The Effect of Phenyl Substitution at the Double Bond of Δ^3-Cyclopentenylethyl *p*-Nitrobenzenesulfonate upon the Rate of Acetolysis to Norbornyl Products[1]

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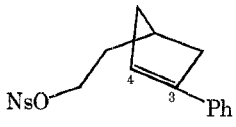
The relative rates of acetolysis of 2-cyclopentylethyl, 2-(Δ^3-cyclopentenyl)ethyl, 2-(3-phenyl-Δ^3-cyclopentenyl)ethyl, and 2-(3,4-diphenyl-Δ^3-cyclopentenyl)ethyl *p*-nitrobenzenesulfonates at ~60° are 0.011, 1.0, 1.70, and 0.87, respectively. The latter two substrates give, within experimental precision, only 2-phenylnorbornene and 1,2-diphenylnorbornene, respectively, as products under the conditions of acetolysis, 60.4° in acetic acid containing sodium acetate and a trace of acetic anhydride. A transition state resembling a classical 2-phenylnorbornyl cation therefore appears to be excluded, and it is concluded, based on analogies, that π-route transition states generally resemble π complexes.

We have synthesized and studied the acetolysis rates and products of 2-(3-phenyl-Δ^3-cyclopentenyl)ethyl and 2-(3,4-diphenyl-Δ^3-cyclopentenyl)ethyl *p*-nitrobenzenesulfonates (nosylates, ONs), **1** and **2**, for comparison with similar substances studied by others. It was anticipated by analogy with the unsubstituted and mono- and dimethyl-substituted species[2-4] that closure to the norbornyl skeleton by the π route would occur upon acetolysis and that the 2-phenyl-2-norbornyl and 1,2-diphenyl-2-norbornyl cations would be intermediates, respectively. Since these anticipated cations are known to be classical through NMR studies in acidic solutions,[5-8] it would be expected that the acetolysis transition states would closely resemble a classical 2-norbornyl cation–nosylate anion pair.[9]



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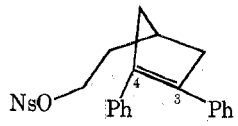

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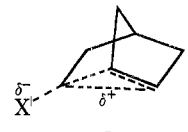
However, information on the methyl-substituted analogs of **1** and **2** indicates that the π-route transition state is nearly symmetrically bridged and not close to a classical 2-norbornyl cation–nosylate anion pair, in that a methyl group at carbon 3 increases the rate of acetolysis 7-fold, while methyl groups at both carbons 3 and 4 increase the rate 38.3-fold.[10] If the transition states for acetolysis of the unsubstituted, 3-methyl, and 3,4-dimethyl derivatives are symmetrically bridged, then the rate enhancement for the monomethyl derivative should be approximately $(38.3)^{1/2} = 6.2$, quite close to the observed 7-fold effect. In contrast, the rate enhancement for monomethyl should be approximately $38.3/2 = 19.2$ if all three transition states are classical. Also, both the relatively small rate effect of methyl substitution at the double bond and the pattern of multiplicative rather than additive behavior in the rate enhancement of methyl relative to dimethyl substitution indicate a symmetrically bridged transition state equilibrium nuclear geometry (ENG), **3**, rather than a classical, nonsymmetrically bonded ENG, **4**, by comparison with other reactions of olefins generally throught to proceed via bridged (peracetic acid oxidation) or classical (acid-catalyzed hydration) transition states.[10]



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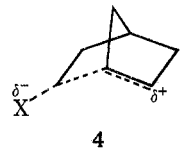

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Subsequently, it was shown that methanolysis of optically active 1,2-dimethyl-*exo*-2-norbornyl *p*-nitrobenzoate[11] and chloride[12] leads to optically active product of partially retained configuration. The amount of retention was found to be independent of both counterion and temperature, a result seemingly consistent solely with totally unassisted ionization to a nonbridged intermediate, which only subsequently, with understandably little selectivity regarding counterion or temperature, partially racemizes.[12] It has also been shown that the 2-methyl-2-norbornyl cation[13] and the 1,2-dimethylnorbornyl cation[14,15] in highly acidic solvents exist essentially entirely in the classical (tertiary cation) form, although a "partially delocalized" ENG has been suggested from NMR and photoelectron spectroscopic evidence.[16,17] A symmetrically bridged structure has been suggested for the 2-norbornyl cation itself.[6,17]

The evidence in the methyl system thus suggests that the π-route transition state is bridged, but that the σ-route transition state is not bridged, and the intermediate cations are classical in the case of both mono- and dimethyl substitution. Great controversy still exists over whether the σ-route transition state is bridged,[18,19] and even over the nature of the 2-norbornyl cation.[17,18] It is generally agreed that the σ-route transition state for solvolysis of 2-phenyl-2-norbornyl derivatives is classical,[7,18] whereas there is not agreement about the classical vs. bridged character in the transition state for solvolysis of 1-phenyl-2-norbornyl derivatives.[18,20,21]

In view of the results with methyl-substituted compounds, it seems probable that systems which can solvolyze through a classical transition state by the σ route nevertheless go through a bridged transition state when carried through the π route. Since it is also probable that σ-route transition states may not be bridged even if there is some degree of bridging in the more electron-demanding carbonium ions,[7] it is of interest to determine whether the acetolysis of **1** and **2** is best described by transition state **3** or **4**.

