Thermal and Solvolytic Studies with the 2-Phenylbicyclo[1.1.1]pentan-2-ol System[1]

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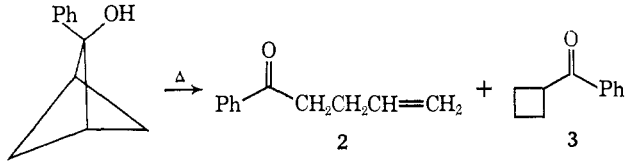
Abstract: Phenylbicyclo[1.1.1]pentan-2-ol (**1**) was found to rearrange thermally to 1-phenyl-4-penten-1-one and cyclobutyl phenyl ketone. Kinetic data and deuterium labeling studies showed that the rearrangement proceeded predominantly *via* a 1,5-H transfer from the diradical obtained from cleavage of the bridgehead carbon–carbon bond. In basic media the bicyclopentanol isomerized to cyclobutyl phenyl ketone. Deuterium labeling experiments indicated that an intramolecular 1,3-proton transfer successfully competes with protonation of the initially formed carbanion. The bicyclopentanol (**1**) was found to be extremely unstable to acidic conditions and rearranged to 3-phenyl-3-cyclopenten-1-ol. The rearrangement was rationalized as proceeding *via* a bicyclo[2.1.0]-pentyl cation intermediate. Kinetic evidence obtained from the solvolysis of the *p*-nitrobenzoate ester of **1** suggests that the ionization proceeds with participation of the one-carbon bridge adjacent to the departing *p*-nitrobenzoate group.

The very high degree of bond angle distortion in small-ring bicyclic systems has made this class of compounds particularly suitable for the study and testing of theories concerned with molecular structure, bonding, and reactivity.[3] The distorted geometry of bicyclo[1.1.1]pentane suggests that it and its substituted derivatives may show the effects of bond angle deformation in the form of unusual chemical behavior. The previously reported syntheses of this system are tedious and are not amenable to the preparation of sufficient quantities of functionalized material for extensive studies.[4-7] We previously reported on a simple photochemical synthesis of 2-phenylbicyclo-[1.1.1]pentan-2-ol[8] and made mention of some of its chemistry.[9] This paper amplifies the earlier report, presents the results of our thermal, base, and solvolytic investigations, and discusses the mechanistic implications.

A study of the thermal reaction of **1** is of interest since the results are expected to provide insight into the reactivity of this ring system. Thermal decomposition of 2-phenylbicyclo[1.1.1]pentan-2-ol (**1**) was carried out at 135° in evacuated Pyrex tubes which had been sealed under nitrogen. Under these conditions



1 2 3

1-phenyl-4-penten-1-one (**2**) (65%) and cyclobutyl phenyl ketone (**3**) (35%) were the only products. The products were isolated by vapor phase chromatography and their structures established by comparison with authentic samples. The product ratios were found to be independent of pressure over the range 10–100 mm. The reaction followed good first-order kinetics, and rate constants were determined from three runs each at three different temperatures. Kinetic data on the pyrolysis of **1** are given in Table I. An Arrhenius plot

Table I. Kinetics of Thermal Decomposition of 2-Phenylbicyclo[1.1.1]pentan-2-ol (**1**)

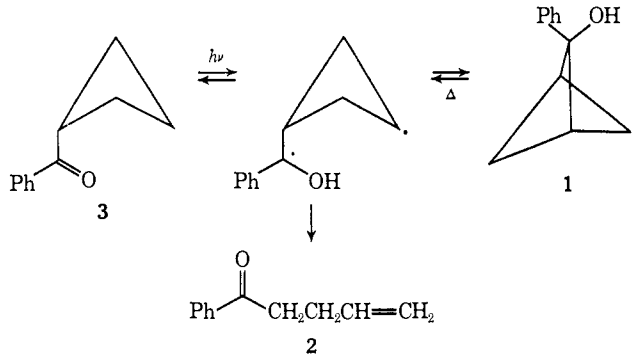
Temp, °C	k, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
135	3.3×10^{-6}		
182	5.4×10^{-4}	36.6	+2.43
208	3.0×10^{-3}		

gives $E_a = 37.6 \pm 0.5$ kcal/mol and $\log A = 13.36$ at 182°, from which values of $\Delta H^{\ddagger} = 36.6$ kcal/mol and $\Delta S^{\ddagger} = +2.43$ eu can be calculated. Extrapolation of the data to 305° indicates that **1** rearranged 4.8×10^3 times more rapidly than the parent bicyclo[1.1.1]-pentane[5] and 19×10^3 times more rapidly than 1,3-dimethylbicyclo[1.1.1]pentane.[10]

The thermal cleavage of both cyclopropane and cyclobutane, as well as many other molecules which incorporate either of these ring systems, has been explained in terms of a diradical intermediate.[11] The initial step in the thermolysis of **1** is most reasonably formulated as involving rupture of the bridgehead carbon–carbon bond and formation of a 1,4-diradical intermediate. The thermal lability of **1** as compared to the parent system can be attributed to the stabilizing effects of both the hydroxyl and phenyl substituents on the incipient diradical. The formation of a mixture of **2** and **3** implies that the thermally generated diradical behaves in a fashion analogous to that observed in the

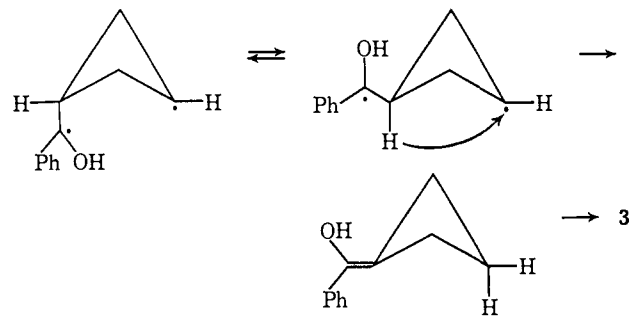
(1) This work was presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.
(2) Fellow of the Alfred P. Sloan Foundation, 1968–1970.
(3) J. Meinwald and Y. C. Meinwald, *Advan. Alicyclic Chem.*, **1**, 1 (1966).
(4) K. B. Wiberg and D. S. Connor, *Tetrahedron Lett.*, 531 (1964); *J. Amer. Chem. Soc.*, **88**, 4437 (1966).
(5) K. B. Wiberg and V. Z. Williams, *J. Org. Chem.*, **35**, 369 (1970).
(6) R. Srinivason and K. H. Carlough, *J. Amer. Chem. Soc.*, **89**, 4932 (1967).
(7) J. Meinwald, W. Szkrybalo, and D. R. Dimmel, *Tetrahedron Lett.*, 731 (1967).
(8) A. Padwa and E. Alexander, *J. Amer. Chem. Soc.*, **89**, 6376 (1967).
(9) A. Padwa and E. Alexander, *ibid.*, **90**, 6871 (1968).
(10) R. Srinivason, *ibid.*, **90**, 2752 (1968).
(11) S. W. Benson, *J. Chem. Phys.*, **34**, 521 (1961).

