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(80) Professor Paul D. Bartlett has kindly informed us of work by himself, Maurice J. Nugent, Raymond Owyang, and Saul Cherkovsky on a variety of substituted Δ^3-cyclopentenylethyl nosylates and related compounds. Their data on 1 and 2 agree with ours. They have also succeeded in making the mono- and dianisyl analogs, which solvolyze only ~3 and 5 times faster than 1 and 2, respectively.

Acetolysis of 3,3-Disubstituted Cyclobutyl Tosylates[1]

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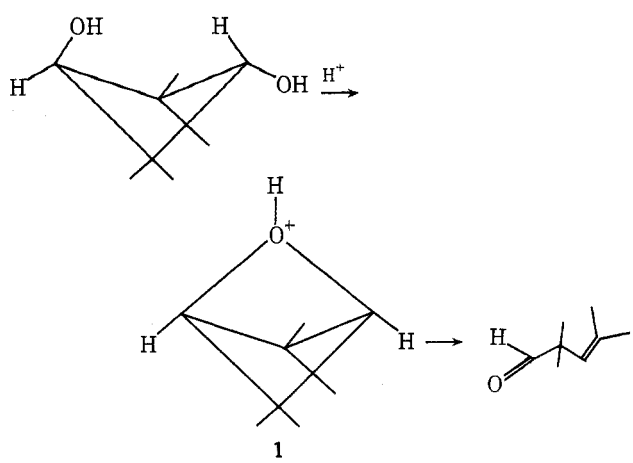
The syntheses and acetolyses of 3,3-diphenyl- and 3,3-dimethylcyclobutyl tosylates have been carried out. The diphenyl compound was prepared from the corresponding cyclobutanone which, in turn, was obtained in the reaction of diphenylketene with diazomethane. The dimethyl compound was prepared by a multistage synthesis. The compounds were solvolyzed in acetic acid containing excess sodium acetate. The activation parameters for the acetolyses were for the diphenyl compound $\Delta H^{\ddagger} = 27.6$ kcal/mol, $\Delta S^{\ddagger} = -9.6$ eu, and for the dimethyl $\Delta H^{\ddagger} = 26.1$ kcal/mol, $\Delta S^{\ddagger} = -5.8$ eu. The products of the reactions as well as the kinetic evidence suggest ionization concerted with rearrangement, which finally result in ring opening. The mechanistic details are discussed.

The solvolysis of the cyclobutyl system has been one of the most thoroughly studied reactions in physical organic chemistry. The solvolysis of 3-substituted cyclobutyl derivatives, however, has received little attention until relatively recently. Part of the reason for this has been the relative difficulty of making such compounds.

Hasek, Clark, and Chaudet[2] reported that the acid-catalyzed ring opening of *trans*-2,2,4,4-tetramethyl-1,3-cyclobutanediol was very much faster than that of the cis isomer. To explain this curious result they suggested that there was participation of the trans hydroxyl to give the bicyclic oxonium ion **1**.

That this hypothesis was untenable was shown by the work of Wilcox and his coworkers[3] and Dolby and Wilkins.[4] The latter workers, using both *cis*- and *trans*-3-hydroxy-2,2,4,4-tetramethylcyclobutyl tosylates, found that, indeed, the trans/cis ratio was about 100 but that the faster rate of the trans compound was not due to the across-the-ring participation. They concluded that the ionization of the tosylate was concerted with the breaking of the 2,3 carbon–carbon bond. They further assumed that the ring opening was disrotatory and hence the cis 3-hydroxyl would interact



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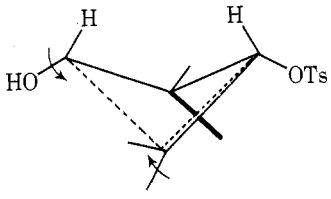
strongly with the methyl substituent on carbon 2, as shown in **2**. Thus the rate of the cis isomer was slow and the rate of the trans was "normal". Indeed, introduction of the fifth methyl group in place of the hydrogen at C-3 reduced the trans/cis ratio to only about 4.

