viously for $Mn(CO)_5(SO_2C_4H_5)$ and $C_5H_5Mo(CO)_3(SO_2C_4H_5)$.[4] An analysis of the entire multiplet pattern in terms of an ABX_3 spin system gives for II the chemical shifts τ 7.60 (CH_3), 4.81, and 4.45 (CH_2), and the coupling constants $|J_{AB}| = 14$ Hz and $|J_{AX}| = |J_{BX}| \sim 2$ Hz. These are to be compared with τ 7.80–7.95 (CH_3), 4.87–4.94, and 4.48–4.57 (CH_2), and $|J_{AB}| = 14.5$–15 Hz and $|J_{AX}| = |J_{BX}| \sim 2$ Hz for the other two compounds. In the infrared spectra of II and other SO_2-containing derivatives of 2-alkynyl transition metal complexes reported, the S–O stretching bands are observed in the ranges 1115–1100 and 910–890 cm^{-1}.[2,4,6,12] These spectral resemblances undoubtedly reflect the same type of structure for the $SO_2C_3H_2R$ (R = H and CH_3) moieties as is found in II (Figure 1).

Work in progress is concerned with reactions between 2-alkynyl metal carbonyls and other electrophilic substrates and with attempts at desulfonylation of the complexes reported herein. Particular interest attaches to an observation that II in CH_2Cl_2 solution undergoes partial (~45%) reconversion to I upon chromatography on alumina.

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(12) The product of the reaction between $(C_6H_5)_3SnCH_2C{\equiv}CH$ and SO_2 shows S—O stretching bands in the region 990–950 cm^{-1} and is best formulated as $(C_6H_5)_3SnOS(O)CH{=}C{=}CH_2$, as suggested by the authors: W. Kitching, C. W. Fong, and A. J. Smith, *J. Amer. Chem. Soc.*, 91, 767 (1969).

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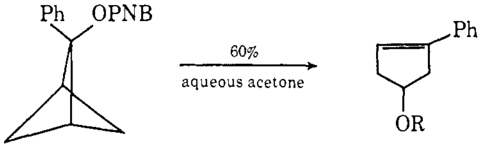
Solvolytic Reactivity of 2-Phenylbicyclo[1.1.1]pentan-2-ol *p*-Nitrobenzoate

Sir:

The generation of carbonium ions in strained ring systems has produced a host of highly interesting and important results of practical and theoretical interest.[1,2] While the solvolytic behavior of some bicyclo[*n*.1.1] systems has received considerable attention,[3] others have remained virtually unexplored. A study of the reaction rate and products of the 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.[4] Our recent photochemical entry into the bicyclo[1.1.1]pentanol system[5] makes these molecules available for a variety of physical organic studies. We now wish to report on the anchimeric assistance present in the solvolysis of 2-phenylbicyclo[1.1.1]pentan-2-ol *p*-nitrobenzoate (**1**).

The preparation of the desired *p*-nitrobenzoate **1**, mp 78–80°, was carried out in the usual way by treating 2-phenylbicyclo[1.1.1]pentanol with *p*-nitrobenzoyl chloride in dry pyridine.[6] The ester was allowed to solvolyze in 60% aqueous acetone, and the course of the reaction was followed titrimetrically using standard techniques. For comparison purposes the related 1-phenylcyclobutanol (**2**) and dimethylphenylcarbinol (**3**) *p*-nitrobenzoates were prepared and their solvolytic behavior was also investigated. Table I lists the rates of solvolysis, and the associated thermodynamic parameters of **1**, **2**, and **3**, together with the rate of solvolysis of 7-phenyl-7-norbornyl *p*-nitrobenzoate (**4**)[7,8] for comparison purposes.

The solvolysis of **1** proceeded *via* rearrangement to the 3-cyclopenten-1-ol system giving 6% internal return to **5** and 92% 3-phenyl-3-cyclopenten-1-ol (**6**). The structure of alcohol **6**, mp 79–81°, is inferred from its composition, spectral data, and chemical behavior. The infrared spectrum of **6** 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 τ 3.98 (J = 2.3 Hz, 1 H), multiplets at τ 5.45 (1 H) and 7.39 (4 H), and a singlet at τ 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 **6** to 3-phenylcyclopentanol (**7**) followed by oxidation of **7** to 3-phenylcyclopentanone (**8**).[9] Structure **8** was compared to an authentic sample prepared from the catalytic reduction of 3-phenyl-2-cyclopent-1-one (**9**).[11]



1

R = PNB (5)
R = H (6)

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 (**11**) which

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(1) J. A. Berson in "Molecular Rearrangements," Vol. I, P. deMayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963.

(2) R. C. Fort and P. von R. Schleyer, *Advan. Alicycl. Chem.*, 1, 283 (1966).

(3) J. Meinwald and Y. C. Meinwald, *ibid.*, 1, 1 (1966).

(4) The solvolytic reactivity of 1-chlorobicyclo[1.1.1]pentane has recently been described; see K. B. Wiberg and V. Z. Williams *J. Amer. Chem. Soc.*, **89**, 3372 (1967); see also K. B. Wiberg, R. A. Fenoglio, and V. Z. Williams, *ibid.*, **92**, 568 (1970).

(5) A. Padwa and E. Alexander, *ibid.*, **89**, 6376 (1967).

(6) All compounds analyzed satisfactorily. Complete spectroscopic and degradative details will be given in our full manuscript.

