mL) and extracted five times with ether. After the usual workup, solvent removal gave 72 mg of the acid **9**: $[\alpha]^{23}_{589}$ −115.5° (*c* 1.42, chloroform); IR 3400–2400, 1740 cm^{-1}; NMR δ 1.00–3.00 (9 H, m), 10.96 (1 H, s, COOH).

(1*R*,2*R*,5*R*)-(+)-Bicyclo[3.3.0]oct-7-en-2-ol (1). A solution of (+)-**2a** (3.0 g, 9.86 mmol) in ethanol (150 mL) was mixed with a solution of potassium hydroxide (1.5 g) in water (20 mL) and refluxed for 1.5 h. After the usual workup, the reaction product was chromatographed on silica gel (10 g) with benzene–ether (2:1) to give a colorless oil of **1** (1.14 g, 92.7%): bp 50 °C at 3 mmHg; $[\alpha]^{20}_{589}$ +210.6° (*c* 0.729, methanol); IR 3350, 3045 cm^{-1}; NMR δ 1.00–3.50 (9 H, m), 4.23 (1 H, m, –CH–O), 5.78 (2 H, m, olefinic); UV (methanol) ε 4300 (197 nm);[14] CD (methanol) Δε +11.4 (195 nm).[14]

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.00; H, 9.85.

Registry No.—(+)-**1**, 68366-26-7; (±)-**1**, 68317-62-4; **2a**, 68317-63-5; **2b**, 68422-21-9; **3**, 68317-64-6; **4**, 54200-35-0; **5**, 68366-27-8; **6**, 68317-65-7; **7**, 68317-66-8; **8**, 68366-28-9; **9**, 2630-37-7; **10**, 2630-38-8; (−)-camphanyl chloride, 39637-74-6.

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(10) Footnotes 41 and 43 in ref 8.
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Rate Decelerations in the Acetolysis of Substituted Cyclopentyl Tosylates

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A comparison of the acetolysis rates of geminally polymethylated secondary cyclopentyl tosylates to cyclopentyl tosylate showed a small rate deceleration in each case.[1] Two factors were considered to be responsible for the rate decelerations: (a) nonbonded repulsions in the transition state greater than in the ground state, and (b) a steric inhibition of effective solvation at the back side of the departing tosyloxy group at the transition state.

In an attempt to separate these factors, it was of interest to study the acetolysis rates of 2-indanyl tosylate (III) and 1,1,3,3,-tetramethyl-2-indanyl tosylate (IV). In this model indanyl system, the importance of factor (a) is greatly reduced (if not eliminated entirely) and the five-membered ring is probably in an envelope conformation of limited mobility.[2] More importantly, inspection of a model of IV suggests that the methyl substituents exert an "umbrella" effect in shielding the approach of solvent to the rear or the front of the carbon bearing the leaving group. The purpose of this paper is to present some data on these systems and discuss them in the light of solvolyses which are limiting (k_c) and/or nucleophilically solvent assisted (k_s).[3,4]

Inspection of the data in Table I reveals that a decrease in the acetolysis rate results when geminal dimethyl groups are adjacent to the reaction site. This rate retardation is most striking in the case of IV. Compound IV undergoes acetolysis 14 250 times slower than I. Moreover, despite similar conformational requirements and the same rate-retarding inductive effect of the benzene ring, IV undergoes acetolysis 299 times slower than III at 25 °C.