Table I
First-Order Constants and Activation Parameters for Acetolysis of Cyclobutyl Tosylates

Tosylate	Temp, °C	k, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta H^{\ddagger}$, eu[a]	Rel rate
3,3-Dimethylcyclobutyl	86.6	5.81×10^{-5}, 5.82×10^{-5}	26.1	−5.8	1/30
	95.0	1.33×10^{-4}, 1.34×10^{-4}			
	103.0	2.99×10^{-4}, 2.94×10^{-4}			
3,3-Diphenylcyclobutyl	127.0	5.86×10^{-5}, 5.70×10^{-5}	27.6	−9.6	1/1000
	136.2	1.02×10^{-4}, 1.06×10^{-4}			
	142.2	2.13×10^{-4}, 2.33×10^{-4}			
Cyclobutyl[b]	50.0	3.58×10^{-5}	23.8	−5	1
	74.8	5.42×10^{-4}			

[a] The $\Delta S^{\ddagger}$ data are probably not better than ±4 eu. [b] Unpublished data: J. Longanbach, Yale University. Personal communication from Professor Wiberg.



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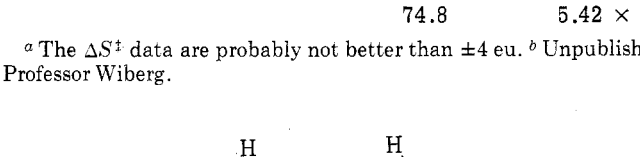
Other data, however, indicated that introduction of any aryl or alkyl substituents into the 3 position of a cyclobutyl tosylate caused a decrease in the rate of solvolysis, relative to the unsubstituted case.[5-7] The cis isomer was generally slower than the trans. Wiberg, Hess, and Ashe[8] suggested that the available data indicated that the 3-substituted cyclobutyl tosylates rearranged stereospecifically initially to the cyclopropylcarbinyl ion, which then opened to the allylcarbinyl ion.

In this paper we describe the preparation and the acetolysis of 3,3-diphenyl- and 3,3-dimethylcyclobutyl tosylates.

Results and Discussion

Preparation of Tosylates. The preparation of 3,3-diphenylcyclobutyl tosylate was carried out according to the following sequence. This preparation was based on the formation of 3,3-dimethylcyclobutanone from dimethylketene and diazomethane.[9] The important difference in the present reaction was that the solution of the ketene was poured into the solution of the diazomethane. In this way the diazomethane was always in excess and moderate yields of the cyclobutanone could be obtained. If the reverse addition was used the reaction took a different course. Very little cyclobutanone was formed; the principal isolated product (20–30%) was the keto ester **4**. This product was formed



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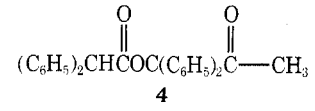

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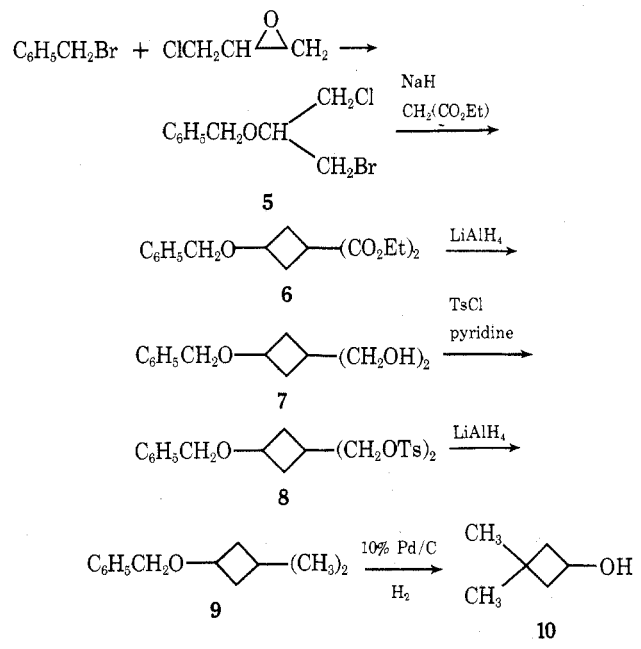
from the addition of diphenylacetic acid to the intermediate cyclopropanone. It was not formed immediately, but crystallized out of the reaction mixture after a few hours of standing.