Results

The substrates were prepared as described in the Experimental Section.

For product determination, the acetolyses were carried out at the same temperature, 60.4°, used for the rate studies. The *p*-nitrobenzenesulfonates **1** and **2** were solvolyzed in anhydrous acetic acid in the presence of excess sodium acetate to neutralize the strong acid released from the reactions. The product isolated from acetolysis of **1** was 95% 2-phenyl-2-norbornene and that from **2** was 95% 1,2-diphenyl-2-norbornene, as shown by comparison with authentic samples prepared by known routes.

Table I
Rate Constants for Acetolysis of RCH_2CH_2ONs

R	Temp, °C	10^4k, sec^{-1}	Relative rate
Cyclopentyl	60	0.0116[a]	0.011
Δ^3-Cyclopentenyl	60	1.10[a]	1.0
	61.83	1.31[b]	
3-Phenyl-Δ^3-cyclopentenyl	60.4	1.865 ± 0.015[c]	1.70
3,4-Diphenyl-Δ^3-cyclopentenyl	60.4	0.955 ± 0.014[c]	0.87

[a] Reference 2. [b] Reference 3. [c] Error limits are the standard deviations of mean values.

For rate studies, solutions of ~1–2 × 10^{-4} *M* for compound **1** and ~5–10 × 10^{-5} *M* for compound **2** in anhydrous acetic acid buffered with 0.03 *M* sodium acetate were heated at 60.4°, the rates being followed spectrophotometrically. The rate constants are given in Table I. These rate constants, since they are much larger than that for the saturated analog (R = cyclopentyl), clearly demonstrate participation of the double bond in the rate-determining step of solvolysis, leading essentially exclusively to the observed ring-closure products. Ring closure is therefore the process by which the double bond accelerates acetolysis.

Discussion

Three kinds of rate comparisons can be made for the phenyl- and diphenyl-substituted compounds **1** and **2**: the rate effect of phenyl substitution at the double bond relative to the rate effect of the double bond alone, all in comparison with the saturated compound; the nature of the cumulative effects of one and two phenyl groups on the double bond; and the effects of phenyl substitution in this acetolysis reaction relative to the effects of phenyl substitution in other, known reactions of carbon–carbon π bonds which are analogous.

Noting the rate effects in Table I, which are ~100-fold for all three Δ^3-cyclopentenyl substrates relative to cyclopentyl, it can be seen that significant double-bond participation is not accompanied by any significant additional effect of one or two phenyl groups attached in conjugation with the double bond. These observations strongly suggest that the participation of the double bond does not involve appreciable development of classical carbonium ion character at either carbon atom in the transition state, nor does it involve appreciable steric interactions in the case of phenyl substitution. Fortuitous near equality of inductive and delocalization effects may well be involved, but the near cancellation required by the small rate effects can only be expected if little development of classical carbonium ion character has ocurred at the double-bond carbon atoms in the transition state.

The rate effects of phenyl substitution do not match either the additive behavior expected for a nonsymmetric transition state ENG **4**, or the multiplicative behavior expected for symmetric **3**.[10,22,23] There clearly are steric interactions of the phenyl groups in analogous compounds such as *cis*-α,α'-dimethylstilbene and *trans*-α,β-dimethylstyrene (*cis*-methyl groups).[24] Had phenyl substitution produced the large rate enhancements expected for mechanisms involving appreciable classical carbonium ion character at the doubly bonded carbon atoms, steric interactions would probably have had only a minor influence on the cumulative effects of one and two phenyl groups. However, in view of the observed very small effect of phenyl substitution, it is hardly surprising that steric effects, different in the monophenyl and diphenyl substrates and transition states, preclude a priori use of the cumulative effect to decide between transition state types **3** and **4**. Considerable effort was directed toward making mono- and dianisyl derivatives, but these compounds were not forthcoming.

Typical electrophilic reactions of olefins include acid-catalyzed hydration, halogen addition, and peroxy acid epoxidation.[25] Trends with methyl-substituted ethylenes have been discussed previously in connection with the methyl-substituted 2-(Δ^3-cyclopentenyl)ethyl nosylates.[10] There is not a large volume of data on phenyl-substituted systems, but enough examples are available to characterize the trend of phenyl substitution. Substitution of one phenyl group onto a carbon–carbon double bond enhances the rate of electrophilic attack, in amounts varying from very large to relatively small, depending on the nature of the electrophilic reagent. However, substitution of a second phenyl group at the other end of the double bond tends to decrease the rate relative to the monophenyl compound.