Norrish type II elimination of cyclobutyl phenyl ketone. While the formation of **2** can be accounted for by ring opening of the diradical, the mechanistic origin of



cyclobutyl phenyl ketone is less clear. One possible path may involve ring inversion of the initially produced diradical followed by a 1,3-H shift (path A). The

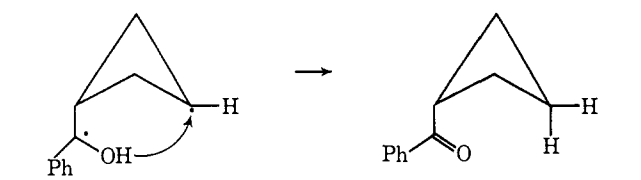
Path A



cyclobutyl ring is quite flexible and exhibits a dynamic ring bending equilibrium which has been termed "pseudorotation" and allows for conformational equilibration of monosubstituted cyclobutanes.[12] A similar ring inversion might be anticipated for the diradical obtained by thermal ring opening of **1**. There are a number of reports in the literature that provide reasonable precedent for this scheme.[13] Jorgenson has proposed that a 1.3,-hydrogen shift of a diradical is an important path in the thermal decomposition of a substituted bicyclo[2.1.0]pentane.[14]

An alternate route that could also account for the formation of **3** would involve a 1,5-hydrogen transfer (path B). Analogies for this route are also available in

Path B



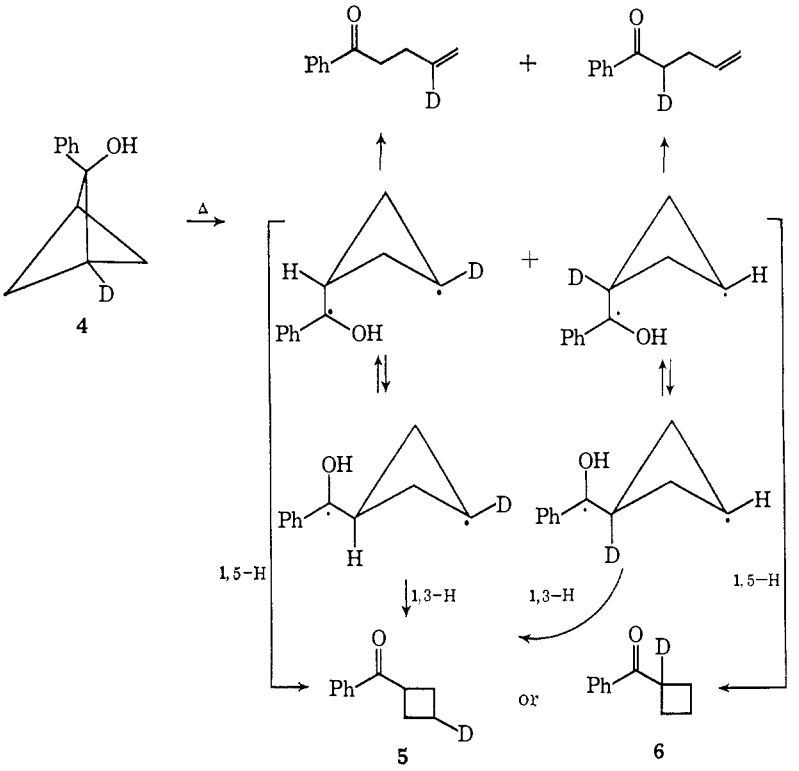
the literature. Wagner has suggested that the triplet state of ketones containing γ-hydrogens will give a biradical intermediate which may revert to the starting ketone or proceed to give product.[15] The lines of evidence implicating the reverse 1,5-hydrogen transfer step in the photochemistry of ketones containing γ-hydrogens are based on kinetic data[16–18] and are reinforced by stereochemical[19–21] and deuterium isotope effects.[22,23]

Evidence concerning the mechanism of cyclobutyl phenyl ketone formation from the thermolysis of **1** was obtained from the thermal rearrangement of 2-phenylbicyclo[1.1.1]pentan-2-ol-d_1 (**4**). The synthesis of this compound, containing 98% deuterium at the bridgehead carbon as determined by nmr and mass spectroscopy, was carried out by irradiating cyclobutyl phenyl ketone-1-d_1 (**6**).[24] If we neglect for the moment the isotope effect on the cleavage of the bridgehead carbon–carbon bond, then formation of cyclobutyl phenyl ketone *via* the 1,3-H transfer route should only lead to cyclobutyl phenyl ketone-3-d_1 (**5**), while a 1,5-H transfer sequence would be expected to give equivalent amounts of **5** and cyclobutyl phenyl ketone-1-d_1 (**6**) (Scheme I). The products obtained from the thermolysis of **4** were isolated by vpc and were analyzed for their total deuterium content by mass spectroscopy. The fraction of the deuterium atoms attached to the carbon adjacent to the carbonyl was then determined by washing out these atoms with sodium methoxide and methanol, rechromatographing by vpc, and analyzing the resultant products for the remaining deuterium. Analysis of the cyclobutyl phenyl ketone obtained from the thermolysis of **4** indicated that it contained only 50% of the deuterium, thus providing support for the 1,5-H transfer mechanism. The unsaturated ketone (**2**), isolated from the thermolysis of **4**, retained only 50% of the deuterium after the exchange. Its nmr spectrum showed that the remaining deuterium was located exclusively on the 4-carbon atom. These observations are consistent with ring opening of the diradical as shown in Scheme I.

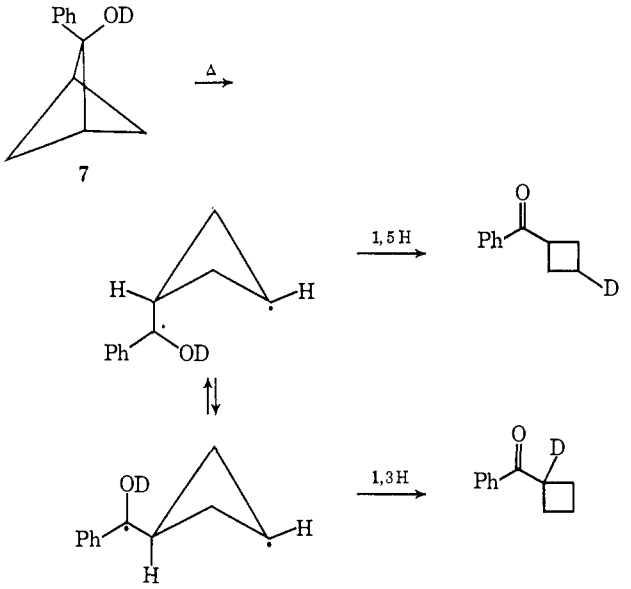
Surprisingly, the route to give cyclobutyl phenyl ketone on pyrolysis of deuterated alcohol **7** did not proceed exclusively by means of a 1,5-H transfer. This conclusion derives from examination of the distribution of deuterium in the product after proton exchange. For this case, 60% of the cyclobutyl phenyl ketone contained deuterium and the remaining 40% was devoid of deuterium. Control experiments demonstrated that no exchange of starting alcohol occurred under the reaction conditions employed. Since only 60% of the deuterium appeared on the cyclobutyl ring, the 1,3-H transfer route must have occurred. An attractive explanation to account for the difference noted between the two systems might be based on the existence of a deuterium isotope effect. Substitution of deuterium for hydrogen on the alcohol portion of the molecule may sufficiently retard the 1,5-H transfer to allow for competitive ring inversion