Although 3,3-dimethylcyclobutanone could be prepared by the reaction of dimethylketene with diazomethane,[9] the fact that it is formed together with the 2,2 isomer led us to consider an alternative route, since the two isomers are relatively difficult to separate on a larger scale. The procedure used is outlined below.



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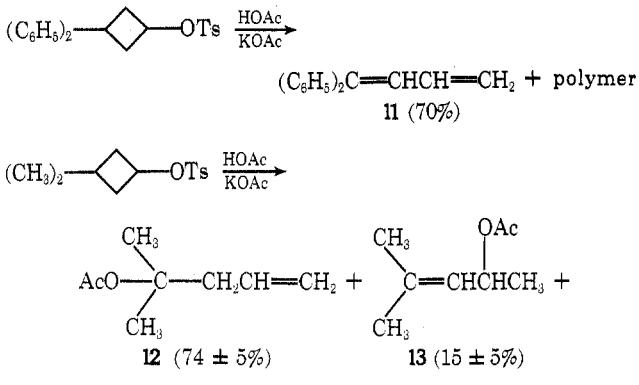
The advantage of this procedure was that in spite of the large number of steps involved, high-purity 3,3-dimethylcyclobutanol could be prepared without the use of the very pyrophoric dimethylketene and large quantities of equally unpleasant diazomethane. All the steps, except the cyclization step, proceeded in relatively high yields and could be carried out on any scale desired. The detailed procedure is given in the Experimental Section.

Kinetics and Product Studies. The rates of acetolysis were determined using the ampoule technique.[10] Solutions of the cyclobutyl tosylates in glacial acetic acid containing 1% of acetic anhydride and an excess of potassium acetate were sealed in a dozen ampoules and placed in a temperature-regulated oil bath. The temperatures were held constant to better than 0.1°. At periodic intervals the ampoules were withdrawn, the reaction was quenched by cooling, and the contents of the tube were titrated with perchloric acid. Because of discoloration of the solutions past 50% reaction the end points were determined using a pH meter. The rates were linear for better than 85% reaction. The rates and activation parameters are summarized in Table I. The rate constants were calculated using the LSKIN-1 program adapted for the IBM 360/65 computer.[11]

All the products of both solvolyses resulted from ring-opening reactions. In the diphenyl case the only characteri-

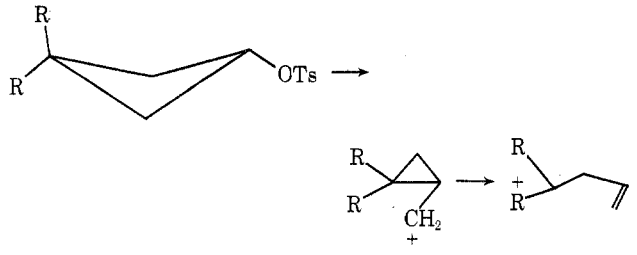
zable product was 1,1-diphenylbutadiene (**11**). This was formed in 56.5% isolated yield (70% crude yield). The compound was isolated by column chromatography. Its spectral (ir, NMR) characteristics were identical with those of an authentic sample.[12] The rest of the reaction mixture resulted from polymerization and/or oligomerization of the butadiene. A similar mixture was obtained from the authentic butadiene when it was heated in glacial acetic acid under solvolysis conditions.

The products of the dimethyl compound were slightly more complex. The principal product (74 ± 5% of the crude reaction mixture) was 4-acetoxy-4-methyl-1-pentene (**12**), formed by the reaction of the dimethylallylcarbinyl ion with acetate. There also was obtained a 15 ± 5% yield of 2-methyl-4-acetoxy-2-pentene (**13**). This product was also formed when authentic 4-methyl-1,3-pentadiene (Aldrich Chemical Corp.) was heated in glacial acetic acid under solvolysis conditions. Thus it apparently arises from the pentadiene, which is thus probably one of the original products of the solvolysis. No pentadiene was observed in the final products. The rest of the material could also be accounted for as having arisen from the pentadiene. These results are summarized in the following reactions. The acetolysis of



3,3-dimethylcyclobutyl brosylate has been reported.[13] The main product of the reaction was **12** (62% yield).