In general, increasing the conformational rigidity of the five-membered ring results in a decrease in the solvolysis rates of cyclopentyl derivatives. Meinwald[8] noted that the tosylate of *trans*-bicyclo[3.2.0]heptan-3-ol (half-chair conformation) solvolyzed 55 times slower than cyclopentyl tosylate at 75 °C. Winstein and Sonnenberg[9] subjected Δ^3-cyclopentenyl tosylate and *trans*-3-bicyclo[3.1.0]hexyl tosylate (envelope conformation) to acetolysis conditions at 50 °C and found the rates to be 8.3 and 16 times slower than cyclopentyl tosylate, respectively. The methanolysis of 2-indanyl tosylate has been reported to proceed 20 times slower than the methanolysis of cyclopentyl tosylate at 50 °C.[10]

In the results reported here, it is suggested that the effect of methyl participation is not of importance in system IV. If this were the case, methyl bridging should lead to a rate enhancement by formation of the methyl-substituted 1-indanyl cation as the first intermediate. A rate accelerating inductive effect due to the methyl groups should also be operative. Conformational effects and the effect of π-participation would also not seem to be of primary importance in the rate comparisons of III and IV. The relevant carbonyl stretching frequencies (measured in dilute carbon tetrachloride solution with a calibrated Perkin-Elmer Model 21 spectrophotometer) for the ketones corresponding to III and IV are 1755 and 1751 cm^{-1}—a trend of predicted faster acetolysis for IV compared to III based on the angle effect.[11]

Recently, Schleyer and co-workers carried out a detailed study of secondary systems without participating neighboring groups. The key compound in this work was 2-adamantyl tosylate for which nucleophilic participation by the solvent was expected to be a minimum. Support was convincing for a highly destabilized transition state resulting from severe steric interaction between the entering and leaving groups and the axial hydrogen atoms of the ring system.[3,4] Once nucleophilic solvent assistance was shown to be small for 2-adamantyl derivatives, it became possible to use the adamantyl system as a standard against which solvent assistance in the solvolysis of other secondary derivatives could be compared.[4]

Arguments similar to these proposed by Schleyer and coworkers for the slow rate of solvolysis of 2-adamantyl tosylate are applicable to the slow acetolysis rate of IV. Indeed, models of this system suggest that IV might even more severely inhibit solvent approach to the incipient electropositive carbon than 2-adamantyl tosylate. Hence, it appears that the main factor influencing the observed rate deceleration of IV (299 times

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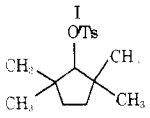
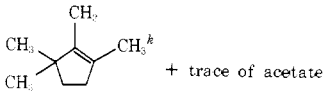
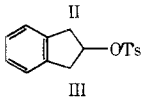
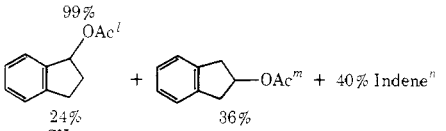
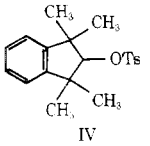
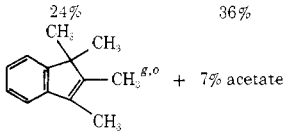
Table I. Rate Comparisons and Products from the Acetolysis of Cyclopentyl-Type Tosylates

tosylate	registry no.	temp, °C	k, s^{-1} [a]	rel k (25 °C)	products[b]
 I	3558-06-3	25.0	1.69×10^{-6}	285	61% cyclopentyl acetate[i] + 39% cyclopentene[d,j]
		65.0	2.06×10^{-4}		
		80.0	9.41×10^{-4} [c]		
 II	15587-83-4	25.0	8.09×10^{-8} [e]	13.6	 + trace of acetate
		65.0	1.38×10^{-5}		
		80.0	7.03×10^{-5}		
 III	17783-69-6	25.0	3.55×10^{-8} [e]	5.98 (285)[f]	 99% OAc[l] + OAc[m] + 40% Indene[n] 24% 36%
		80.0	3.76×10^{-5}		
		117.1	1.37×10^{-3}		
 IV	67969-41-9	25.0	1.19×10^{-10} [e]	0.02 (0.95)[f]	 + 7% acetate
		80.0	3.19×10^{-7} [e]		
		117.1	1.93×10^{-5}		
		134.8	1.04×10^{-4}		
2-adamantyl-OTs (V)		25.0	5.94×10^{-9} [h]	1.0	