In acid-catalyzed hydration, phenyl substitution typically increases the rate by a few thousandfold.[25] This reaction is clearly "classical", as even methyl substitution increases the rate by on the order of a thousandfold or more (depending on reaction conditions), but a second methyl group at the other end of the double bond decreases that rate enhancement somewhat.[26]

Bromination and chlorination of olefins show the same kinds of trends, with monophenyl substitution giving faster rates by on the order of a few hundred to over 1000, but with diphenyl substitution giving rates only a few times (up to 20) faster than the unsubstituted olefin.[25,27-31] A mechanism involving a bridged, though possibly unsymmetrically bridged, transition state for bromination has been suggested, and it was concluded that this type of transition state leads to a bromonium ion in the case of alkyl-substituted olefins, but it leads to an open α-bromocarbonium ion in the case of phenyl-substituted olefins.[31] The latter case was noted[31] as something of a problem with respect to Hammond's postulate,[9] and thus the bromination data parallel the present data on **1** and **2**, presenting the following problem. Why should a reaction leading to a classical carbonium ion structure proceed through a rate-determining transition state ENG which seems not to resemble the classical carbonium ion so much as it resembles a bridged, nonclassical structure?

Peracid epoxidation of olefins is a mildly electrophilic reaction,[32] which is thought generally to proceed through a cyclic rate-determining transition state and not to a carbonium ion, or even an oxonium ion.[25] Data on phenyl-substituted ethylenes,[33] making reasonable allowances for temperature differences, indicates that substitution of a single phenyl group onto an olefin increases the rate of peracetic acid oxidation by factors of ~15–60, while a second phenyl group at the other end of the double bond decreases this enhancement by factors of ~2–8. The epoxidation rates maintain the same pattern seen in halogenation and in the π-route solvolyses, while bridging the gap in rate enhancements produced by phenyl substitution, which are only somewhat larger in the case of epoxidation than in solvolysis.

These experimental analogies show that one cannot distinguish between classical and bridged transition states directly on the basis of the cumulative effects of mono- and diphenyl substitution of the double bond, since both classical (hydration) and bridged (halogenation, epoxidation) mechanisms are slowed by substitution of a second phenyl group at the other end of the double bond. While steric effects are no doubt the cause of this difficulty, it is never-

theless possible to compare the *orders of magnitude* expected for additive (classical mechanism) and multiplicative (bridged mechanism) effects. If one phenyl group increases the rate by 10^3, then two phenyl groups should give 2×10^3 (classical) or 10^6 (bridged); other sets of corresponding numbers are 10^2, 2×10^2, 10^4; and 10, 20, 100. With very large rate enhancements, as in olefin hydration, the discrepancy between experiment and prediction for the bridged mechanism is enormous. With lower rate enhancements, the classical prediction still is closer to experiment, but the discrepancy between the bridged prediction and experiment is not so large, and may readily be interpreted as a steric effect. Unsymmetrically bridged transition states would reduce the discrepancy still further (approaching in the limit the classical mechanism).

Based on the above three kinds of rate comparisons, we conclude that the small rate effects of phenyl substitution on the double bond of the Δ^3-cyclopentenylethyl system relative to the large (100-fold) effect of the double bond itself rule out a transition-state structure closely resembling a classical norbornyl cation. The transition state in the phenyl-substituted case (**1** and **2**) appears to be bridged, but with little electron deficiency in the participating π system. Expectations of relatively small substituent effects, particularly for phenyl groups, in bridged cationic structures appear to reinforce the idea that these π-route transition states are not like classical carbonium ions and are probably bridged.[20,34]

Substantial π-bond assistance is evident in these reactions, since the Δ^3-cyclopentenylethyl compounds undergo acetolysis 100 times faster than the corresponding saturated-ring compound which uses solvent assistance. The major feature of these π-route solvolyses thus appears to be an almost "vertical" interaction of the π bond, distorting the π-electron distribution so little that substitution of the π-bonded carbon atoms produces little additional effect. The transition state may thus be thought of as similar to a π complex,[35-36] although it may, of course, be unsymmetrically bridged in cases such as **1** and **2**. This interpretation is further supported by evidence that π-route transition states do not resemble classical cations in solvolytic cyclizations involving unsymmetrical participation by double and triple bonds.[37]

There appears to be substantial carbon–oxygen bond breaking at the transition state, since the rate ratio for leaving groups ONs/OTs is 12.4 (Δ^3, 62°) or 11.1 (saturated, 101°).[10] The near equality of these ratios and the effective ρ values of a little more than unity indicate that the sulfonate anions are rather completely formed at the transition state (as expected for the solvent-assisted reaction of the primary, saturated system). Molecules may generally be expected to avoid primary carbonium ions as intermediates, but this does not preclude transition states resembling ion-paired primary carbonium ions. In the π-route transition state, this reasoning suggests that the structure is like a loose π complex of a primary carbonium ion with relatively little charge deficiency in the π system itself.