The data presented in this report are in line with those reported by others[8] on the solvolysis of 3-substituted cyclobutyl tosylates. The important findings in the present work are that both the 3,3-diphenyl- and the 3,3-dimethylcyclobutyl tosylates solvolyzed more slowly than the unsubstituted cyclobutyl tosylate and that no cyclic products were formed during the reaction.[14] The slowness of the reaction seems to militate against the concerted ring opening to the allylcarbinyl ion accompanying ionization. In both cases the substituents in the 3 position would have stabilized the developing positive charge. On the other hand, the lack of any cyclobutyl products suggests that the initial formation of the cyclobutyl ion does not occur either. Wiberg et al.[8] suggest that all 3-substituted cyclobutyl derivatives (except 3-ethoxycyclobutyl tosylate) ionize initially to the cyclopropylcarbinyl ions, which then undergo a rapid ring opening to the corresponding allylcarbinyl ions. Our data are in line with this hypothesis. It must be said, however, that none of the data at hand (ours and other) prove the mechanism above. In fact, if the rate of cyclopropylcarbinyl ion opening is exceedingly fast, then its existence as an intermediate may be questioned. In that limiting case the solvolysis would be via a concerted ionization and disrotatory[15] ring opening. The rate of such a reaction, which would be governed by strict orbital symmetry control considerations, would depend on the steric interactions in the attainment of the transition state leading to the allylcarbinyl ion. This type of a mechanism was proposed by Dolby and Wilkins[4] to explain their data on the solvolysis of the highly substituted cyclobutyl tosylates.



Experimental Section

Melting points and boiling points are uncorrected. Infrared spectra were measured with a Perkin-Elmer Model 237 spectrophotometer. The NMR spectra were measured with Varian A-60, A-60D, and HA-100 spectrometers. The calculations were carried out on the University of Nebraska IBM 360/65 computer. Analyses were performed by A. Bernhardt, Elbach über Engelskirchen, West Germany.

3,3-Diphenylcyclobutanone. Diphenylketene.[16] A solution of 50 g (0.23 mol) of diphenylacetic acid in 150 ml of dry benzene was placed into a 500-ml three-necked flask equipped with a reflux condenser and an addition funnel and protected by a drying tube. The solution was heated at reflux and 132 g (1.1 mol) of thionyl chloride was added dropwise during 30 min. The heating was continued for 7 hr. At the end of that time the benzene and the excess thionyl chloride were removed by distillation to leave a pale yellow oil. To remove the last traces of thionyl chloride, 10 ml of benzene was added and the solution was again distilled. The residue was dissolved in 100 ml of hot, anhydrous hexane. The solution was treated with charcoal, filtered, and chilled at 0°. The product crystallized out as white plates. The crystals were recrystallized twice from dry hexane and dried in vacuo at room temperature. The yield of diphenylacetyl chloride was 36 g (73%), mp 52–53° (lit.[16] mp 51–53°).

A solution of 9.7 g (0.042 mol) of diphenylacetyl chloride in 100 ml of dry ether and 75 ml of dry hexane was placed in a 500-ml three-necked flask equipped with a magnetic stirrer, a gas inlet tube, an addition funnel, and a drying tube. The solution was chilled in an ice bath and was flushed thoroughly with dry nitrogen. To this solution 4.4 g (0.044 mol) of dry triethylamine was added dropwise with stirring over a period of 30 min. Triethylamine hydrochloride began precipitating immediately and the supernatant solution became bright yellow. After the addition was complete the flask was stoppered tightly and was kept at 0° for 4 hr. The hydrochloride was filtered using a sintered glass filter which could be attached directly to the reaction vessel via a standard taper. The filtration was accomplished by simply inverting the reaction flask so that the contents flowed into the filter. The filtrate flowed into another flask attached to the fiter via a second standard taper. Suction was applied to the system through a side arm on the filter, below the sintered glass disk. In this way the ketene solution was not exposed to the atmosphere or to moisture. The yellow ketene solution was used in the next step without further isolation. Pure ketene in yields of about 60–70% could be obtained by rapid distillation of the solution.[16]