[a] Acetolysis rates were obtained from a least-squares treatment of the data on an IBM 1130 computer. [b] In the product studies, quantitative infrared analysis was utilized to determine the acetate percentages resulting from the acetolysis of II and IV. The structures of all the products were readily ascertained by NMR analysis and in a few cases by comparison to authentic samples. [c] This experimentally obtained value is close to the extrapolated value obtained from the data of H. C. Brown and G. Ham.[5] [d] These products were obtained by J. D. Roberts and J. C. Chambers.[6] [e] Extrapolated from data at higher temperatures. [f] Numbers in parentheses are corrected for the inductive effect of the aromatic ring. [g] Spectral data agree well with the literature.[7] [h] See ref 4. [i] Registry no. 933-05-1. [j] Registry no. 142-29-0. [k] Registry no. 65378-75-8. [l] Registry no. 26452-98-2. [m] Registry no. 4254-31-3. [n] Registry no. 95-13-6. [o] Registry no. 4705-87-7.

slower than III at 25 °C) is the steric inhibition of solvation at the back side of the departing tosyloxy group at the transition state or a steric inhibition of solvation of the leaving group itself. In addition to the rate data, support for this idea is found in the product distribution from these acetolysis reactions (Table I). The decreased percentage of acetates found in the products as a function of increased methyl substitution in the reactants is striking.

The data in Table I show that compound IV solvolyzes in acetic acid at 1/50 of the rate of 2-adamantyl tosylate. However, correction for the decelerating inductive effect of the aromatic ring (an estimated factor of 47.6 if conformational differences are neglected in the comparison of I and III) in IV provides a rate constant which should be independent of the benzenoid inductive effect and a function solely of k_c and k_s. This adjusted acetolysis rate of IV at 25 °C is remarkably close to the acetolysis rate of 2-adamantyl tosylate. The significance of this comparison is perhaps not entirely clear because of the obvious structural differences in the substrate but might be attributable to both compounds having similar k_c values. It appears that this substituted indanyl system is another interesting example of the necessity for nucleophilic participation of the solvent at the transition state of the acetolysis of secondary systems.

Experimental Section

All melting points are corrected. The vapor phase chromatographic analyses were performed on the Aerograph A-90-P. All percentage data from the GLC studies are based on areas calculated by the peak-height, half-width procedure. The Perkin-Elmer Model 21 infrared spectrophotometer was used for quantitative information. The Perkin-Elmer Model 237B was used for qualitative work. The NMR spectra were taken from a Varian A-60 spectrophotometer.

Materials. Alcohols (tosylate precursors) were prepared in greater than 90% yields via lithium aluminum hydride reduction of the ketones. The ketones were either commercially available or they were prepared via alkylation of commercially available precursors.[12,13]

The 2,2,5,5-tetramethylcyclopentyl tosylate (II) was prepared in 82% yield via the reaction of 2,2,5,5-tetramethylcyclopentanol with p-toluenesulfonyl chloride in pyridine according to Tipson's procedure.[14] The 1,1,3,3-tetramethyl-2-indanyl tosylate (IV) was prepared in 88% yield by reacting 1,1,3,3-tetramethylindan-2-ol with an ethereal solution of methyllithium first and then adding an ethereal solution of p-toluenesulfonyl chloride according to Brown et al.[15] The tosylate esters were stored in a desiccator over phosphorus pentoxide in a freezer. The pertinent data for the new tosylates are listed in Table II.

Table II

compd	mp, °C	calcd, % C	calcd, % H	found, % C	found, % H
2,2,5,5-tetramethylcyclopentyl tosylate (II)	95–96.5	64.84	8.16	64.94	8.44
1,1,3,3-tetramethyl-2-indanyl tosylate (IV)	135.5–136	69.75	7.02	69.70	6.99

Kinetic Procedures. The acetolysis procedures and conditions using the infinity titer aliquot technique were the same as those described in a previous publication except that the sealed ampule infinity titer technique was employed at temperatures above 80 °C.[16] (Rates obtained by the sealed ampule technique at 80 °C were virtually identical to those obtained by the aliquot technique.) A least-squares treatment of the data on an IBM 1130 computer was used to determine the rate constants.

