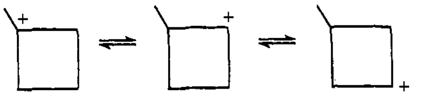

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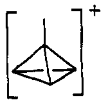

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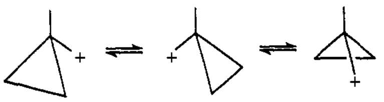

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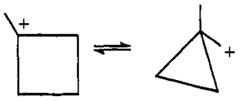

(4)

ing cyclopropylcarbinyl cation; (4) the cyclobutyl cation could be in rapid equilibrium with the corresponding cyclopropylcarbinyl cation.

Mechanisms 2, 3, and 4 would produce ^{13}C satellites at positions appropriate for the various coupling constants.[6,7] Mechanism 1, however, would require ^{13}C satellites of triple the normal intensity at spacings corresponding to one-third the normal splittings due to averaging of direct and indirect coupling constants.

The calculated theoretical shift for the ring hydrogen peak for explanations 2 or 3 (this value is based on shifts from ion III (see below); it is the weighted average of τ 5.6 for the four cyclopropyl hydrogens and 0.5 for the two carbinyl protons) is τ 3.9. This is far below the observed value. A similarly calculated shift (this value is the weighted average of τ 5.8 for the four α-methylene hydrogens and 7.5 for the two β-methylene hydrogens which are derived from data on the methylcyclopentyl cation[5]) for a methylcyclobutyl ion whose α and β hydrogens are all averaged by rapid interchange is τ 6.4, approximately the experimental value. Mechanism 4, with the equilibrium favoring the cyclobutyl cation, fits the data best.

Our observation that similar treatment of 1-chloromethyl-1-methylcyclopropane[8] gives a cation with an nmr spectrum identical with that of the ion from I is also consistent with possibility 4.

At $-25°$, the ion from I isomerized slowly (assuming a normal log A, we obtained an E_a of about 20 kcal/mol) to III whose spectrum consisted of a multiplet at τ 0.49 (1 H), a multiplet centered at 5.6 (5 H), and a doublet at 6.63 (3 H), J = 6.3 Hz (coupling constant measured on both 100- and 60-MHz instruments). Comparison with cyclopropylcarbinyl-type cations[9] leads to the assignment of (methyl)cyclopropylcarbonium ion (III) as its structure. To check the assignment, 1-chloroethylcyclopropane was prepared.[10] The ion from this chloride was found to be identical with III. This mixture of ions was allowed to reach equilibrium at room temperature (several minutes). A final low-temperature spectrum indicated that about 2% of the cyclobutyl ion remained. This corresponds to a K_{equil} of 50 and a ΔF of approximately 2 kcal/mol.

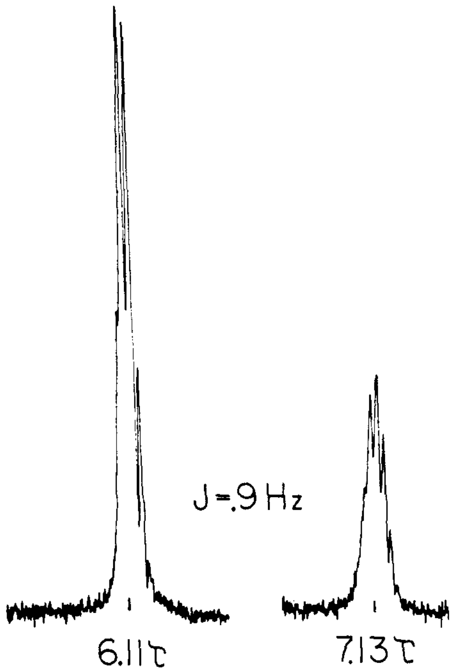

Figure 1.

Isomerization of the trideuteriomethylcyclobutyl cation was also carried out. The ratio of the ring hydrogen to methyl hydrogen peaks in the *unrearranged* material remained unchanged during the reaction, *i.e.*, there was no significant amount of mixing of ring and methyl hydrogen.