Diazomethane was prepared from Aldrich Chemical Co. Diazald (*N*-methyl-*N*-nitroso-*p*-toluenesulfonamide) using the procedure for obtaining the ethanol-free product.[17] The diazomethane solution was dried over solid potassium hydroxide.

Diphenylcyclobutanone. To a solution of excess diazomethane in ether contained in a 1-l. erlenmeyer flask was added a solution of diphenylketene, prepared as described above. The addition was accomplished simply by slowly pouring one solution into the other, with intermittent swirling. The evolution of nitrogen started immediately. After standing for several hours the solution was greenish-blue in color. Evaporation of solvent in vacuo gave a dark oil which showed a prominent peak at 1780 cm^{-1} in its infrared spectrum.

The crude reaction mixture (8.4 g) was applied to a chromatography column made from 200 g of silicic acid and 50 g of Celite. The column was initially eluted with 1 l. of Skellysolve B, then with 1 l. of Skellysolve B containing 1% ether. The latter solvent eluted 0.6 g of 1,1-diphenylethylene from the column. The polarity of the solvent was increased gradually to 3.5% ether in Skellysolve B for 2 l. of eluting solvent. During this time various uncharacter-

ized oils were eluted. There was then a break in fractions and the desired product was eluted. The yield of 3,3-diphenylcyclobutanone was 1.5 g (22% of total products, 16% of theory): mp 84–85°; ir (CCl_4) 1793 cm^{-1}; NMR (CCl_4) δ 7.2 (s, 10 H), 3.67 (s, 4 H).

Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.36. Found: C, 86.31; H, 6.36.

3,3-Diphenylcyclobutyl Tosylate (3). A solution of 3.14 g (0.015 mol) of 3,3-diphenylcyclobutanone in 25 ml of dry ether was added dropwise to a stirred solution of 0.32 g (0.08 mol) of lithium aluminum hydride in 50 ml of dry ether. After the addition was complete the reaction mixture was stirred for an additional 6 hr. After this period the excess reducing agent was decomposed with 50 ml of water. The ether layer was separated and the water layer was washed three times with ether. The combined ether solutions were dried and the solvent was evaporated off. The crude 3,3-diphenylcyclobutanol was recrystallized from 200 ml of hexane. The yield was 2.78 g (84%): mp 104–105°; ir (CCl_4) 3610 cm^{-1}; NMR ($CDCl_3$) δ 7.19, 7.29 (10 H), 4.20 (1 H), 3.06, 2.48 (4 H), 2.88 (1 H).

Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.88, H, 7.10.

The NMR spectrum of the cyclobutanol is of some interest because of the large cross-ring coupling. The spectrum was calculated using the LAOCN3 program.[18] Table II lists the calculated coupling constants and the chemical shifts.

The tosylate from the above cyclobutanol was prepared by the sodium hydride method. The yield from 3.74 g of the alcohol was 2.99 g (47%), after three recrystallizations: mp 117–118°; ir (CCl_4) 2900, 1290 s, 1450 w, 1500 s, 1185 s, 1200 s, 1045 s, 1110 s, 950, 700 cm^{-1}; NMR ($CDCl_3$) δ 7.0–8.0 (14 H, aromatic), 4.68 (m, 1 H), 2.00 (m, 4 H), 2.35 s, 3 H).

Anal. Calcd for $C_{23}H_{22}O_3$: C, 73.00; H, 5.82; S, 8.47. Found: C, 72.98; H, 5.52; S, 8.35.

