chromium trioxide with vigorous stirring. After the yellow pyridine–chromium trioxide complex precipitated 10.6 g (0.0625 mole) of ketal alcohol **8** was added followed by stirring overnight. The reaction mixture was poured into 1 l. of water and the mixture was continuously extracted with ether for 6 days. The ether extracts were dried over anhydrous magnesium sulfate and filtered, and the solvent removed on a rotary evaporator. The resulting crude product was distilled *in vacuo* to yield 8.57 g (81%) of **9**, bp 70–72° (0.5 mm). A sample was redistilled for analysis, $n^{26.6}D$ 1.4883.

Anal. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.28; H, 6.99.

***endo*-2-Hydroxybicyclo[2.2.1]heptan-7-one Ethylene Glycol Ketal (10).** A solution of 7.0 g (0.0416 mole) of ketone **9** and 13.5 g of aluminum isopropoxide in 400 ml of isopropyl alcohol was slowly distilled over a 5-hr period. The resulting viscous liquid was dissolved in 500 ml of 10% aqueous sodium hydroxide. The aqueous solution was extracted with three 100-ml portions of ether and the combined ether extracts were dried over anhydrous magnesium sulfate. The ether solution was filtered and the ether removed on a rotary evaporator. The product was fractionally distilled *in vacuo* to yield 6.33 g (90%) of alcohol **10**, bp 95–97° (0.6 mm). Upon standing the alcohol crystallized, mp 51–52°.

Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.37; H, 8.27.

***endo*-2-Acetoxybicyclo[2.2.1]heptan-7-one Ethylene Glycol Ketal (16).** A solution of 980 mg (5.76 mmoles) of ketal alcohol **10** and 646 mg of acetic anhydride in 15 ml of dry pyridine was stirred at room temperature for 12 hr. The solution was poured into 50 ml of saturated aqueous sodium bicarbonate followed by three extractions with 25-ml portions of ether. The combined ether extracts were washed twice with 25-ml portions of dilute hydrochloric acid, dried over anhydrous magnesium sulfate, and filtered, and the solvent removed on a rotary evaporator. The product was distilled *in vacuo* to yield 1.04 g (85%), bp 87–90° (0.25 mm), of the ketal acetate **16**, $n^{26.6}D$ 1.4773.

Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.24; H, 7.55.

***endo*-2-Tosyloxybicyclo[2.2.1]heptan-7-one Ethylene Glycol Ketal (4).** To a cooled solution of 2.58 g (0.0152 mole) of alcohol **10** in 20 ml of dry pyridine was added with stirring 3.2 g of *p*-toluenesulfonyl chloride. The solution was allowed to come to room temperature while stirring for 12 hr. The mixture was poured onto 50 ml of water and the aqueous solution was extracted three times with 20-ml portions of chloroform. The combined chloroform extracts were washed three times with 20-ml portions of water followed by drying over anhydrous magnesium sulfate. The solution was filtered and the solvent removed on a rotary evaporator. The last traces of pyridine were removed under vacuum to yield 3.65 g (74%) of a clear oil which did not crystallize. Drying of a sample over calcium chloride and removal of the drying agent and solvent under vacuum yielded a sample which analyzed for **4**.

Anal. Calcd for $C_{16}H_{20}SO_5$: C, 59.25; H, 6.22; S, 9.87. Found: C, 59.23; H, 6.36; S, 9.71.

Tricyclo[2.2.1.0^{3,5}]heptan-2-one Ethylene Glycol Ketal (13). A solution of 1.0 g (0.00927 mole) of nortricyclanone[13] and 4 g of ethylene glycol in 50 ml of benzene was stirred at reflux with 0.5 g of IR-120 acid ion exchange resin while the water was removed azeotropically. After 3 hr the solution was filtered and extracted twice with 50-ml portions of water. The benzene layer was dried over anhydrous magnesium sulfate and filtered, and the solvent removed by distillation through a 12-in. Vigreux column. The resulting crude product was distilled *in vacuo* to yield 0.90 g (64%) of the ketal **13**, bp 85–87° (11 mm), $n^{26.6}D$ 1.4859.

Anal. Calcd for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 70.92; H, 7.84.

Δ^3-Cyclohexenylcarbinol (14). A solution of 3.0 g (0.027 mole) of commercially available Δ^3-cyclohexenylcarboxaldehyde in 50 ml of ether was added slowly to a mixture of 2.0 g of lithium aluminum hydride in 100 ml of ether. After stirring for 1 hr, 8.0 g of 10% aqueous sodium hydroxide was added cautiously and stirring was continued for 1 additional hr. The solution was filtered and the solvent removed by distillation. The resulting oil was distilled *in vacuo* to yield 1.75 g (58%), bp 98–100° (18 mm), of the desired carbinol, **14**.