Acknowledgment. This work was supported by a grant from the National Science Foundation.

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[6] G. A. Olah and M. B. Comisarow, *J. Amer. Chem. Soc.*, **88**, 1818 (1966).

[7] G. A. Olah and A. M. White, *ibid.*, **91**, 3954 (1969).

[8] W. Kirmse, M. Kapps, and R. B. Hager, *Chem. Ber.*, **99**, 2855 (1966).

[9] C. U. Pittman and G. A. Olah, *J. Amer. Chem. Soc.*, **87**, 5123 (1965).

[10] M. Hanack and H. Eggensperger, *Justus Liebigs Ann. Chem.*, **663**, 31 (1963).

(11) Fellow of the Alfred P. Sloan Foundation.

(12) National Institutes of Health Predoctoral Fellow.

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Received October 20, 1969

Characteristics of the Abrupt Change from the Participation to the Nonparticipation of a Neighboring Group

Sir:

Most changes in molecular structure which result in a change in neighboring group participation also involve a change in the steric environment of the centers being studied. At this time we wish to report our results on a series of molecules of essentially identical steric environment in the vicinity of the reactive sites. In this series we observe an abrupt cessation of neighboring group participation with a resultant dramatic change in the characteristics of the reaction being studied.

In a previous report[1] we presented data on the solvolysis of the systems represented by **1** and **2** where **X** was p-methoxy, hydrogen, and p-trifluoromethyl. These compounds solvolyzed over a rate range of 10^7 and provided definitive evidence that in certain cases neighboring group participation is a linear function of

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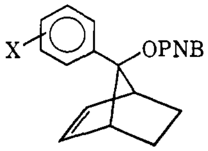
[1] P. G. Gassman and A. F. Fentiman, Jr., *J. Amer. Chem. Soc.*, **91**, 1545 (1969).

Table I. Measured and Extrapolated Rates of *syn*-7-Aryl-*anti*-7-norbornenyl *p*-Nitrobenzoates in 70:30 Dioxane–Water at 25°

Compd	Aryl group	k_n, sec^{-1}	σ^+	k_n/k_{10}	log (k_n/k_{10})
3	4-Dimethylaminophenyl	1.08×10^{-2}	−1.70	1.06×10^{8}	8.02
4	4-Methoxyphenyl	5.18×10^{-7}	−0.78	5.08×10^{3}	3.71
5	Phenyl	4.23×10^{-9}	0.00	4.15×10^{1}	1.62
6	4-Trifluoromethylphenyl	2.94×10^{-10}	0.61	2.88×10^{0}	0.46
7	3,5-Bis(trifluoromethyl)phenyl	3.06×10^{-11}	1.04	3.00×10^{-1}	−0.52

Table II. Measured and Extrapolated Rates of 7-Aryl-7-norbornyl *p*-Nitrobenzoates in 70:30 Dioxane–Water at 25°

Compd	Aryl group	k_n, sec^{-1}	σ^+	k_n/k_{10}	log (k_n/k_{10})
8	4-Dimethylaminophenyl	2.42×10^{-2}	−1.70	2.37×10^{8}	8.38
9	4-Methoxyphenyl	1.54×10^{-7}	−0.78	1.51×10^{3}	3.18
10	Phenyl	1.02×10^{-10}	0.00	1.00×10^{0}	0.00
11	4-Trifluoromethylphenyl	8.52×10^{-15}	0.61	8.35×10^{-5}	−4.08
12	3,5-Bis(trifluoromethyl)phenyl	1.20×10^{-16}	1.04	1.18×10^{-6}	−5.93
13	3,5-Dichloro-4-cyanophenyl	6.30×10^{-18}	1.22	6.18×10^{-8}	−7.21



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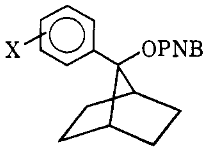

2

the electron demand of the incipient carbonium ion. By varying the nature of **X** we now have been able to extend our studies of **1** and **2** over a rate range of greater than 10^{15}. As a result of this extensively expanded view of the solvolytic behavior of the systems represented by **1** and **2**, we are able to illustrate the striking differences between the presence and absence of neighboring group participation.