3,3-Dimethylcyclobutanol. 1-Chloro-2-benzyloxy-3-bromopropane (5). The procedure of Nenitzescu et al.[19] was followed. A mixture of benzyl bromide (254 g, 1.48 mol), epichlorohydrin (138 g, 1.48 mol), and 0.25 g of mercurous chloride was heated for 12 hr at 150–160°. The product was separated from the dark brown reaction mixture by distillation through a 12-in. Vigreux column: yield 211 g (54.3%); bp 142–145° (0.3 mm) [lit.[19] bp 146–150° (5 mm)]; NMR (CCl_4) δ 7.26 (s, 5 H), 4.58 (s, 2 H), 3.34–3.9 (m, 4 H).

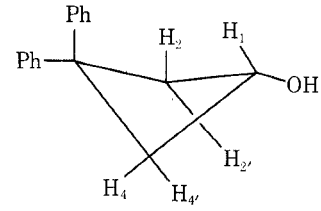
Diethyl 3-Benzyloxycyclobutane-1,1-dicarboxylate (6). The procedure of Beard and Burger[20] was followed. In a 3-l., three-necked flask equipped with a stirrer, an addition funnel, and a reflux condenser and which was swept with dry nitrogen was placed 19.8 g (0.8 mol) of sodium hydride in 500 ml of dry dioxane. To this stirred mixture 128 g (0.8 mol) of diethyl malonate was added dropwise over 20 min. After this addition was complete 211 g (0.8 mol) of **5** was added dropwise in 20 min. Upon completion of the reaction the solution became red but changed to yellow on standing. The mixture was heated at reflux for 44 hr. After cooling to room temperature 19.8 g of sodium hydride in a little dioxane was added to the mixture and heating at reflux was continued for an additional 120 hr. The solvent was partially removed under reduced pressure and the mixture was treated with 500 ml of water. The organic layer was extracted into ether. The ether extracts were dried and concentrated and the residue was distilled under reduced pressure. The distillate, which formed two immiscible layers, was collected at 174–176° (0.9 mm). The heavier layer was the desired product: yield 100.9 g (40.5%) [lit.[20] bp 157° (0.45 mm)]; NMR (CCl_4) δ 7.23 (s, 5 H), 4.13 (q, 4 H, J = 7 Hz), 4.34 (s, 2 H), 4.0–4.7 (m, 1 H), 2.2–3.0 (m, 4 H), 1.23 (t, 6 H, J = 7 Hz).

1,1-Di(hydroxymethylene)-3-benzyloxycyclobutane (7).[21] Diethyl 3-benzyloxycyclobutane-1,1-dicarboxylate (50 g, 0.16 mol) was reduced by 11.4 g of lithium aluminum hydride in 100 ml of ether in the usual manner. There was obtained 24 g (71%) of **9:** mp 66–68° (lit.[21] mp 71°); NMR ($CDCl_3$) δ 7.36 (s, 5 H), 4.41 (s, 2 H), 3.3–4.2 (m, 7 H), 1.4–2.4 (m 4 H).

1,1-Di(tosyloxymethylene)-3-benzyloxycyclobutane (8). To a solution of 48 g (0.22 mol) of **7** in 150 ml of dry pyridine was added 85 g (0.44 mol) of *p*-toluenesulfonyl chloride. The reaction mixture was kept at about 5° overnight. The mixture was poured into water and the product was extracted with ether. The ether extracts were washed thoroughly with 5% hydrochloric acid, 5% potassium carbonate, and finally with water. After drying and concentration of the ether solution the ditosylate crystallized, yield 84.2 g (74.3%), mp 85–86° (lit.[21] mp 86–87°).

1-Benzyloxy-3,3-dimethylcyclobutane (9). The ditosylate **8** (84.2 g, 0.16 mol] was added as a solid, in portions, to a stirred suspension of 12 g of lithium aluminum hydride in 1000 ml of dry ether. The reaction mixture was flushed with nitrogen and chilled in an ice bath. After the addition was complete the mixture was heated at reflux for 24 hr. After the decomposition of the excess hydride with water the mixture was extracted with ether. The ethereal extracts were dried and concentrated and the residue was distilled to give 20.5 g (71%) of the product: bp 127–132° (12–15 mm); NMR (CCl_4) δ 7.25 (s, 5 H), 4.21 (s, 2 H), 3.95 (q, 1 H), 1.4–D.4 (m, 4 H), 1.12 (s, 3 H), and 1.09 (s, 3 H).