Since the unsubstituted and methyl-substituted Δ^3-cyclopentenylethyl substrates appear to go through transition states which are symmetrically bridged, it is of interest to ask whether a symmetrically bridged intermediate is required. Such a single, symmetrically bridged rate-determining transition state is required by the symmetry of the reaction coordinate motion to lead initially to a symmetric ENG.[38-40] However, there are still two possibilities, for this symmetric ENG may be either an intermediate or a transition state—a nonclassical ion or the symmetrically bridged transition state for the rapid Wagner–Meerwein (W–M) rearrangement of two classical ions. A sketch of the latter

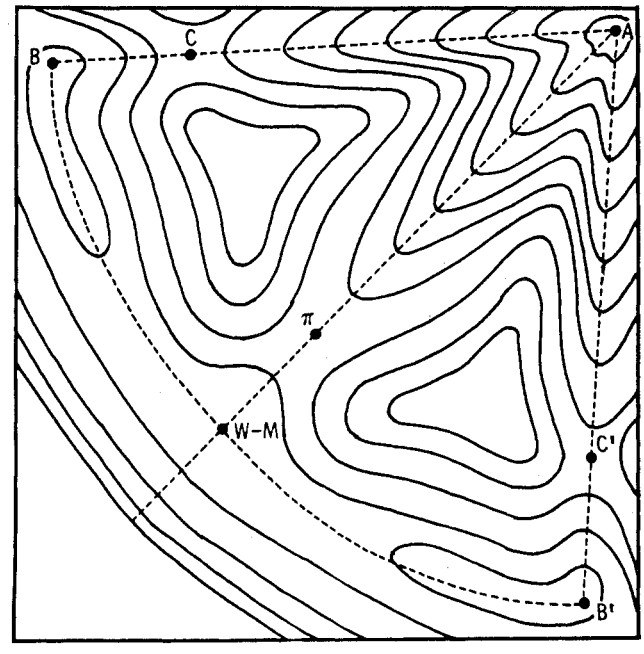

Figure 1. Sketch of possible potential energy surface for 1,2-dimethylnorbornyl cation system. Starting from 2-(3,4-dimethyl-Δ^3-cyclopentenyl)ethyl nosylate, A, the lowest energy route involves passage through transition state, π to a symmetrical ENG, **W–M**, which is itself the transition state for Wagner-Meerwein rearrangement of the classical 1,2-dimethylnorbornyl cations B $\rightleftarrows$ B′. The two coordinates plotted are the C_2–C_6 and the C_6–C_1 distances (norbornyl numbering). It is assumed that other nuclear coordinates have been relaxed to the most stable nuclear geometry for the given values of the C_2–C_6 and C_6–C_1 distances. The bond from carbon (C_6) to nosylate in A is assumed to be broken as the carbonium ions are formed, and ENG's B, B′, and **W–M** are assumed not to have the (already formed) nosylate anion associated with them. C and C′ are unsymmetrical, higher energy transition states for direct formation of the classical carbonium ions. The energy contours might represent ~3 kcal mol^{-1} increments.

situation is shown in Figure 1. The essential feature can be described, with some looseness of meaning as this: What *was* the symmetric reaction coordinate of the π-route transition state becomes a true vibration of the W–M transition state, while the antisymmetric stretching vibration of the partially formed carbon–carbon bonds of the π-route transition state becomes the reaction coordinate of the W–M transition state. Thus, both transition states are well-defined ENG's.

A surface involving a nonclassical ion in equilibrium with classical ions would be similar to Figure 1, except that the region around **W–M** would be a basin rather than a saddle point. By suitable changes, π could be made higher in energy than C and C′, or B and B′ could be made higher in energy than **W–M**, or made nonexistent as ENG's. Unsymmetrically bridged π-transition states could result by changing the routes through π or C and C′, or by having them merge.

In a case such as the reactions of **1** and **2**, it is possible that two π-like transition states exist in *place* of the single transition state π in Figure 1, passing by curved valleys from A near π to B and again from A near π to B′. However, it is difficult to fit such routes onto the same surface and still provide barriers between them and the B $\rightleftarrows$ B′ route. Figure 1 nicely suffices to explain the possibility that the methyl-substituted Δ^3-cyclopentenylethyl systems actually may proceed through a symmetrical transition state, while still forming classical, not bridged, ions as the first intermediate (but not the first ENG).