Acetolysis Products. General Procedure. The tosylate and a 10–15% molar excess of sodium acetate were weighed into a round-bottom flask. Anhydrous acetic acid was added so that the concentrations would be similar to a typical kinetic run. The flask was then fitted with a condenser and a drying tube filled with calcium chloride. The acetolysis was allowed to proceed for at least 10 half-lives in a bath which was kept at the temperature of the fastest kinetic run. The products were isolated by the more appropriate of the following methods:

A. When volatile acetolysis products were expected (as in the case of II), the contents of the flask were poured into a test tube containing an equal volume of ice water. The test tube was kept in an ice bath. The organic layer which separated was drawn off with a small eye dropper and transferred to another small test tube which was also cooled in an ice bath. This organic layer was washed once with water, once with 5% sodium bicarbonate, once more with water and then

dried over potassium carbonate.

B. When relatively high boiling products were expected (i.e., III and IV), the products were extracted with pentane. This was done by pouring the acetolysis products into an equal volume of cold water, extracting the organic layer with pentane, and washing with water, 5% sodium bicarbonate, and once again with water. The pentane solution was dried over potassium carbonate and then concentrated on a rotary evaporator.

From either procedure, acetate percentages were calculated from infrared spectra, nuclear magnetic resonance spectra, and microhydrogenation data. Olefins were identified by NMR analysis and by subjecting the hydrogenated acetolysis products to vapor-phase chromatographic studies.

Acetolysis of 2,2,5,5-Tetramethylcyclopentyl Tosylate (II). The tosylate (2.14 g, 0.072 mol) was added to a solution of 0.783 g (0.095 mol) of sodium acetate in 40 mL anhydrous acetic acid. The procedure for volatile acetolysis products was followed as in general procedure A. There was 0.85 g (95% if all olefin) of product isolated.

The infrared spectrum showed no evidence of acetate. Only one peak appeared in the GLC on a Carbowax on Firebrick column (110 °C). The product absorbed 96% of the calculated amount of H_2 for 1,2,5,5-tetramethylcyclopentene. The NMR (CCl_4) showed no evidence of vinyl protons.

Acetolysis of 2-Indanyl Tosylate (III). A solution of 3.81 g (13.2 mmol) of the tosylate and 1.50 g (18.3 mmol) of sodium acetate in 100 mL of anhydrous acetic acid was kept at 80 °C for 96 h. The acetolysis products were isolated according to general procedure B and this yielded 1.45 g of product (83% if all olefin).

The infrared showed strong acetate absorption at 1740 and 1245 cm^{-1}. In the NMR the region between 6.9 and 7.5 ppm was used as a standard (4 H) to calculate the percentage of indene, 1-indanyl acetate, and 2-indanyl acetate. The absorptions between 3.15–3.30, 2.81–2.85, and 2.75–2.81 ppm were assigned to indene, 1-indanyl acetate, and 2-indanyl acetate, respectively. The ratio of the two acetates was determined after expansion of the sweep width from 500 to 100 Hz. The product mixture contained 40% indene, 24% 1-indanyl acetate, and 36% 2-indanyl acetate. Each acetate was identified by the enrichment technique.

Acetolysis of 1,1,3,3-Tetramethyl-2-indanyl Tosylate (IV). The tosylate (0.645 g, 1.87 mmol) was added to a solution of 0.172 g (2.09 mmol) of sodium acetate in 60 mL of anhydrous acetate acid in a 100-mL round-bottom flask. The end of the flask was sealed with an oxygen flame. The flask was then placed in an oil bath at 135 °C for 72 h. The flask was then removed and allowed to cool. The top of the flask was broken and the contents were poured into a separatory funnel. The flask was washed several times with acetic acid. Ice cold water (50 mL) was then added. The solution was then treated according to general procedure B and this produced 0.310 g of product (96% if all olefin).