Table II
NMR Parameters for 3,3-Diphenylcyclobutyl Alcohol



Coupling constants, Hz	Chemical shifts (60 MHz) Proton	Shift, Hz
$J_{2,4}$ = 5.20		
$J_{2,4'}$ = 0.0	1	251.5
$J_{2,2'}$ = $J_{4,4'}$ = 11.10	2	187.0
$J_{2,4'}$ = $J_{4,2'}$ = −0.60	4	187.0
$J_{1,4}$ = $J_{1,2}$ = 7.00	2'	151.2
$J_{1,4'}$ = $J_{1,2'}$ = 8.20	4'	151.2

3,3-Dimethylcyclobutanol (10). A solution of 10 g (0.052 mol) of benzyl ether **9** in 10 ml of ethanol was mixed with a suspension of 0.3 g of 10% palladium on charcoal in 20 ml of ethanol. The mixture was hydrogenated for 3 hr under 30 psi of hydrogen in a Parr shaker. The catalyst was filtered off and the solvent was evaporated. Distillation of the residue gave 3 g (57%) of 3,3-dimethylcyclobutanol: bp 112–114° (20 mm); NMR (CCl_4) 4.17 (q), 3.84 (s, 1 H), 1.44–2.35 (m, 4 H), 1.12 (s, 3 H), and 1.08 (s, 3 H).

Anal. Calcd for $C_6H_{12}O$: C, 71.95; H, 12.08. Found: C, 71.68; H, 11.86.

3,3-Dimethylcyclobutyl Tosylate. This compound was prepared in the same manner as 3,3-diphenylcyclobutyl tosylate. Starting with 6 g of the cyclobutanol, there was obtained 4.1 g of the pure tosylate, mp 21–22°. The crude tosylate was purified by chromatography over a short (10 in.) column of Florisil, using pentane as the eluent. The product was recrystallized from pentane: NMR (CCl_4) δ 7.47 (d, 4 H), 4.74 (q, 1 H), 2.44 (s, 3 H), 1.60–2.38 (m, 4 H), 1.10 (s, 3 H), and 1.03 (s, 3 H).

Anal. Calcd for $C_{16}H_{18}O_3S$: C, 61.42; H, 7.09; S, 12.60. Found: C, 61.19; H, 7.10; S, 12.49.

Kinetic Procedures. The method used was essentially that of Winstein et al.[10] Solutions of the tosylates (ca. 0.02 *M*) in glacial acetic acid, containing 1% acetic anhydride and 0.045–0.056 *M* in dry potassium acetate, were sealed in Pyrex ampoules and placed in a constant-temperature oil bath. The bath temperature was held constant to better than 0.1° and was measured with a calibrated total immersion thermometer. The ampoules were withdrawn at periodic intervals and accurately measured aliquots were titrated with perchloric acid. The end points were determined with a pH meter; the use of visual indicators was precluded by discoloration of the samples after 50% reaction. The last ampoule was withdrawn after 10 half-lives. The rate constants were calculated using a nonlinear least-squares program, LSKIN-1.[11] The activation parameters were also calculated using a least-squares program. The rates were strictly first order over at least 85% reaction. The statistical analysis of the data (residual plot) showed that all the deviations were random.

Solvolysis Product Studies. In all cases the solvolyses were carried out under the same[22] conditions as the kinetic runs, i.e., the solutions were sealed in ampoules and placed in the constant-temperature bath for at least 10 half-lives.

3,3-Diphenylcyclobutyl Tosylate. A solution containing 1.50 g (0.04 mol) of the tosylate and 0.55 g of dry potassium acetate in 50 ml of glacial acetic acid containing 1% acetic anhydride was divided between and sealed in six ampoules. The tubes were heated in a constant-temperature bath at 136° for 20 hr. At the end of that period the solution was poured into 100 ml of ether, to which was then added 100 ml of water. The solution was neutralized by addition of solid potassium carbonate. The aqueous layer was extracted

with ether (four times) and the combined ethereal layers were dried and concentrated to give 0.86 g of crude product.