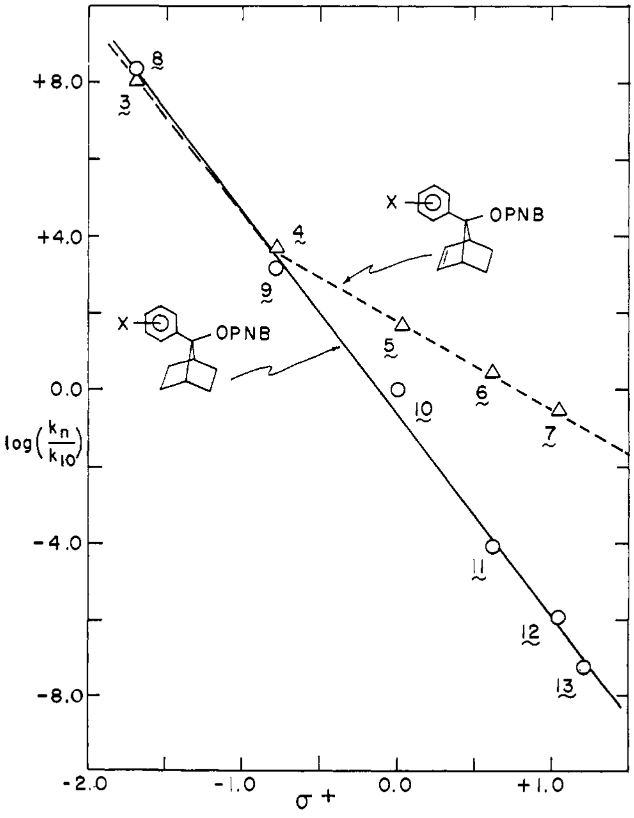

Figure 1. ρ–σ^+ plot of 7-aryl-7-norbornyl and *syn*-7-aryl-*anti*-7-norbornenyl *p*-nitrobenzoates in 70% aqueous dioxane at 25°.

Table I lists the relative rates of solvolysis of the *syn*-7-aryl-*anti*-7-norbornenyl *p*-nitrobenzoates in 70:30 dioxane–water at 25°, while Table II provides the same data for the corresponding 7-aryl-7-norbornyl *p*-nitrobenzoates.[2–7] The ρ–σ^+ plot of these data are shown in Figure 1 with the rate constant of 7-phenyl-7-norbornyl *p*-nitrobenzoate (**10**) being used as the reference point. For the saturated series, **2**, ρ was −5.27 (correlation coefficient 0.999) for six compounds with a spread in rate constants[9] of 3.8×10^{15}. For the unsaturated series, **1**, a sharp break occurred in the ρ–σ^+ plot. For the four compounds **4**–**7**, ρ was −2.30 (correlation coefficient 0.997). Figure 1 shows that the sharp break in the ρ–σ^+ plot occurs at the *p*-methoxyphenyl derivative **4**, with the rate constants of **4** and **3** (the *p*-dimethylaminophenyl derivative) being almost identical with the rate constants for the saturated compounds **9** and **8**, respectively. The sharp break in the ρ–σ^+ plot indicated a dramatic change in the mechanistic aspects of the solvolysis of the unsaturated series. For substituents less capable of stabilizing a carbonium ion than the *p*-methoxyphenyl group, neighboring

[2] The rates for 3 and 8 were measured in 90:10 acetone–water and extrapolated to 70:30 dioxane–water by multiplying the measured rates in 90:10 acetone–water by a factor of 12.0. This factor was determined experimentally by comparing the rates of both **4** and **9** in both solvent systems.

[3] The rates of compounds **4**–**7** and **9**–**13** were extrapolated from higher temperatures.