The NMR (CCl_4) spectrum of the acetolysis products showed sharp singlets (4 H) and (6 H) at 7.03 and 1.10 ppm, respectively. There were also singlets (3 H each) at 2.88 and 2.76 ppm. This spectrum agreed favorably with that of 1,2,3,3-tetramethylindene in the literature.[7]

The infrared spectrum showed a weak carbonyl absorption at 1740 cm^{-1}. The amount of acetate present was found to be 7% by weight. This value was obtained by preparing standard solutions of 1,1,3,3-tetramethyl-2-indanyl acetate in 1,2,3,3-tetramethylindene and then comparing the carbonyl absorption of the acetate in the acetolysis products to the carbonyl absorption of the standard solutions.

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Base-Catalyzed Autoxidation of Cyclic Ketones

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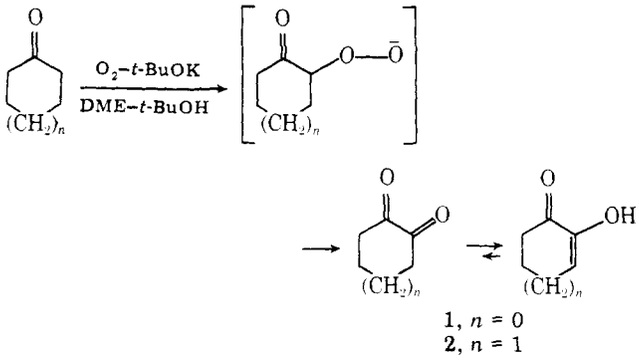
The base-catalyzed autoxidation of ketones yields carboxylic acids.[1] In the case of cyclic ketones, the corresponding dicarboxylic acids are obtained.[1,2] The reaction proceeds via α-ketohydroperoxide anion, followed by carbon–carbon bond cleavage, yielding aldehyde-carboxylic acid which rapidly undergoes further autoxidation to dicarboxylic acid. The intermediate α-ketohydroperoxide can be isolated in the autoxidation of α-substituted ketones. For example, 2-hydroperoxy-2-methylcyclohexanone was obtained from 2-methylcyclohexanone at −50 °C in dimethoxyethane–*tert*-butyl alcohol using potassium *tert*-butoxide as the base.[3] When the reaction was carried out at −8 °C, the major product was 6-ketoheptanoic acid.[3]

If the autoxidation of cyclic ketones is conducted at −20 °C under similar conditions, carbon–carbon bond cleavage is minimized and the intermediate α-ketohydroperoxide eliminates hydroxide ion with formation of α-diketones as the major products.[4] Thus, autoxidation of cyclopentanone in a mixture of dimethoxyethane and *tert*-butyl alcohol (3:2) in the presence of potassium *tert*-butoxide as the base yields 35.7% of cyclopentane-1,2-dione (1) and 18.9% glutaric acid. Autoxidation of cyclohexanone under similar conditions produces 60% of cyclohexane-1,2-dione (2), and 10% adipic acid was isolated from the reaction mixture.



1, n = 0
2, n = 1

Low temperature (−20 °C) autoxidation of cycloheptanone also produces the corresponding diketone. The latter undergoes base-catalyzed aldol condensation with the starting ketone to produce 1-hydroxy-1,1′-bicycloheptyl-2,2′-dione (3). The aldol 3 was formed exclusively when the reaction mixture was worked up without acidification. However, when the reaction mixture was acidified and worked up, along with aldol 3, its dehydration product 1,2,3,4,5,9,10,11-octahydrodicyclohepta[*b*,*d*]furan (4) was isolated as the minor product.

The structures of 3 and 4 were elucidated by NMR (^{13}C and

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