This idea of two consecutive transition states has suggested itself before in studies of imidazole catalysis.[41] It may also apply to some cases of bromination.[31]

The surface also suggests an explanation of why the transition state appears not to resemble the classical carbonium ion, as predicted by Hammond's postulate.[9] The transition state should resemble the consecutively formed ENG closer to it in energy, but this ENG need not be an intermediate; it may be a transition state. In the present case, the transition state π and the classical carbonium ion intermediates B and B′ are not consecutive ENG's, and π resembles **W–M** more closely than it resembles B or B′.

While it is impossible here to review the literature on the norbornyl system,[1b] we would like to revive the interpretation of rapidly equilibrating classical ⇄ nonclassical ⇄ classical ions, which was previously considered unnecessary, as it would still require that the classical ion exhibit high exo/endo selectivity.[42] Classical ions have been implicated in reactions of *endo*-2-norbornyl derivatives.[43-45] Ion-pairing effects can explain differences between exo and endo systems.[44-50] Although NMR studies indicate that the 2-norbornyl cation itself is bridged,[6,17] a carbon-14-labeling experiment, the π-route formolysis of 2-(Δ^3-cyclopentenyl)-2-^{14}C-ethyl nosylate,[51] gives a product ^{14}C distribution, which is incompatible with exclusive formation of a symmetrically bridged ion,[52] and evidence, that in solvolytic reactions *exo*-norbornyl derivatives are unusually fast and that high exo/endo selectivity characterizes bridged structures,[19] has been forcefully held to be inconclusive.[18,53,54]

We would suggest that perhaps exo is unusually fast as a result of carbon–carbon hyperconjugation[36,55,56] in a transition state resembling the classical carbonium ion. The results of the Foote–Schleyer correlation[57,58] may be more readily explained in this way: since steric/torsional effects may be expected to favor exo over endo,[59-62] the near-normal rate for endo may be the result of compensating steric/torsional and hyperconjugative effects. Hyperconjugative effects should be present in the endo transition state as well as the exo, if it resembles a carbonium ion–counterion pair. The fast rate for exo would then result from reinforcement of steric/torsional and hyperconjugative effects, and the exo/endo rate and product ratios would be primarily determined by steric/torsional differences,[18] since the hyperconjugative accelerations would be present for both endo and exo and thus cancel. The ^{14}C-labeling results noted above[51,52] are consistent with the classical ⇄ nonclassical ⇄ classical scheme (even though they are not consistent with a scheme involving only nonclassical ions), if the nonclassical ion does not undergo 6,2 hydride shift appreciably in comparison with the classical ion, for then the 6,2 equilibration process need not give equal amounts of the two acetates which can result from 6,2 hydride shifts.[63] Perhaps this scheme is not the answer, but there is evidence *suggesting*, if not requiring, both classical and nonclassical ions in different phenomena in the 2-norbornyl system, and so it seems not unreasonable to suggest that this scheme be re-examined. The extremely rapid W–M rearrangements of such skeletons are well explained by the presence of a relatively low-energy, bridged intermediate for the interconversion of the classical carbonium ion structures in cases where the classical ENG is more stable than the nonclassical.

Experimental Section

Elemental analyses were by Galbraith Microanalytical Laboratories, Knoxville, Tenn. Melting points, determined with a Thomas-Hoover capillary melting point apparatus, are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 137 Infracord. NMR spectra were run on a Varian Model A-60A spectrometer. Samples were run as dilute solutions in the solvent indicated using tetramethylsilane (TMS) as an internal reference. An Aerograph Model A-700 was used for GLC. Dry pyridine was distilled from BaO and stored over KOH pellets. Petroleum ether had bp 70–90°.

3-Phenyl-Δ^3-cyclopentenecarboxylic Acid. Methylphenylvinylcarbinol, prepared by reaction of vinylmagnesium bromide and acetophenone,[64] was dehydrated by heating with aniline hydrobromide[64] (Eastman) to give 2-phenyl-1,3-butadiene, bp 55–64° (13 mm) [lit.[64] bp 57–63° (13 mm)]. This butadiene was heated with ethyl diazoacetate[65] (Aldrich) at 95 ± 2° for 18 hr to give 1-(1-phenylvinyl)-2-carboethoxycyclopropane, yield 29%, bp 95–104° (0.7 mm). 1-(1-Phenylvinyl)-2-carboethoxycyclopropane was pyrolyzed[10,66] at 500° to give two rearranged products, ethyl 3-phenyl-Δ^3-cyclopentenecarboxylate, and the free acid which was separated by alkaline extraction. The ester was saponified with 10% aqueous KOH solution and acidified, and the combined carboxylic acid was recrystallized from cyclohexane: yield 51%; needles; mp 93–94°; ir (Nujol mull) 1700 cm^{-1} (C=O); NMR ($CDCl_3$) δ 2.67–3.55 (m, 5 H), 6.03 (br, 1 H, vinyl), 7.29 (m, 5 H, aromatic), 12.05 (s, 1 H, COOH).