(12) J. E. Kilpatrick, K. S. Pitzer, and R. Spitzer, *J. Amer. Chem. Soc.*, **69**, 2483 (1947).
(13) R. Kh. Freidlina, *Advan. Free Radical Chem.*, **1**, 211 (1965).
(14) M. J. Jorgenson and T. J. Clark, *J. Amer. Chem. Soc.*, **90**, 2189 (1968).
(15) P. J. Wagner, *ibid.*, **89**, 5898 (1967).
(16) P. J. Wagner, *Tetrahedron Lett.*, 1753 (1967).
(17) J. A. Barltrop and J. D. Coyle, *ibid.*, 3235 (1968).
(18) N. C. Yang, S. P. Elliott, and B. Kim, *J. Amer. Chem. Soc.*, **91**, 7551 (1969).
(19) K. H. Schulte-Elte and G. Ohloff, *Tetrahedron Lett.*, 1143 (1964).
(20) J. Orban, K. Schaffner, and O. Jeger, *J. Amer. Chem. Soc.*, **85**, 3033 (1963).
(21) N. C. Yang and S. P. Elliott, *ibid.*, **91**, 7550 (1969).
(22) R. D. Coulson and N. C. Yang, *ibid.*, **88**, 4511 (1966).
(23) A. Padwa and W. Bergmark, *Tetrahedron Lett.*, 5795 (1968).
(24) A. Padwa, E. Shefter, and E. Alexander, *J. Amer. Chem. Soc.*, **90**, 3717 (1968).

Scheme I

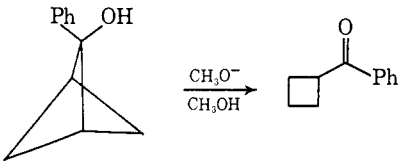


and the occurrence of a 1,3-H shift. It is noteworthy that the rate of rearrangement of **7** is essentially the same as **1** and **4** but the product composition has been slightly altered (80% **2**, 20% **3**). This observation is fully compatible with the dual mechanistic sequence proposed. Alternatively, the difference noted between



the two systems may be attributed to a significant secondary α-deuterium isotope effect in the rupture of the bridgehead carbon–carbon bond of **4**. If we assume an isotope effect of about 1.5, then approximately 20% of the diradical produced from thermolysis of **4** must undergo 1,3-hydrogen transfer. The exact amount of 1,3-hydrogen transfer will be related to the magnitude of the secondary deuterium isotope effect involved in the bond rupture step.

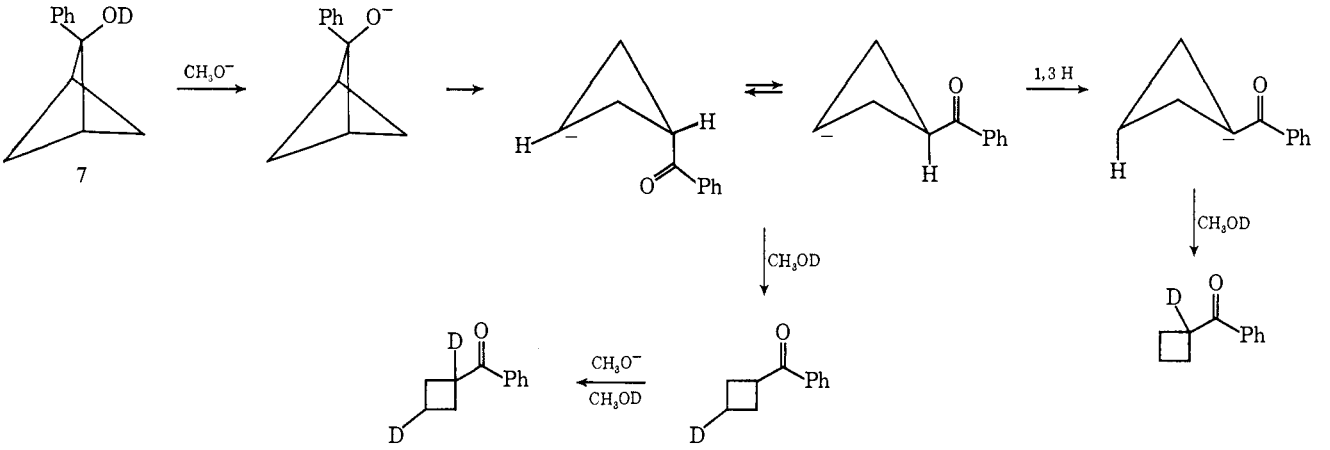
Bicyclopentanol **1** was also noted to be extremely sensitive to basic conditions. When **1** was dissolved in a 0.1% sodium methoxide–methanol solution a mild exotherm resulted with the immediate formation of cyclobutyl phenyl ketone in 95% yield. The reaction appears to be analogous to the base-catalyzed ring opening of cyclopropanols.[25] Several attempts were



made to trap the initially formed alkoxide. A number of organosodium and lithium bases were added to a solution of **1** in hexane at −78°. Methyl iodide (or dimethyl sulfate) was then added and the solution was allowed to stir at −78° for 1 hr and then slowly brought to room temperature. Under these conditions the only product formed was cyclobutyl phenyl ketone. The fact that carbon alkylation did not occur is consistent with the work of Wash[26] who found that the alkylation of enolate anions of benzoyl ketones does not proceed readily at room temperature. These observations suggest that the base induced cleavage of the bicyclopentanol system is much faster than the rate of O-alkylation. When the reaction was quenched with dilute acid, no starting material could be recovered. This result also points to the extremely fast rate of isomerization of **1** in basic media. The driving force for the reaction is probably related to the relief of strain in the transition state for ring opening.

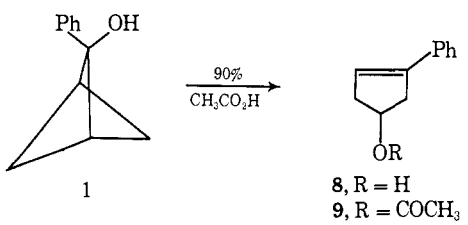
Two different mechanistic pathways can be proposed for the base-catalyzed isomerization. One path would

(25) C. H. DePuy, *Accounts Chem. Res.*, **1**, 33 (1968).
(26) G. Wash, B. Shiver, and H. L. Lochte, *J. Amer. Chem. Soc.*, **63**, 2975 (1941).