Ethylene Glycol Mono-Δ^3-cyclohexenylcarboxylate (20). A solution of 15.5 g (0.125 mole) of commercially available Δ^3-cyclohexenylcarboxylic acid and 25 ml of thionyl chloride was allowed to stand at room temperature for 8 hr. The reaction mixture was then distilled *in vacuo* to yield 16.7 g (93%), bp 80° (50 mm), of the desired acid chloride which was reacted without further purification.

To a solution of 70.7 g (1.16 moles) of ethylene glycol in 100 ml of pyridine was slowly added 16.7 g (0.116 mole) of the acid chloride in 100 ml of pyridine. After stirring for 2 hr, the pyridine solution was poured into 500 ml of water and sodium bicarbonate was added to neutralize the acid. The aqueous solution was extracted three times with 100-ml portions of ether. The combined ether extracts were washed twice with 100-ml portions of water and once with a 100-ml portion of dilute mineral acid. The ether solution was dried over anhydrous magnesium sulfate and filtered, and the solvent removed on a rotary evaporator. The product was distilled *in vacuo* to yield 4.62 g (22%), bp 115–120° (1.6 mm), of pure monoester, **20**, 1.09 g (5.5%) of impure monoester, and 1.69 g of diester Redistillation of the monoester yielded 4.20 g, bp 118–120° (1.5 mm), of the desired ester, $n^{26.6}D$ 1.4815.

Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.38; H, 8.34.

(13) J. Meinwald, J. Crandall, and W. E. Hymans, *Org. Syn.*, **45**, 77 (1965).

2′-Acetoxyethyl Δ³-Cyclohexenylcarboxylate (18). A solution of 4.62 g (0.272 mole) of monoester **20** and 5.5 g of acetic anhydride in 25 ml of pyridine was allowed to stand at room temperature for 12 hr. The solution was poured onto 100 ml of water and extracted three times with 50-ml portions of ether. The ethereal solution was washed twice with 50-ml portions of water, dried over anhydrous magnesium sulfate, and filtered, and the solvent distilled through a 12-in. Vigreux column. The product was distilled *in vacuo* to yield 4.81 g (83%) of the ester acetate **18**, bp 93–97° (0.45 mm), $n^{26.6}$D 1.4628.

Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.32; H, 7.60.

Kinetics. Reagent. Anhydrous acetic acid was prepared by refluxing a solution of acetic anhydride and sodium acetate in glacial acetic acid for 24 hr and subsequent fractional distillation in a dry atmosphere. Standard sodium acetate in acetic acid (*ca.* 0.1 *M*) was prepared by the careful addition of anhydrous acetic acid to a solution of anhydrous sodium carbonate in acetic anhydride, such that *ca.* 1% acetic anhydride remained after the water of neutralization was removed, followed by refluxing in a dry atmosphere for 5 hr[14] (calculated to be 1.325 g of anhydrous sodium carbonate and 3.78 g of acetic anhydride diluted to 250 ml with anhydrous acetic acid). Standard perchloric acid in acetic acid (*ca.* 0.02 *M*) used in titrating acetolysis aliquots was prepared by the careful addition of 70% perchloric acid to a solution of anhydrous acetic acid and acetic anhydride, such that 1% acetic anhydride remained after the water was removed, followed by standing at room temperature for 12 hr. The molarity of the standard perchloric acid in acetic acid was determined by titrating an aliquot *vs.* potassium acid phthalate (primary standard) in anhydrous acetic acid using bromophenol blue as the indicator.

Procedure. The kinetic procedure followed was essentially that of Winstein and coworkers.[15] All rates were determined using an infinity titer. All solvolytic runs for **3** and **4** in buffered anhydrous acetic acid gave linear pseudo-first-order plots through greater than 75% reaction.

Acetolysis Products from 3. A solution of 258.5 mg of tosylate **3** in 10 ml of 0.1 *M* sodium acetate in acetic acid was heated at 110° for 2 hr. The solution was cooled and added dropwise to 100 ml of saturated aqueous sodium bicarbonate. After extraction of the aqueous solution ten times with 25-ml portions of ether the combined ether extracts were added dropwise to 2.0 g of lithium aluminum hydride followed by stirring for 1 hr. The hydride mixture was cautiously neutralized with 8 g of 10% aqueous sodium hydroxide. After stirring for 1 hr and filtration of the solution, the solvent was removed by distillation. The crude oil was combined with 28.5 mg of standard (*o*-chlorophenol) and vpc analyses were run on a 15 ft, 5% Carbowax 20M column at 110°. The yields and per cent composition listed in the discussion part of this paper were the average of four runs.