(7) P. G. Gassman and A. F. Fentiman, *J. Amer. Chem. Soc.*, **91**, 1545 (1969).

(8) The solvolysis of 7-phenyl-7-norbornyl *p*-nitrobenzoate (4) was studied in 70% aqueous dioxane.[7] 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.

(9) Although the above spectral and chemical data are consistent with that of the proposed structure (6), it does not necessarily preclude 3-phenyl-2-cyclopenten-1-ol (10) as an alternate possibility. Alcohol 10 was therefore synthesized[10] and shown to be substantially different from the solvolysis product.

(10) W. Borsche and A. Fels, *Ber.*, **39**, 1922 (1906).

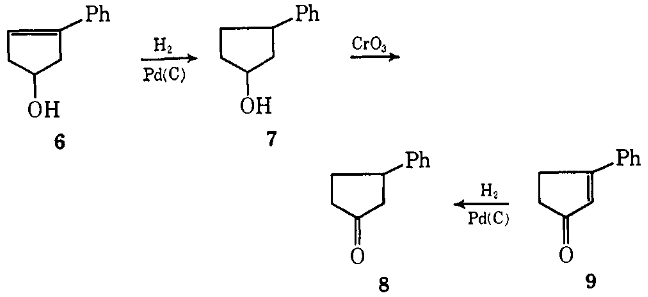
(11) H. O. House and R. L. Wasson, *J. Amer. Chem. Soc.*, **79**, 1490 (1957).

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

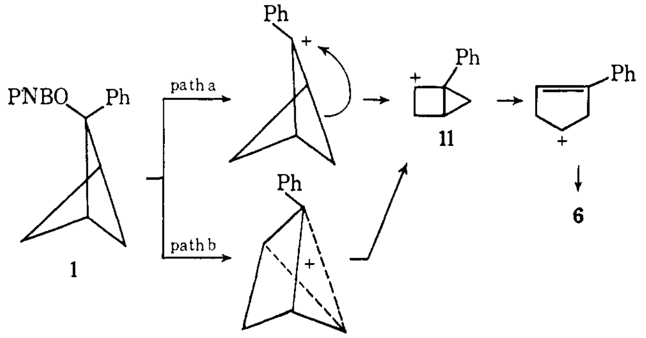
Compd	Temp, °C	Rate, sec^{-1}	k_{rel} at 25°	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
1	50.0 ± 0.01	$(3.97 \pm 0.03) \times 10^{-5}$			
	75.0 ± 0.01	$(3.72 \pm 0.03) \times 10^{-4}$			
	96.0 ± 0.01	$(1.72 \pm 0.01) \times 10^{-3}$			
	25[a]	3.72×10^{-6}	36,400	18.7	−8.28
2	75.0 ± 0.01	$(2.50 \pm 0.02) \times 10^{-5}$			
	101.0 ± 0.01	$(2.77 \pm 0.02) \times 10^{-4}$			
	128.0 ± 0.02	$(1.35 \pm 0.02) \times 10^{-3}$			
	25[a]	2.19×10^{-7}	2,140	20.1	−8.46
3	52.0 ± 0.01	$(2.55 \pm 0.03) \times 10^{-5}$			
	76.0 ± 0.01	$(3.16 \pm 0.03) \times 10^{-4}$			
	100.0 ± 0.01	$(1.35 \pm 0.02) \times 10^{-3}$			
	25[a]	2.51×10^{-6}	24,600	18.9	−8.08
4	25[a]	1.02×10^{-10}	1	26.9	−13.9

[a] Rates at 25° are extracted from higher temperatures.

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.[12]



Although the formation of **5** and **6** can be accounted for in terms of the transient existence of a bicyclo[2.1.0]-2-pentyl cation, its mechanistic origin is less clear. Different theories on the nature of neighboring group participation in rigid bicyclic systems would suggest that **1** could ionize to a classical (path a) or nonclassical (path b) ion.[13] Either of these ions would be expected to collapse to **11**. It should be possible to use the kinetic results to distinguish between these two possibilities. Examination of the rate data listed in Table I shows that the reactivity of **1** is very much greater than that anticipated simply on the basis of geometrical considerations. Schleyer[14] and Foote[15] 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 encountered in the rates of solvolysis of **2**, **3**, and **4**. The bridgehead angle (C_1–C_7–C_4) in bicyclo[2.2.1]heptane has been reported to have a value of 96°.[16] The angle about the methylene carbons of bicyclo[1.1.1]pentane is considerably smaller, having a mean value of 75°.[17] Since the transition state for solvolysis involves partial sp^2 hybridization, one would expect that **4** (with the larger bridgehead angle) would solvolyze at a faster rate than **1**. The fact that **1** undergoes solvolysis some 36,000 times faster than **4** strongly suggests that **1** ionizes with participation of the C-1 bridge adjacent to the departing *p*-nitrobenzoate group, giving the bridged ion directly.

It has been generally accepted that the more stable the carbonium ion center, the less demand that center will make upon neighboring groups for additional stabilization through participation.[18] 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[19] essentially vanishes in the corresponding 7-*p*-anisyl derivatives.[20] They also showed that neighboring group participation is a linear function of the electron demand of the incipient carbonium ion.[7] Their studies established that an unsubstituted phenyl group leveled neighboring group participation by a factor of 10^9. From the above results 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.

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