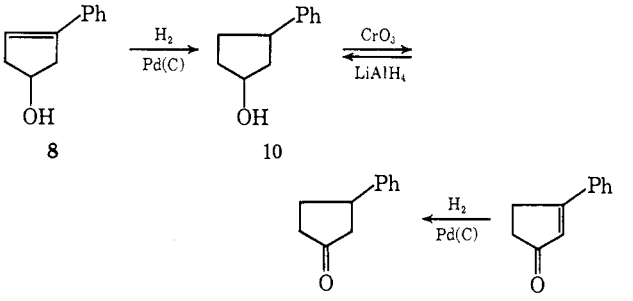


involve inversion of the initially formed cyclobutyl carbanion followed by a 1,3-proton shift and subsequent protonation. The second possibility would simply involve protonation of the initially formed carbanion. Evidence for the correct mechanistic sequence was obtained by treating deuterated bicyclopentanol **7** with sodium methoxide in methanol-d_1. Formation of **3** *via* the 1,3-proton transfer path would be expected to give **3** with the deuterium located only on the C_1 position. The alternate path would lead to **3** with deuterium on both the C_1 and C_3 positions. Control experiments demonstrated that only the α protons exchanged under the conditions employed. The cyclobutyl phenyl ketone isolated from the above reaction was analyzed by nmr and mass spectroscopy for its total deuterium content. The fraction of deuterium adjacent to the carbonyl group was then determined by washing out the deuterium with methanol and reanalyzing the resultant ketone for its remaining deuterium content. Analysis of the ketone indicated that the reaction proceeds by a combination of both paths. This conclusion follows from examination of the distribution of deuterium before and after the methanol wash. Prior to the wash, 54% of the ketone was found to be dideuterated and 46% monodeuterated. After proton exchange with methanol, 54% of the ketone retained its deuterium content. These results indicate that 46% of **3** is formed *via* the 1,3-proton transfer route which successfully competes with protonation of the ring carbanion. Undoubtedly the stability of the enolate anion provides the driving force for the 1,3-proton transfer.

The bicyclopentanol **1** was also found to be extremely unstable to acidic conditions. Treatment of **1** with 90% acetic acid afforded a mixture of 3-phenyl-3-cyclopenten-1-ol (**8**, 40%) and 3-phenyl-3-cyclopentenyl 1-acetate (**9**, 60%). The structure of alcohol **8**,



mp 79–81°, is inferred from its composition, spectral data, and chemical behavior. The infrared spectrum of **8** was characterized by bands at 2.82, 3.50, 8.70, and 9.60 μ. The ultraviolet spectrum in 95% ethanol has a maximum at 255 mμ (ϵ 11,700). The nmr spectrum in deuteriochloroform showed a multiplet at τ 2.75 (5 H), a triplet at 3.98 (J = 2.3 cps, 1 H), multiplets at 5.45 (1 H) and 7.39 (4 H), and a singlet at 7.40 (1 exchangeable proton). The mass spectrum exhibited peaks at m/e 160, 142 (base), 131, 115, and 91. Chemical confirmation was obtained by catalytic reduction of **8** to 3-phenylcyclopentanol (**10**) followed by oxidation of **10** to 3-phenylcyclopentanone (**11**). Structure **11** was then compared to an authentic sample prepared from the catalytic reduction of 3-phenyl-2-cyclopentan-1-one (**12**).[27] Although the above spectral

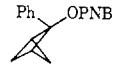
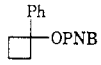
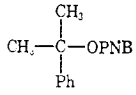
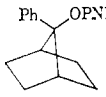


and chemical data are consistent with that of unsaturated alcohol **8**, it does not necessarily preclude 3-phenyl-2-cyclopenten-1-ol (**13**) as an alternate structure. Alcohol **13** was therefore synthesized by the method of Treibs and Weissenfels[28] and shown to be substantially different from the alcohol isolated from **1**. The structure of acetate **9** was established by the reaction of **8** with acetic anhydride. The bicyclopentanol system was also found to smoothly rearrange to 3-phenyl-3-chlorocyclopentene when treated with zinc or aluminum chloride.

The above results point to the exceptional reactivity of the bicyclo[1.1.1]-2-pentyl cation and the high propensity for it to undergo bond reorganization. The products formed can best be rationalized in terms of a bicyclo[2.1.0]-2-pentyl cation intermediate (**14**) which undergoes subsequent reorganization to the 3-cyclopentenyl cation system. Precedence for this type of isomerization is found in the work of Wiberg who showed that bicyclo[2.1.0]-2-pentyl derivatives readily solvolyze to 3-cyclopenten-1-ol *via* a cyclopentenyl cation.[29]

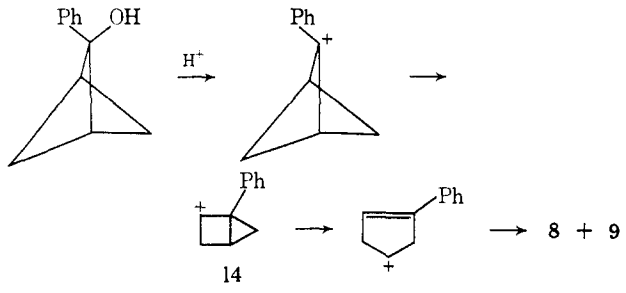
(27) H. O. House and R. L. Wasson, *J. Amer. Chem. Soc.*, **79**, 1490 (1957).
(28) W. Treibs and Weissenfels, *Chem. Ber.*, **93**, 1374 (1960).
(29) K. B. Wiberg, V. Z. Williams, and L. E. Friedrich, *J. Amer. Chem. Soc.*, **90**, 5338 (1968).

Table II. Rates of Solvolysis of Tertiary Benzylic *p*-Nitrobenzoates in 60:40 Acetone–Water

Compd	No.	Temp, °C	Rate, sec^{-1}	k_{rel} at 25°	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
	**15**	50.0 ± 0.01	(3.97 ± 0.03) × 10^{-5}	36,400	18.7	−8.28
		75.0 ± 0.01	(3.72 ± 0.03) × 10^{-4}			
		96.0 ± 0.01	(1.72 ± 0.01) × 10^{-3}			
		25[a]	3.72 × 10^{-6}			
	**17**	75.0 ± 0.01	(2.50 ± 0.02) × 10^{-5}	2,140	20.1	−8.46
		101.0 ± 0.01	(2.77 ± 0.02) × 10^{-4}			
		128.0 ± 0.02	(1.35 ± 0.02) × 10^{-3}			
		25[a]	2.19 × 10^{-7}			
	**18**	52.0 ± 0.01	(2.55 ± 0.03) × 10^{-5}	24,600	18.9	−8.08
		76.0 ± 0.01	(3.16 ± 0.03) × 10^{-4}			
		100.0 ± 0.01	(1.35 ± 0.02) × 10^{-3}			
		25[a]	2.51 × 10^{-6}			
	**19**	25[a,b]	1.02 × 10^{-10}	1	26.9	−13.9

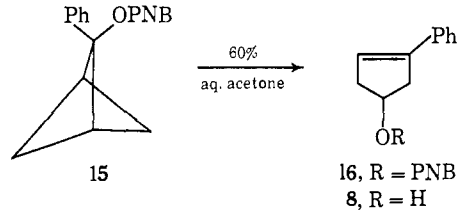
[a] Rates at 25° are extrapolated from higher temperatures. [b] The solvolysis of 7-phenyl-7-norbornyl *p*-nitrobenzoate (**19**) was studied in 70% aqueous dioxane.[34] The *Y* values of 60% acetone and 70% dioxane are similar and consequently there should be small differences (±10%) in rate between the two solvents.