The crude reaction mixture was placed on a chromatography column made up from 32 g of silicic acid and 10 g of Celite. The column was eluted with petroleum ether. The main product of the reaction, 1,1-diphenyl-1,3-butadiene, was obtained in 56.5% yield. The examination of the NMR spectrum of the crude mixture revealed it to be about 70% butadiene. Addition of small amounts of ether to the eluent caused the elution of products which contained an acetate group (20% of the crude mixture). Further addition of ether to the eluent caused the appearance of several trace fractions which were not identified.

The butadiene was identified by its ir and NMR spectrum and comparison with an authentic sample.[12] Authentic 1,1-diphenyl-1,3-butadiene was heated in glacial acetic acid in the presence of potassium acetate under the same conditions as the solvolysis. After an identical work-up and chromatography, polymeric and oligomeric acetates were isolated, virtually identical with those obtained in the solvolysis reaction.

3,3-Dimethylcyclobutyl Tosylate. The product study solvolysis of this compound was carried out using similar conditions to the diphenyl tosylate. A solution of 0.98 g (0.038 mol) of the tosylate and 0.56 g (0.056 mol) of potassium acetate in 40 ml of glacial acetic acid was heated at 105° for 24 hr. The contents of the tubes were dissolved in 75 ml of ether contained in a 250-ml flask equipped with a stirrer and an addition funnel and connected to a Dry Ice trap. The solution was cooled, 50 ml of water was added, and the solution was carefully neutralized with cold, concentrated potassium hydroxide. The solution was then extracted with ether; the extracts were dried and concentrated by careful distillation. No volatile products were recovered from the Dry Ice trap. The solvolysis products were separated by GLC using a 4-ft glass column packed with 5% Apiezon N on Chromosorb W and operated at 50° with 47 ml/min He flow rate. The main component, 74 ± 5% of the crude reaction mixture, was 4-acetoxy-4-methyl-1-pentene **(12)**. It was identified by its ir spectrum ($\nu_{C=O}$ 1735 cm^{-1}) and NMR spectrum (CCl_4) [δ 1.44 (s, 6 H), 1.94 (s, 3 H), 2.56 (d, 2 H), and 4.9–6.25 (m, 3 H)]. The NMR spectrum was essentially identical, except for the acetate methyl group, with the spectrum of 4-hydroxy-4-methyl-1-pentene, prepared by the addition of allylmagnesium bromide to acetone.

Another fraction, formed in 15 ± 5% yield, was identified as 2-methyl-4-acetoxy-2-pentene **(13)**: ir (CCl_4) 1730, 1600 cm^{-1}; NMR (CCl_4) δ 1.28 (d, 3 H, J = 6.0 Hz), 1.66, 1.68 (two s, 6 H), 1.89 (s, 3 H), 4.0–5.7 (m, 1 H), 1.5–2.0 (m, 1 H, buried under Me resonances). The same product was formed when authentic 4-methyl-1,3-pentadiene (Aldrich Chemical Co.) was heated in acetic acid under the solvolysis conditions.

Two other minor (1–2%) volatile components, which were not identified, were isolated. These were also obtained when the pentadiene was heated in acetic acid.

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Registry No.—**3,** 54166-14-2; **5,** 54307-67-4; **6,** 54166-15-3; **7,** 20061-24-9; **8,** 20440-61-3; **9;** 54166-16-4; **10,** 54166-17-5; **10** tosylate, 54166-18-6; **11,** 4165-81-5; **12,** 926-22-7; **13,** 54166-19-7; 3,3-diphenylcyclobutanone, 54166-20-0; diphenylketene, 525-06-4; diphenylacetic acid, 117-34-0; diphenylacetyl chloride, 1871-76-7; 3,3-diphenylcyclobutanol, 54166-21-1; *p*-toluenesulfonyl chloride, 98-59-9.

References and Notes

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