The identity of the products was determined by comparison of vpc retention times on three columns (a 10-ft 10% SE-30 column; a 15-ft 5% Carbowax 20M column; and a 10-ft 5% PDEAS column) with those of authentic samples. The solvolysis mixture enriched with authentic samples showed appropriate peak height and area increases when chromatographed on the same three columns.

The compounds identified were the ketal olefin **6**, tricyclic ketal **13**, the ketal alcohols **8** and **10**, and Δ³-cyclohexenylcarbinol (**14**). The cyclohexenylcarbinol arose from the reduction of the ester acetate **18**. The ester acetate **18** was isolated from the reaction mixture prior to reduction and the ir and nmr were compared with those of an authentic sample. The alcohols **8** and **10** resulted from the reduction of **15** and **16**.

Acetolysis Products of 4. A solution of 318.8 mg of tosylate **4** in 10 ml of 0.1 *M* sodium acetate in acetic acid was heated for 1 hr at 130°. The solution was cooled and added dropwise to 200 ml of saturated aqueous sodium bicarbonate. The aqueous solution was continuously extracted with ether for 3 hr and the ether extract was added dropwise to 4.0 g of lithium aluminum hydride. After stirring for 1 hr 16.0 g of 10% aqueous sodium hydroxide was cautiously added to destroy the excess hydride and stirring was continued an additional 8 hr. The solution was filtered and the solvent removed by distillation. The crude oil was combined with 44.9 mg of standard (*o*-chlorophenol) and the identity of the products was determined by comparison of vpc retention times on three columns (a 10-ft 10% SE-30 column; a 15-ft 5% Carbowax 20M column; and a 10-ft 5% PDEAS column) with those of authentic samples. The solvolysis mixture enriched with authentic samples showed appropriate peak height and area increases when chromatographed on the same three columns. The compounds identified were ketal olefin **6**, tricyclic ketal **13**, the ketal alcohols **8** and **10**, and Δ³-cyclohexenylcarbinol (**14**). The yield and per cent composition reported in the discussion are the average of three runs.

Stability of 13 to the Solvolysis Conditions. A solution of 119.4 mg of ketal **13** in 10 ml of 0.1 *M* sodium acetate in acetic acid was heated at 130° for 1 hr. The solution was added dropwise to 400 ml of saturated aqueous sodium bicarbonate. The aqueous solution was extracted three times with 50-ml portions of ether and the combined ether extracts were dried over anhydrous magnesium sulfate. The solution was filtered and the solvent removed by distillation to yield 105.3 mg (89%) of starting material which was 95% pure by vpc. The ir was identical with that of starting material.

Stability of 6 to the Solvolysis Conditions. A solution of 117.9 mg of ketal olefin **6** in 10 ml of 0.1 *M* sodium acetate in acetic acid was heated at 130° for 1 hr. The solution was added dropwise to 400 ml of saturated aqueous sodium bicarbonate. The aqueous solution was extracted three times with 50-ml portions of ether. The combined ether extracts were dried over anhydrous magnesium sulfate and filtered, and the solvent was removed by distillation to yield 108.3 mg (92%) of product which was 95% pure by vpc. The ir was identical with that of starting material.

Stability of 15 to the Solvolysis Conditions. A solution of 102.1 mg of *exo*-acetate **15** in 10 ml of 0.1 *M* sodium acetate in acetic acid was heated at 130° for 1 hr. The solution was added dropwise to 400 ml of saturated aqueous sodium bicarbonate. The aqueous solution was extracted three times with 50-ml portions of ether and the combined ether extracts were dried with magnesium sulfate. The solution was filtered and the solvent removed by distillation to yield 95.2 mg (93%) of product which was 95% pure by vpc. The ir was identical with that of starting material.

Stability of 16 to the Solvolysis Conditions. A solution of 73.3 mg of ketal acetate **16** in 5 ml of 0.1 *M* sodium acetate in acetic acid was heated at 110° for 7 hr. The solution was added dropwise to 200 ml of saturated aqueous sodium bicarbonate followed by five extractions with 25-ml portions of ether. The combined ether extracts were dried over anhydrous magnesium sulfate and filtered, and the solvent removed on a rotary evaporator. The crude product, 71.0 mg (97%), was greater than 99% pure by vpc and its ir was identical with that of the starting acetate.

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(15) S. Winstein, E. Grunwald, and L. L. Ingraham, *ibid.*, 70, 821 (1948).