[4] Due to the inert character of the *p*-nitrobenzoates **12** and **13**, the rates of these compounds could not be determined directly. Thus, the rates of the corresponding tosylates were determined in anhydrous acetic acid and extrapolated to *p*-nitrobenzoates in 70:30 dioxane–water by dividing the rates of the tosylates by a factor of 6.3×10^{9}. This factor was determined experimentally by comparing the rate of solvolysis of **11** in 70:30 dioxane–water with the rate of solvolysis of the corresponding tosylate in anhydrous acetic acid.

[5] The σ^+ values listed in Tables I and II, with the exception of that for **13**, were those of H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4979 (1958).

[6] The σ^+ value for the 3,5-dichloro-4-cyanophenyl moiety was determined experimentally to be +1.22 by measuring the rate of solvolysis of the corresponding cumyl chloride according to the procedure of Brown and Okamoto.[8] The details of the synthesis and utilization of this strongly electron-withdrawing aryl grouping will be presented in a forthcoming publication.

[7] Satisfactory elemental analyses have been obtained on all new compounds.

[8] Y. Okamoto and H. C. Brown, *J. Amer. Chem. Soc.*, **79**, 1909 (1957).

[9] To our knowledge this is the largest rate spread over which a ρ–σ^+ study has been carried out for a solvolysis reaction.

group participation by the π electrons of the norbornenyl double bond was important. For substituents such as *p*-dimethylaminophenyl, which are better at stabilizing carbonium ions than the *p*-methoxyphenyl group, neighboring group participation by the π electrons of the norbornenyl double bond was not needed and hence did not occur. Figure 1 gives mute testimony to the abrupt cessation of this participation. The occurrence of the sharp break in the ρ-σ^+ plot at the point for **4** showed that the *p*-methoxyphenyl group was just sufficient to overcome the π-electron neighboring group participation.[10]

In addition to the evidence provided by the ρ-σ^+ plot on the difference between participation and nonparticipation, product studies gave confirmation of the clear-cut division between the involvement and noninvolvement of a neighboring group. Compounds represented by **5**, **6**, and **7** solvolyzed in a stereospecific manner and gave only unrearranged products with complete retention of the nucleophile in the *anti* position in yields of 100, 85, and 94%, respectively. In sharp contrast was the fact that **3** and **4** gave almost identical mixtures of 8% *syn* and 92% *anti* products in yields of 86% and 95%, respectively. Again the disappearance of the stereospecificity of the reaction was consistent with the cessation of neighboring group participation.

The data discussed above demonstrate unequivocally that significant differences exist between the presence and absence of neighboring group participation. In addition this study proves that the use of substituent effects over a broad range of σ^+ values can provide definite evidence for the presence (or absence) of neighboring group participation.

Acknowledgment. We are indebted to the Petroleum Research Fund, administered by the American Chemical Society, for a grant in support of this work.

[10] Comparison of the rate constants of 4 and 9 indicates that the *p*-methoxyphenyl group can overcome or "level" neighboring group participation of *ca.* 3 × 10^{10} (for the origin of this value see ref 1). Utilizing this same approach it can be predicted that the *p*-dimethylaminophenyl moiety should be able to "level" neighboring group participation of *ca.* 10^{13}.

[11] Alfred P. Sloan Foundation Research Fellow, 1967–1969.

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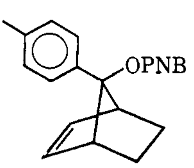
Received January 13, 1970

Aryl Delocalization *vs.* Cyclopropyl Participation

Sir:

We recently demonstrated that the *p*-anisyl group was capable of compensating neighboring group participation[1,2] with a "leveling" effect of *ca.* 3 × 10^{10}. This value was obtained by balancing the aryl delocalization by the *p*-anisyl moiety against π-electron participation of the double bond in *syn*-7-*p*-methoxyphenyl-*anti*-7-norbornenyl *p*-nitrobenzoate (**1**) and comparing the rate of solvolysis of **1** with the rate of solvolysis of the saturated ester, **2**. Since **1** solvolyzes only three times faster than **2**, the rate difference of 10^{11} observed in the parent molecules[3] must have been leveled by a factor of *ca.* 3 × 10^{10} by the presence of the *p*-anisyl group. In order to test whether the "leveling" capacity of 3 × 10^{10} was a general property of the *p*-anisyl group, we pitted *p*-anisyl delocalization against neighboring group participation by cyclopropane. We now wish to report the results of this study.