2-(3-Phenyl-Δ^3-cyclopentenyl)acetic Acid. Reduction of 3-phenyl-Δ^3-cyclopentenecarboxylic acid with $LiAlH_4$[67] gave (3-phenyl-Δ^3-cyclopentenyl)methanol, yield 81%, mp 49–50° (from benzene–pentane). This alcohol was converted to the tosylate with tosyl chloride,[68] yield 84%, mp 78–80°. The tosylate was then heated with KCN in ethylene glycol[69] at 100° for 2.5 hr. The crude nitrile without further purification was refluxed with 20% aqueous KOH solution for 20 hr. The product was isolated by acidification of the aqueous solution to give crude acid: yield 68% based on the tosylate; mp 105–107°; ir (Nujol mull) 1710 cm^{-1} (C=O); NMR ($CDCl_3$) δ 2.0–3.3 (m, 7 H), 6.02 (br, 1 H, vinyl), 7.24 (m, 5 H, aromatic), 11.42 (s, 1 H, COOH).

2-(3-Phenyl-Δ^3-cyclopentenyl)ethyl *p*-Nitrobenzenesulfonate (1). Reduction of the above acid with $LiAlH_4$[67] gave 2-(3-phenyl-Δ^3-cyclopentenyl)ethanol, yield 93%, mp 50–51° (from petroleum ether). This alcohol was converted to the nosylate with *p*-nitrobenzenesulfonyl chloride:[70] yield 56%; mp 102–103° (from benzene–pentane); ir (Nujol mull) no trace of OH, 1530, 1350 (nitro group), 1368, 1190 cm^{-1} (sulfonate); NMR ($CDCl_3$) δ 1.66–3.04 (m, 7 H), 4.21 (t, 2 H, J = 6.4 Hz), 6.03 (br, 1 H, vinyl), 7.26 (br, 5 H, aromatic), AA′BB′ pattern centered at 8.17 (4 H).

Anal. Calcd for $C_{19}H_{19}NO_5S$: C, 61.12; H, 5.13; N, 3.75; S, 8.57. Found: C, 61.14; H, 5.10; N, 3.64; S, 8.43.

3,4-Diphenyl-Δ^3-cyclopentenone. 4-Hydroxy-3,4-diphenyl-Δ^2-cyclopentenone, prepared by the reaction of benzil and acetone,[71] was converted to 4-chloro-3,4-diphenyl-Δ^2-cyclopentenone with acetyl chloride,[72] yield 65%, mp 117–118° (lit.[72] mp 116–117°). This chloride was reduced to the ketone with Zn and CH_3CO_2H in ether:[73] yield 95%; light yellow needles (from acetone); mp 143–144° (lit.[73] mp 147°); ir (Nujol mull) 1750 cm^{-1} (C=O); NMR ($CDCl_3$) δ 3.42 (s, 4 H, methylene), 7.16 (s, 10 H, aromatic).

3,4-Diphenyl-Δ^3-cyclopentenylacetic Acid. Reduction of 3,4-diphenyl-Δ^3-cyclopentenone with $LiAlH_4$[74] in ether gave, after recrystallization from cyclohexane, 3,4-diphenyl-Δ^3-cyclopentenol, yield 93%, colorless crystals, mp 103–104° (lit.[75] mp 102–104°). This alcohol was converted to the tosylate with tosyl chloride,[68] yield 95%, mp 103–104°. The tosylate was condensed with sodium diethylmalonate[76] in ethanol solution to give a brown oil, which upon hydrolysis with 10% aqueous KOH for 20 hr produced, after acidification with 10% sulfuric acid, a pale yellow, crystalline solid. Decarboxylation of the crude diacid in refluxing pyridine[76] gave, after recrystallization from 95% ethanol, colorless needles: yield 39% based on tosylate; mp 160–161°; ir (Nujol mull) 1700 cm^{-1} (C=O); NMR ($CDCl_3$) δ 2.42–3.42 (m, 7 H), 7.1 (s, 10 H, aromatic), 11.45 (s, 1 H, COOH).