The generation of carbonium ions in strained ring systems has produced a host of highly interesting and important results of practical and theoretical interest.[30,31] While the solvolytic reactivity of the bicyclo[2.1.1]hexane system has received considerable attention,[32] the homologous bicyclo[1.1.1]pentane system



has remained virtually unexplored.[33] A study of the reaction rate and products of solvolysis of the *p*-nitrobenzoate ester of bicyclo[1.1.1]pentan-2-ol would be of considerable interest since it should provide additional information on what effects ring size and strain have on the course of cyclobutyl carbonium ion type rearrangements. In this connection, we have studied the solvolytic reactivity of 2-phenylbicyclo[1.1.1]pentan-2-ol *p*-nitrobenzoate (**15**). The ester **15** was prepared in the standard manner without difficulty and was allowed to solvolyze in 60% aqueous acetone. The course of the reaction was followed titrametrically using the standard ampoule technique for rate determinations. The solvolysis proceeded *via* rearrangement to the 3-cyclopenten-1-ol system giving 6% internal return to **16** and 92% 3-phenyl-3-cyclopenten-1-ol (**8**). The rate data are listed in Table II together with the rates of solvolysis and associated thermodynamic parameters of the *p*-nitrobenzoates of 1-phenylcyclobutanol (**17**), dimethylphenylcarbinol (**18**), and 7-phenyl-7-norbornanol (**19**) for comparison purposes.[34]

The rates of solvolysis of **15**, **17**, and **18** were not very different, the fastest (**15**) being only 17 times more



rapid than the slowest (**17**). The surprising feature of the rate comparison was that **15** was *ca.* 36,000 times faster than **19**. The reactivity of **15** is very much greater than that anticipated simply on the basis of geometrical considerations. Schleyer[35] and Foote[36] have pointed out that the internal C–C–C angle at the carbon atom from which the anion departs plays a predominant role in determining the rate of ionization. This correlation between angle strain and expected reaction rate satisfactorily accounts for the differences in the rates of solvolysis of **17**, **18**, and **19**. The bridgehead angle (C_1–C_7–C_4) in bicyclo[2.2.1]heptane has been reported to have a value of 96°.[37] The angle about the methylene carbons of bicyclo[1.1.1]pentane is considerably smaller, having a mean value of 75°.[24] Since the transition state for solvolysis involves partial sp^2 hybridization, one would expect that **19**, with the larger bridgehead angle, would solvolyze at a faster rate than **15**. The fact that **15** undergoes solvolysis some 36,000 times faster than **19** strongly suggests that **15** ionizes with participation of the one-carbon bridge adjacent to the departing *p*-nitrobenzoate group.

There have been numerous reports in the literature which suggest a dimunition in driving force for the

(30) J. A. Berson in "Molecular Rearrangements," Vol. I, P de Mayo, Ed., Interscience, New York, N. Y., 1963.
(31) R. C. Fort and P. v. R. Schleyer, *Advan. Alicyclic Chem.*, **1**, 283 (1966).
(32) J. Meinwald and P. G. Gassman, *J. Amer. Chem. Soc.*, **85**, 57 (1963); J. Meinwald, P. G. Gassman, and J. J. Hurst, *ibid.*, **84**, 3722 (1962).
(33) See however, K. B. Wiberg and V. Z. Williams, *ibid.*, **89**, 3372 (1967); K. B. Wiberg, R. A. Fenoglio, V. Z. Williams, and R. Ubersax, *ibid.*, **92**, 568 (1970).
(34) P. G. Gassman and A. F. Fentiman, *ibid.*, **91**, 1545 (1969); **92**, 2549, 2551 (1970).
(35) P. v. R. Schleyer, *ibid.*, **86**, 1854 (1964).
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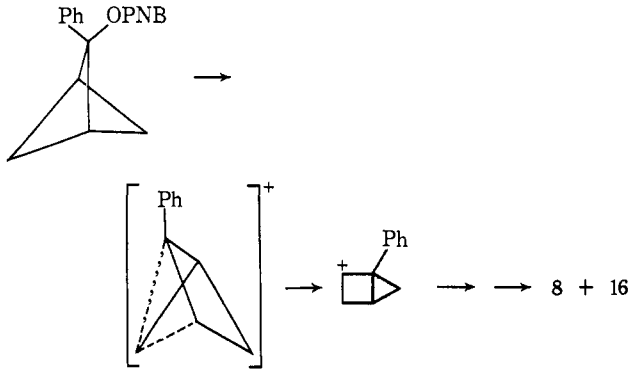
(37) A. C. MacDonald and J. Trother, *Acta Crystallogr.*, **19**, 456 (1965).



formation of bridged intermediates when competing modes of charge stabilization exist.[38,39] For example, Roberts has shown that replacement of the α-hydrogen by a methyl group in cyclobutyl derivatives reduces the bicyclobutonium ion character in the solvolyses of these derivatives.[40] Gassman and coworkers recently demonstrated that the 10^{11} acceleration arising from participation of the double bond in the solvolysis of *anti*-7-dehydronorbornyl derivatives[41] essentially vanishes in the corresponding 7-*p*-anisyl derivatives.[42] They also showed that neighboring group participation is a linear function of the electron demand of the incipient carbonium ion.[34] Their studies established that an unsubstituted phenyl group leveled neighboring group participation by a factor of 10^9. From the results outlined above it appears that the phenylbicyclo[1.1.1]pentyl system is another case where stabilization of the incipient carbonium ion by a phenyl group is not efficient enough to overcome neighboring group participation.

Wiberg and coworkers have recently studied the solvolysis of the 3,5-dinitrobenzoate of bicyclo[1.1.1]pentan-2-ol (**20**).[33] Comparison of the relative rates of the unsubstituted cyclobutyl and the bicyclo[1.1.1]pentyl systems shows that the methylene bridge brings about a 60-fold rate acceleration.[43] When the phenyl substituted systems are compared, the rate factor is 17. This appears to be consistent with the arguments outlined above.

Experimental Section[44]

Thermolysis of 2-Phenylbicyclo[1.1.1]pentan-2-ol. Thermal reactions were carried out in 25-ml Pyrex tubes that had been thoroughly cleansed and dried in an oven. A Neslab Instruments constant temperature apparatus, accurate to ±0.01°, was used with GE-SF-1017 as the bath oil. In each run 0.02 g of bicyclopentanol[24] was added to a tube which was subsequently evacuated and sealed at 0.05 mm. Thermolysis mixtures were analyzed by vpc using nitrobenzene as an internal standard. In the kinetic experiments, two runs were taken for each time period and the results obtained were averaged. At the end of each time interval the tubes were quenched (−78°) and 6.8 mg of nitrobenzene in 1 ml of benzene was added to each tube. The sides of the tube were washed with 3 ml of benzene and the solvent then removed under reduced pressure until the residual volume amounted to *ca.* 0.1 ml. The mixture was then analyzed on a 5 ft × 0.25 in. 10% Degs on 60–80 mesh Chromosorb W column at an oven temperature of 120° and at a helium flow rate of 60 ml/min. The areas under the peaks due to the standard (nitrobenzene) and products were measured using a planimeter. Each set of chromatograms was measured twice in this way and the results were converted to per cent reaction based on starting alcohol. The results are summarized in Table I.