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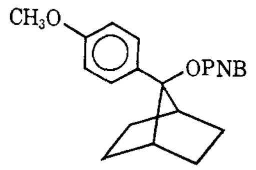

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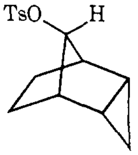
The ability of a cyclopropyl ring to stabilize an incipient carbonium ion by neighboring group participation is best demonstrated by the rate difference of 10^{14} in the rates of solvolysis of **3** and **4**.[4–6] Since **3** solvolyzes 10^{14} times faster than **4**, replacement of the hydrogen at C-8 of **3** by a *p*-anisyl group should be insufficient to overcome the neighboring group participation by the cyclopropyl ring if the *p*-anisyl group was only good for a factor of 3 × 10^{10}. In fact, a residual rate factor of *ca.* 3 × 10^3 would be predicted for the difference in the rate of solvolysis of **2** and **5**.



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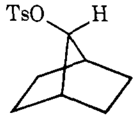
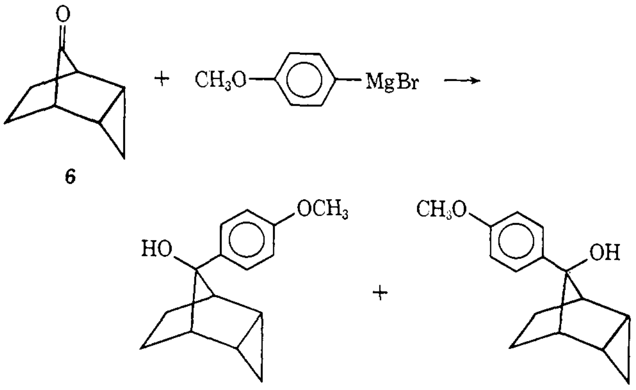


4

Reaction of the known[6,7] ketone **6** with *p*-anisyl-Grignard reagent in refluxing tetrahydrofuran gave, after aqueous work-up and chromatographic separation, 5.4% of **7**, mp 92.0–93.0°, and 51% of **8**, mp 82–83°.[8,9] Treatment of **7** with *p*-nitrobenzoyl chloride



6
7
8

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[1] P. G. Gassman and A. F. Fentiman, Jr., *J. Amer. Chem. Soc.*, **91**, 1545 (1969).

[2] P. G. Gassman and A. F. Fentiman, Jr., *ibid.*, **92**, 2549 (1970).

[3] S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *ibid.*, **77**, 4183 (1955); S. Winstein and M. Shatavsky, *ibid.*, **79**, 505 (1957).

[4] H. Tanida, T. Tsuji, and T. Irie, *ibid.*, **89**, 1953 (1967).

[5] M. A. Battiste, C. L. Deyrup, R. E. Pincock, and J. Haywood-Farmer, *ibid.*, **89**, 1954 (1967).

[6] J. S. Haywood-Farmer and R. E. Pincock, *ibid.*, **91**, 3020 (1969).

[7] S. C. Clarke, K. J. Frayne, and B. L. Johnson, *Tetrahedron*, **25**, 1265 (1969).

[8] Satisfactory elemental analyses were obtained on all new compounds.

[9] The stereochemical assignment was based primarily on hydrogen bonding studies. Whereas 7 showed only a free O–H stretching vibration at 3630 cm^{-1}, 8 showed a free O–H stretching vibration at 3623 cm^{-1} and a hydrogen-bonded O–H stretching vibration at 3587 cm^{-1}.