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.

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[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}.

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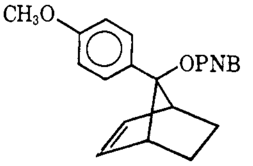
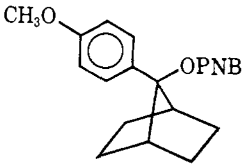
Aryl Delocalization *vs.* Cyclopropyl Participation

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.

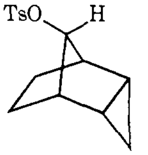


1



2

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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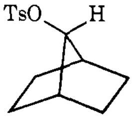
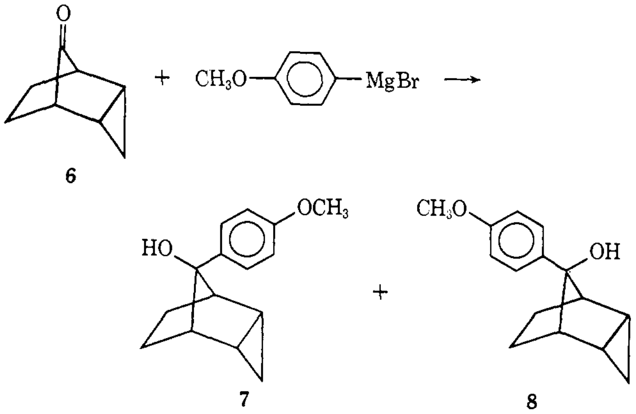


4

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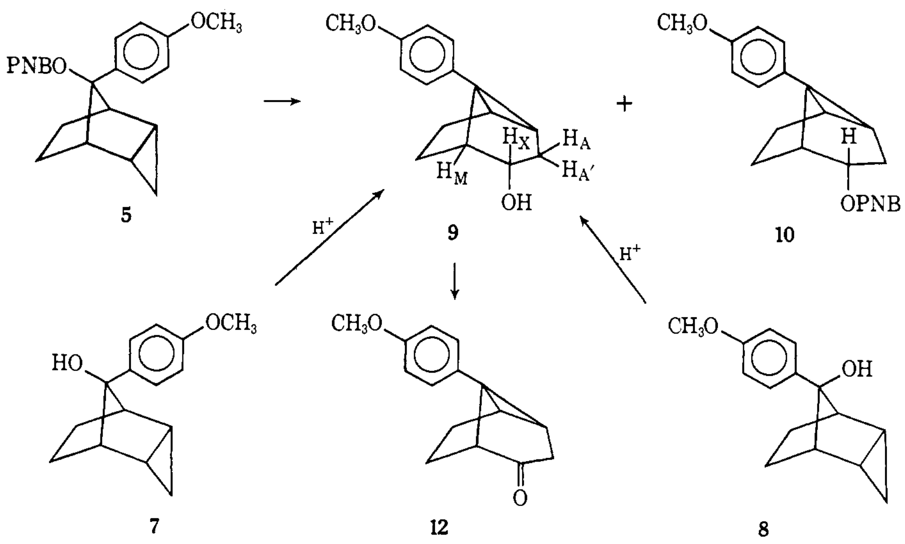
[6] J. S. Haywood-Farmer and R. E. Pincock, *ibid.*, **91**, 3020 (1969).

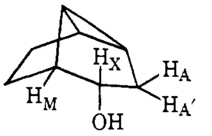
[7] S. C. Clarke, K. J. Frayne, and B. L. Johnson, *Tetrahedron*, **25**, 1265 (1969).

[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.



in pyridine gave **5**, mp 112.5–113.0°. The kinetic data obtained from the solvolysis of **5** in 90:10 acetone–water produced a plot with a constantly decreasing rate curve when the theoretical infinity titer was used in the calculations. In addition only 67% of the theoretical amount of *p*-nitrobenzoic acid was liberated. This behavior was characteristic of a reaction involving initial formation of an ion pair followed by partial formation of hydrolysis product and partial internal return to a new, relatively unreactive *p*-nitrobenzoate.[4–6,11] Product studies confirmed these suspicions. Under the solvolysis conditions **5** was found to give a 2:1 mixture of **9** and **10**, respectively. The structure of **9** was established primarily on the basis of nmr spectroscopy. A comparison of the nmr spectrum of **9** with the published[6] data for **11** (the major alcoholic product obtained from **3**) showed that many similarities were present. In particular, the six-peak, one-proton signal for H_X of **9** observed at *ca.* τ 5.4 corresponded to the X part of an AA'MX system, with $J_{AX} = J_{A'X} =$ 9.0 Hz and $J_{MX} =$ 6.5 Hz. Spin-decoupling experiments confirmed that the coupling constants observed for **9** were practically identical with those observed for **11**.[6] Chromic anhydride in pyridine oxidation of **9** gave **12**, mp 74–75°, which had nmr and infrared spectra consistent with the assigned structure. The tricyclic alcohol **9** could also be obtained through the acid-catalyzed rearrangement of either **7** or **8**. The structural relationship between **9** and **10** was shown by the lithium aluminum hydride reduction of **10** to give **9** and by the reaction of **9** with *p*-nitrobenzoyl chloride in pyridine which gave **10**.



11

When the observed infinity titers were used in plotting the rate data obtained in the solvolyses of **5**, good first-order rate plots were observed. The rate constant obtained from the slope of these plots corresponded to the sum of the rate constants for solvolysis and rearrangement ($k_{\text{obsd}} = k_{\text{rearr}} + k_{\text{solvys}}$).[6,11] Thus, the observed rate constant for the solvolytic disappearance of **5** at 25.0 ± 0.01° in 90:10 acetone–water was (4.76 ± 0.14) $\times 10^{-5}$ sec^{-1}. However, the rate of solvolysis of **2** at 25° in the same solvent system has been found[12] to be 1.25 $\times 10^{-8}$ sec^{-1}. Thus, even with the *p*-anisyl group in the 8 position of **5**, neighboring group participation by the cyclopropyl ring provides a rate acceleration of 3.8 $\times 10^{3}$, in excellent agreement with predictions! It is interesting to note that, in overwhelming the stabilization which the *p*-anisyl group could provide *via* delocalization, the cyclopropyl moiety controlled product formation. Even though a cation at C-8 would be tertiary and stabilized by the *p*-anisyl group, the charge tends to reside primarily at C-2 which leads eventually to **9**. It was demonstrated that **9** and not **7** was the product of kinetic control by establishing that under the reaction conditions **7** was only slowly converted to **9**.

This study provided convincing evidence that an aryl group has a definite upper limit to the amount of stabilization it can provide *via* delocalization of a positive charge on a benzylic position. For the *p*-anisyl group, this limit appears to be equated with a rate factor of 3 $\times 10^{10}$. These results can be extrapolated to the other aryl groups for which "leveling" capacities have been established.[1,2] This extrapolation would appear dependable since the results discussed above show that the "leveling" capacity of the *p*-anisyl group remains constant even in going from one participating group to another.

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

The 36-cm^{-1} difference observed between the two types of O–H stretching vibrations in **8** was in good agreement with the $\Delta\nu$ of 35 cm^{-1} observed for the parent system.[10] In addition the nmr spectra of **7** and **8** were consistent with the assigned structures.

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