Thermolysis of Deuterated Bicyclopentanols 4 and 7. In a typical case, 0.080 g of bicyclopentanol was placed in a sealed evacuated tube and heated to the appropriate temperature. After thermolysis, the crude reaction mixture was dissolved in 10 ml of methylene chloride. A 5.0-ml aliquot of the above solution was taken, the solvent evaporated, and the remaining oil analyzed by vapor phase chromatography. The solvent was removed from the remaining 5-ml sample, which was then allowed to reflux for 3 days in a 5% sodium methoxide–methanol solution. The methanol was removed under reduced pressure and the resulting oil washed with 20 ml of water and then extracted with methylene chloride. Evaporation of the methylene chloride afforded an oil which was subjected to preparative vpc. The products isolated were analyzed for their total deuterium content by nmr and mass spectroscopy. In the case of deuterated alcohol **4**, the products obtained retained 50% of their deuterium content after refluxing in the protic medium. For the other deuterated alcohol **7**, 40% of the cyclobutyl phenyl ketone isolated was devoid of deuterium and 60% contained deuterium on the three-carbon atom of the ring. Control experiments using a sodium methoxide–methanol-*d* solvent system indicated that the only acidic α proton was exchanged under these conditions.

The peak occurring at (*m/e*) 55, which corresponds to the cyclobutyl fragment, was used in determining the deuterium content of the cyclobutyl phenyl ketone. No fragment ions were seen at (*m/e*) 56 or 57 for nondeuterated ketone, whereas the monodeuterated ketone possesses a peak at (*m/e*) 56. Dideuterated cyclobutyl phenyl ketone possesses a peak at (*m/e*) 57. In order to test the accuracy of the mass spectral analysis, standard mixtures containing 1:1 and 2:1 ratios of nondeuterated and monodeuterated ketones were subjected to mass spectral analysis. The results obtained indicated that the percentages of the nondeuterated to monodeuterated ketones were experimentally the same as the actual percentages used.

Deuterated bicyclopentanol **7** was prepared by allowing 0.150 g of **1** to stir in a 30% D_2O–dioxane mixture for 2 days. The solvent was removed under reduced pressure leaving behind a crystalline material. Nmr and infrared analysis of this component showed that greater than 95% exchange had taken place.

Treatment of Deuterated Bicyclopentanol 7 with Sodium Methoxide in Methanol-d_1. A 0.070-g sample of bicyclopentanol **7** was dissolved in 10 ml of methanol-d_1. To the above solution was added 5 ml of a 0.1% sodium methoxide–methanol-d_1 solution. The mixture was allowed to stir for 3 hr. The solvent was subsequently removed under reduced pressure and the residual oil obtained was dissolved in 10 ml of methylene chloride. A 5-ml aliquot of the above solution was removed, the solvent was evaporated, and the oil remaining was subjected to preparative vpc. Nmr and mass spectral analysis of the products showed that 54% of the cyclobutyl phenyl ketone isolated was dideuterated and 46% was monodeuterated. The remaining 5 ml of the methylene chloride solution was concentrated and the residual oil was taken up in 10 ml of methanol and then treated with 5 ml of a 5% sodium methoxide–methanol solution. The resulting solution was allowed to reflux for 3 days. Analysis of the system showed that 54% of the cyclobutyl phenyl ketone retained deuterium.

Treatment of Bicyclopentanol 1 with Organosodium and Lithium Bases. The bases used were amylsodium, *n*-butyllithium, and phenyllithium. In a typical case, 0.050 g (0.31 mmol) of bicyclopentanol **1** was dissolved in 10 ml of hexane and the resulting solution was allowed to stir under nitrogen for 10 min at −78°. An

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(40) E. F. Fox, M. C. Caserio, M. S. Silver, and J. D. Roberts, *ibid.*, **83**, 2719 (1961).
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(42) P. G. Gassman, J. Zeller, and J. T. Lumb, *Chem. Commun.*, 69 (1968).
(43) The rate difference was obtained by extrapolation of Wiberg's data[33] for 20–25° and by assuming an approximate factor of 3×10^7 for the difference in rate between a tosylate in acetic acid and a dinitrobenzoate in 60% acetone. This factor was determined by comparing the rate of solvolysis of *endo*-bicyclo[2.1.1]hexyl 5-tosylate in anhydrous acetic acid with the rate of solvolysis of the corresponding 3,5-dinitrobenzoate in 60% acetone.
(44) All melting points are corrected and boiling points uncorrected. Elemental analyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark, and Alfred Bernhardt Laboratories, Hohenweg, Germany. The infrared absorption spectra were determined on a Perkin-Elmer Infracord spectrophotometer, Model 137. The ultraviolet absorption spectra were measured with a Cary recording spectrophotometer, using 1-cm matched cells. The nuclear magnetic resonance spectra were determined at 60 MHz with the Varian Associate high-resolutions spectrometer. Tetramethylsilane was used as an internal standard.

equimolar amount of base was injected into the reaction mixture by means of a syringe and the solution was allowed to stir for an additional 30 min at −78°. At this point either 1 ml of methyl iodide or dimethyl sulfate was added. The reaction mixture was allowed to stir for an additional hour at −78° and then slowly brought to room temperature. The resulting solution was washed with water, extracted with methylene chloride, and dried over sodium sulfate. Removal of the solvent under reduced pressure, followed by infrared and vpc analysis, showed the presence of only cyclobutyl phenyl ketone. Similar results were obtained when sodium hydride was used as the base.

Treatment of Bicyclopentanol 1 with 90% Acetic Acid. A 0.2-g sample of 2-phenylbicyclo[1.1.1]pentan-2-ol was added to 5 ml of 90% acetic acid and the resulting solution was allowed to stir for 6 hr at room temperature. The acetic acid was removed at 20° under reduced pressure. Fractional crystallization of the residue with heptane as the solvent gave 0.083 g of 3-phenyl-3-cyclopenten-1-ol (**8**). Sublimation of the product at 75° (0.3 mm) afforded pale yellow crystals, mp 79–81°.

Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.65; H, 7.71.

The infrared spectrum (CCl_4) was characterized by bands at 2.82, 3.50, 6.70, 6.91, 8.70, and 9.60 μ. The ultraviolet spectrum showed a maximum at 255 mμ (ε 11,700). The nmr spectrum ($CDCl_3$) showed a multiplet τ 2.75 (5 H), a triplet at 3.98 (J = 2.3 Hz, 1 H), multiplets at 5.45 (1 H) and 7.39 (4 H), and a singlet at 7.40. The mass spectrum exhibited peaks with m/e 160 (M^+) base peak, 142, 131, 117, 115, and 91.

A second component was isolated from the mother liquors and amounted to 0.126 g. Sublimation of this material at 45° (0.3 mm) gave a white crystalline material, mp 42–44°, which was subsequently identified as 3-phenyl-3-cyclopentenyl 1-acetate (**9**).

Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.23; H, 6.93. Found: C, 76.93; H, 6.90.

The infrared spectrum (CCl_4) was characterized by bands at 5.75, 7.31, 8.03, 8.36, and 9.65 μ. The nmr spectrum ($CDCl_3$) showed a singlet at τ 2.80 (5 H), a triplet at 4.80 (J = 2.3 Hz, 1 H). and 7.25 (4 H), and a singlet at 8.12 (3 H). The mass spectrum exhibited peaks with (m/e) 202 (M^+), base peak 142, 143, 141, 115, and 43.

Preparation of 3-Phenyl-3-cyclopentenyl 1-Acetate from 8 and Acetic Anhydride. A 0.128-g sample of 3-phenyl-3-cyclopenten-1-ol **8** in 10 ml of benzene was added to 1.2 ml of anhydrous pyridine. The solution was stirred at room temperature while 0.480 g of acetic anhydride was slowly added. After refluxing for 1 hr, the solvent was removed under reduced pressure. The residual yellow oil was washed with heptane and then sublimed at 45° (0.3 mm) to give 0.85 g of 3-phenyl-3-cyclopentenyl 1-acetate **9**, mp 42–44°. The melting point and spectral properties of this compound were identical in every way with those of the acetate isolated previously.

Establishment of the Structure of 3-Phenyl-3-cyclopenten-1-ol (8). A 0.8-g sample of 3-phenyl-2-cyclopenten-1-ol **8** was dissolved in 150 ml of ethanol and hydrogenated at 50 lb pressure over a 10% palladium on carbon catalyst. Filtration of the catalyst followed by evaporation of the solvent under reduced pressure gave 0.8 g of a yellow oil.

The infrared spectrum (CCl_4) was characterized by major bands at 2.95, 6.23, 6.63, 6.81, 7.45, 9.25, and 9.60 μ. The nmr spectrum showed a singlet at τ 2.75 (5 H), a multiplet at 5.60 (1 H), a broad singlet at 7.09 (1 H), and a multiplet centered at 8.10 (7 H). The mass spectrum included peaks at (m/e) 162 (M^+), base peak, 144, 143, 129, 118, 117, 107, 105, and 104.

The yellow oil obtained was dissolved in 2 ml of acetone. To the above solution was added 10 drops of a 2.65 M potassium dichromate solution and the solution was allowed to stir for an additional 15 min. The reaction mixture was extracted with ether, and the ethereal extracts were washed several times with water, and dried over sodium sulfate. Evaporation of the ether afforded 3-phenylcyclopentanone as a clear liquid.

The infrared spectrum (CCl_4) was characterized by bands at 3.31, 5.69, 6.60, 6.80, 7.03, 7.32, and 8.71 μ. The nmr spectrum ($CDCl_3$) showed a multiplet at τ 2.70 (5 H) and a broad envelope centered at 7.70 (7 H). A 2,4-dinitrophenylhydrazone derivative was prepared mp 149–153° (reported[27] 154°). The spectral properties of this material were identical in every respect with those of ketone **11** obtained from the catalytic reduction of 3-phenyl-2-cyclopentenone (**12**).[27]

Treatment of Bicyclopentanol 1 with Zinc Chloride. To 0.05 g of 2-phenylbicyclo[1.1.1]pentanol (**1**) dissolved in 20 ml of anhydrous dioxane was added 200 mg of zinc chloride. The heterogeneous mixture was stirred at room temperature for 24 hr, washed with a saturated sodium bicarbonate solution, and extracted with methylene chloride. Evaporation of the methylene chloride left 0.05 g of a yellow oil which was subjected to preparative gas phase chromatography. The chromatographic separation employed a 5 ft × 0.25 in. aluminum column packed with 5% Degs on Chromosorb W at a flow rate of 60 ml/min and at a column temperature of 145°. The chromatogram showed one major peak with a retention time of 4 min which was subsequently identified as 4-chloro-1-phenylcyclopentene (60%). This same compound was obtained when **1** was treated with aluminum chloride in methylene chloride or with thionyl chloride.

The infrared spectrum (CCl_4) was characterized by major bands at 3.28, 6.65, 6.88, 7.61, 7.87, and 10.77 μ. The nmr spectrum (CCl_4) showed a multiplet at τ 2.83 (5 H), an unsymmetrical triplet at 4.05 (J = 2.0 Hz, 1 H), a multiplet at 5.50 (1 H), and a multiplet centered at 7.20 (4 H). The mass spectrum exhibited peaks with (m/e) 180, 178 m^+, base peak 143, 128, 105, 51, and 37.

Preparation of *p*-Nitrobenzoate Esters 15, 17, and 18. A mixture of 1.0 g of 2-phenylbicyclo[1.1.1]pentan-2-ol, 2.0 g of *p*-nitrobenzoyl chloride, and 1.0 g of pyridine was refluxed in 70 ml of benzene for 5 hr. At the end of this time the solution was cooled to room temperature, filtered, and concentrated under reduced pressure to give 1.5 g of a yellow oil. Recrystallization from heptane gave 1.1 g of 2-phenylbicyclo[1.1.1]pentan-2-ol *p*-nitrobenzoate (**15**) as a pale yellow solid, mp 78–80°.

Anal. Calcd for $C_{18}H_{15}NO_4$: C, 69.89; H, 4.89; N, 4.53. Found: C, 69.65; H, 4.88; N, 4.30.

The infrared spectrum (CCl_4) was characterized by major bands at 5.80, 6.58, 7.42, 7.70, 8.90, 9.10, and 10.33 μ. The nmr spectrum (CCl_4) shows a singlet at τ 1.95 (4 H), a multiplet at 2.65 (5 H), a singlet at 6.65 (2 H), a multiplet at 7.58 (1 H), and a multiplet at 8.31 (3 H).

1-Phenylcyclobutyl *p*-nitrobenzoate (**17**) was prepared from the reaction of 1-phenylcyclobutanol[45] with *p*-nitrobenzoyl chloride. A 1.0-g sample of 1-phenylcyclobutanol was added to a mixture of 2.0 g of *p*-nitrobenzoyl chloride and 0.80 g of pyridine. The mixture refluxed in 70 ml of benzene for 5 hr. The reaction mixture was cooled to room temperature, filtered, and the solvent removed under reduced pressure to afford 1.5 g of a yellow oil. Recrystallization of the oil from heptane led to 0.95 g of **17** as a white solid, mp 97–99°.

Anal. Calcd for $C_{17}H_{15}NO_4$: C, 68.67; H, 5.08; N, 4.71. Found: C, 68.58; H, 5.19; N, 4.72.

The infrared spectrum (CCl_4) was characterized by bands at 5.79, 6.53, 7.42, 7.81, and 9.10 μ. The mass spectrum exhibited peaks at (m/e) 167, 150, 130, 129 base peak, 128, 115, and 102.

The *p*-nitrobenzoate ester of dimethylphenylcarbinol (**18**) was prepared in a similar fashion. To 3.0 g of dimethylphenylcarbinol in 70 ml of benzene was added 3.7 g of *p*-nitrobenzoyl chloride and 2.5 g of pyridine. The mixture was refluxed for 5 hr, cooled to room temperature, and filtered. The solvent was removed under reduced pressure to give 5.9 g of **18** as a white solid, mp 130–132°.