2-(3,4-Diphenyl-Δ^3-cyclopentenyl)ethyl *p*-Nitrobenzenesulfonate (2). Reduction of 3,4-diphenyl-Δ^3-cyclopentenylacetic acid with $LiAlH_4$[67] in ether gave, after recrystallization from benzene–petroleum ether, 2-(3,4-diphenyl-Δ^3-cyclopentenyl)ethanol, yield 84%, colorless fibrous crystals, mp 71–72°. This alcohol was converted to the nosylate with *p*-nitrobenzenesulfonyl chloride[70] (Eastman): yield 52%; pale yellow crystals; mp 99–100° (blue melt); ir (Nujol mull), no trace of OH, 1545, 1355 (nitro group), 1372, 1183 cm^{-1} (sulfonate); NMR ($CDCl_3$) δ 1.93 (br quin, 2 H, $J \simeq J' \simeq 6$ Hz), 2.25–3.12 (m, 5 H), 4.22 (t, 2 H, J = 6 Hz), 7.06 (s, 10 H, aromatic), AA′BB′ pattern centered at 8.16 (4 H).

Anal. Calcd for $C_{25}H_{23}NO_5S$: C, 66.81; H, 5.16; N, 3.12; S, 7.12. Found: C, 66.74; H, 5.43; N, 3.14; S, 7.09.

2-Phenyl-2-norbornene and 1,2-diphenyl-2-norbornene were prepared from the corresponding 2-norbornanols by pub-

Table II
Comparison of Molar Absorptivity of Spent Reaction Mixture (10 Half-Lives) with Total Molar Absorptivity of Authentic Samples of Acetolysis Products[a]

λ, nm	$10^{-3}\epsilon_{Ph_1}$ or $10^{-3}\epsilon_{Ph_2}$	$10^{-3}\epsilon_{nos}$	$10^{-3}\epsilon_{tot}$	$10^{-3}\epsilon_{inf}$
		Compound 1		
281	3.62 ± 0.12	5.2 ± 0.2	8.8 ± 0.2	9.1 ± 0.4
283	2.80 ± 0.08	4.6 ± 0.2	7.4 ± 0.2	7.5 ± 0.2
285	2.10 ± 0.06	4.1 ± 0.2	6.2 ± 0.2	6.3 ± 0.2
288	1.49 ± 0.04	3.4 ± 0.2	4.9 ± 0.2	5.0 ± 0.2
		Compound 2		
283	1.57 ± 0.04	4.6 ± 0.2	6.2 ± 0.2	6.5 ± 0.4
285	1.42 ± 0.03	4.1 ± 0.2	5.5 ± 0.2	5.6 ± 0.3
288	0.78 ± 0.02	3.4 ± 0.2	4.2 ± 0.2	4.6 ± 0.2
293	0.34 ± 0.01	2.5 ± 0.1	2.8 ± 0.1	3.2 ± 0.2

[a] Error limits are standard deviations of mean values. The compound for measurement of ϵ_{Ph1} had to be freshly purified.

lished procedures,[77-79] for use as authentic samples of the acetolysis products of **1** and **2**, respectively.

Kinetics. Anhydrous acetic acid was prepared by allowing glacial acetic acid to reflux with 5% added acetic anhydride and a trace of sodium acetate for at least 24 hr, followed by fractional distillation in a dry atmosphere. A solution containing 0.03 *M* sodium acetate was prepared by careful addition of anhydrous acetic acid to a solution of anhydrous sodium carbonate in acetic anhydride, such that ~0.5% acetic anhydride remained after the water of neutralization was removed.

Solutions for kinetics were prepared by weighing 4–6 mg of **1** or 2–4 mg of **2** into a 100-ml volumetric flask, diluting to the mark with anhydrous acetic acid containing 0.03 *M* sodium acetate, and transferring ~5-ml aliquots to Pyrex ampoules which were chilled and sealed. The ampoules were allowed to equilibrate in a constant temperature bath at 60.40 ± 0.04° for at least 20 min before the first kinetic point was taken; the infinity point was taken after 10 half-lives. Ampules were quenched in Dry Ice–acetone. Before ultraviolet measurements, the ampoules were allowed to warm to room temperature, the contents were transferred to a quartz cell, and the absorbance was read at 281 nm for **1** and 293 nm for **2** with a Cary Model 16 spectrophotometer. Rate constants were calculated by fitting the absorbance data to the first-order rate equation by means of a nonlinear least-squares computer program.

Acetolysis Products. A solution of 155 mg (4.2 mmol) of **1** and 50.4 mg (6.2 mmol) of anhydrous sodium acetate in 50 ml of anhydrous acetic acid was heated in a sealed glass tube at 60.4° for 15.5 hr (~15 half-lives). The solution was cooled, poured into 100 ml of ice–water, and exhaustively extracted with purified ether. The combined ether extracts were successively washed with water, 5% aqueous Na_2CO_3, water, and saturated NaCl solution and dried over anhydrous Na_2SO_4. Evaporation of the ether left 67.1 mg (95%) of a viscous light yellow oil with a very strong camphorlike odor (like that of authentic 2-phenyl-2-norbornene). This crude oil had the same NMR pattern as the authentic sample, except for a small amount of impurity, probably ether solvent. Integration of the vinyl and other protons demonstrated that little acetate product could be present. The infrared spectrum of the crude oil was essentially identical with that of the authentic sample. GLC on a 6.2 m × 0.94 cm column, packed with 20% SE-30 on 60–80 mesh Chromosorb W at 180°, helium flow rate 85 ml/min, showed only one peak, retention time 22.3 min, identical with that of the authentic sample.