Anal. Calcd for $C_{16}H_{15}NO_4$: C, 67.36; H, 5.30; N, 4.91. Found: C, 67.34; H, 5.45; N, 4.93.

The infrared spectrum (KBr) was characterized by bands at 5.80, 6.59, 7.25, 9.05, 11.80, 13.10, 13.94, and 14.40 μ. The mass spectrum exhibits peaks at (m/e) 167, 118 base peak, 117, 103, 78, and 77.

Solvolysis of 2-Phenylbicyclo[1.1.1]pentan-2-ol *p*-Nitrobenzoate (15). A 300-mg sample of 2-phenylbicyclo[1.1.1]pentanol *p*-nitrobenzoate (**15**) was dissolved in 10 ml of 60% acetone–water and heated in a sealed tube at 100° for 3 hr. After allowing the mixture to cool to room temperature, the sealed tube was opened and the contents poured onto 85 ml of a saturated solution of sodium bicarbonate. The aqueous layer was extracted with ether and the ethereal extracts were washed with several portions of water, dried over sodium sulfate, and evaporated under reduced pressure. Gas chromatographic analysis of the residue indicated the absence of bicyclo[1.1.1]pentanol **1**. Sublimation of the residual oil afforded 0.107 g of 3-phenyl-3-cyclopenten-1-ol (**8**).

The residue left behind in the sublimation apparatus was recrystallized from ethanol and gave 0.023 g of **16** as a white solid, mp 143–145°. The infrared spectrum (KBr) was characterized by bands at 5.88, 6.60, 7.44, 7.75, 8.90, 9.05, 13.25, and 14.00 μ. The mass spectrum exhibited peaks at (m/e) 143, 142 base peak, 141, and 115.

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In order to establish the structure of this material as 3-phenyl-3-cyclopentene 1-*p*-nitrobenzoate (**16**) a mixture of 0.05 g of 3-phenyl-3-cyclopenten-1-ol **8**, 0.05 g of pyridine, and 0.071 g of *p*-nitrobenzoyl chloride was dissolved in 40 ml of benzene. The mixture was heated to reflux for 4 hr, cooled to room temperature and filtered from the precipitated salts. The solvent was removed under reduced pressure to afford 0.060 g of a yellow oil. Recrystallization from ethanol led to 0.03 g of a white crystalline product whose properties were identical with those of ester (**16**) isolated from the solvolysis of **15**.

Kinetic Experiments. Standard solutions consisting of 0.400 g of the appropriate *p*-nitrobenzoate ester in 100 ml of anhydrous acetone were prepared. In each run a 3.0-ml aliquot was taken from the standard solution and placed in a Carius tube. To each tube was added 2.0 ml of doubly distilled water. The tubes were then sealed. The rates were determined in duplicate for each temperature. A Neslab Instruments constant temperature apparatus, accurate to +0.1°, was used for the measurements. The reaction mixtures were titrated with a 0.00857 *N* sodium hydroxide solution using bromothymol blue as the indicator. All of the solvolyses followed first-order kinetics up to at least 75% conversion and furnished the theoretical amount of *p*-nitrobenzoic acid. The results obtained are summarized in Table II.

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Evidence for an Anion–Carbene Pair[1]

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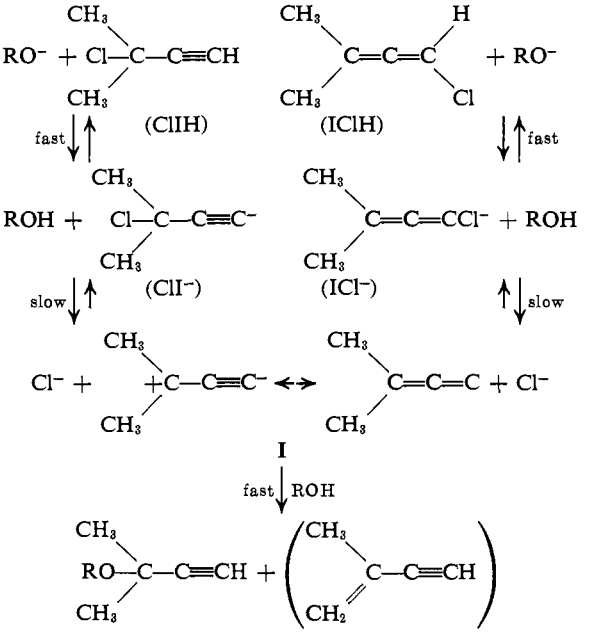
Abstract: The activation volume of the base-promoted solvolysis of 1-chloro-3-methylbuta-1,2-diene in an ethanol–water mixture 80:20 vol/vol at 25° equals +5 cm³/mol. A combination of this value with that measured earlier for 3-chloro-3-methylbut-1-yne and with the densities of these two substrates shows that the two transition states have virtually identical volumes. This suggests that the two precursor anions are on their way to a common intermediate, an anion–carbene pair, preceding the carbene 3,3-dimethylpropenylidene. The acetylenic chloride isomerizes to a small extent (0.30%) to the allenic halide during solvolysis. The yield of the isomer depends on the concentration of added chloride in a way which is compared to those that theoretically characterize external and internal return; this analysis leads to the conclusion that 33% of the isomerization results from internal return and 67% from external return. Both the yield of the isomer and the fraction of internal return increase (to 0.86 and 82%, respectively) if large concentrations of bromide are also present, and the same is true if a solvent consisting of a 50/50 mixture of ethanol and *t*-butyl alcohol is used (3.21 and 84%, respectively).

Several authors have considered the mechanisms of the base-promoted solvolyses of 3-halo-3-methylbut-1-yne and of 1-halo-3-methylbuta-1,2-diene (it is convenient to symbolize these compounds by XIH and IXH, respectively). Hennion and Maloney[2] proposed in 1951 that the reactions of the chlorides, first order in base and in the organic substrate, take place *via* rate-limiting proton abstraction to give the anions ClI⁻ and ICl⁻, respectively, followed by rapid loss of chloride to yield the common intermediate I (3,3-dimethylpropenylidene); I would subsequently react with the solvent to give ROIH. Since then Shiner[3,4] has found that BrIH and IBrH in a basic deuterated solvent undergo exchange much faster than solvolysis; that result requires that the loss of bromide ion rather than the proton abstraction is rate determining. With that modification, the Hennion–Shiner mechanism still stands today (see Scheme I).

Scheme I



It is further known now that a small common ion effect operates, so that some capture of the intermediate I by halide ion must be occurring; that BrIH reacts approximately 50 times faster than IBrH, and that a small amount (about 1%) of the latter is formed during basic solvolysis of the former.[3,4] Hartzler[5,6] has demonstrated that I can be generated and captured under nonsolvolytic conditions in styrene to give the expected

(1) Paper XVIII in the series "Chemical Reactions under High Pressure."
(2) G. F. Hennion and D. E. Maloney, *J. Amer. Chem. Soc.*, 73, 4735 (1951).
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