A solution of 248 mg (5.5 mmol) of **2** and 69.3 mg (8.4 mmol) of anhydrous sodium acetate in 50 ml of anhydrous acetic acid was heated in a sealed glass tube at 60.4° for 23 hr (~11 half-lives), and the product was worked up as described above for **1**. Evaporation of the ether left 130 mg (95%) of a crude yellow solid which had the same NMR pattern as the authentic sample of 1,2-diphenyl-2-norbornene, except for impurity, probably ether. Integration of the vinyl and other protons demonstrated again that little acetate product could be present. The infrared spectrum of the crude solid was essentially identical with that of the authentic sample. The crude product was recrystallized once from pentane, giving colorless needles, mp 103–104°, undepressed by admixture with authentic sample (mp 103–104°).

Ultraviolet Absorbance Studies. Absorbance measurements were made on reaction mixtures after 10 half-lives, at four different wavelengths. The molar absorptivities, ϵ_{inf}, were compared with the sum of molar absorptivities, ϵ_{tot}, of authentic product 2-phenyl-2-norbornene, ϵ_{Ph_1}, or 1,2-diphenyl-2-norbornene, ϵ_{Ph_2}, respectively, and authentic nosylate ion, ϵ_{nos}, as shown in Table II. The agreement is considered to be adequate to demonstrate that the reactions proceed to give the products previously isolated, and that the ultraviolet method of following the kinetics provides a real measure of the progress of the reactions.[80]

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Registry No.—**1**, 49698-52-4; **2**, 49698-53-5; 3-phenyl-Δ^3-cyclopentenecarboxylic acid, 54143-11-2; methylphenylvinylcarbinol, 6051-52-1; aniline hydrobromide, 542-11-0; 2-phenyl-1,3-butadiene, 2288-18-8; ethyl diazoacetate, 623-73-4; 1-(1-phenylvinyl)-2-carboethoxycyclopropane, 54143-12-3; 2-(3-phenyl-Δ^3-cyclopentenyl)acetic acid, 54143-13-4; (3-phenyl-Δ^3-cyclopentenyl)methanol, 54143-14-5; (3-phenyl-Δ^3-cyclopentenyl)methyl tosylate, 54143-15-6; 2-(3-phenyl-Δ^3-cyclopentenyl)ethanol, 54143-16-7; *p*-nitrobenzenesulfonyl chloride, 98-74-8; 3,4-diphenyl-Δ^3-cyclopentenone, 7402-06-4; 4-hydroxy-3,4-diphenyl-Δ^2-cyclopentenone, 5587-78-0; 3,4-diphenyl-Δ^3-cyclopentenylacetic acid, 54143-17-8; 3,4-diphenyl-Δ^3-cyclopentenol, 4997-50-6; 3,4-diphenyl-Δ^3-cyclopentenyl tosylate, 35115-43-6; 2-(3,4-diphenyl-Δ^3-cyclopentenyl)ethanol, 54143-18-9.

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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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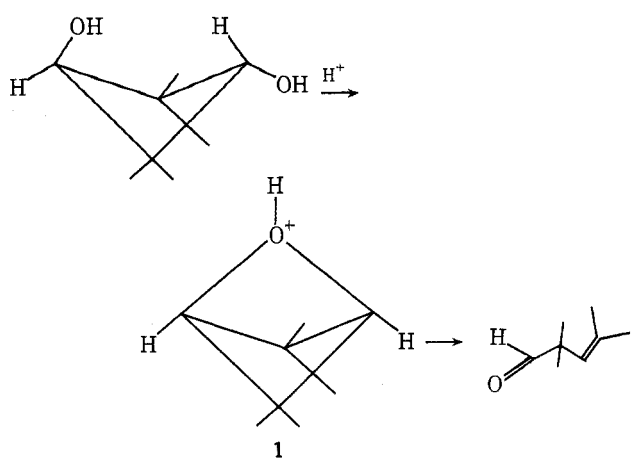
The syntheses and acetolyses of 3,3-diphenyl- and 3,3-dimethylcyclobutyl tosylates have been carried out. The diphenyl compound was prepared from the corresponding cyclobutanone which, in turn, was obtained in the reaction of diphenylketene with diazomethane. The dimethyl compound was prepared by a multistage 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



1

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.