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ON THE VALIDITY OF THE ARYL DELOCALIZATION "LEVELING" CONCEPT AS A GENERAL PROBE OF NEIGHBORING GROUP PARTICIPATION

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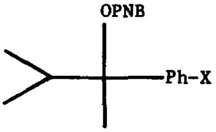
The efficacy of aryl substitution as a probe for and means of eliminating or "leveling" neighboring group participation (NGP) has been well established in the 7-norbornyl skeleton.[1] More recently, this method has been applied to 2-norbornyl and related systems to ascertain the level of sigma participation, if operative, in the solvolysis of *exo*-2-norbornyl derivatives.[2] The results of this approach have been interpreted as being consistent with the absence of such participation[3] in the *exo*-2-norbornyl system.

We now wish to point out an alternative evaluation of the kinetic studies previously obtained for the solvolysis of 2-aryl-3-methyl-2-butyl (1)[2c], 1-aryl-1-cyclopropyl-1-ethyl (2)[2c], 3-aryl-3-nortricyclyl (3)[2d], 2-aryl-*endo*-2-norbornyl (4)[2b], and 2-aryl-*exo*-2-norbornyl (5)[2b] p-nitrobenzoates. Our analysis raises some important questions which must be answered before previous[3] "no sigma participation" conclusions can be accepted.

Previous analysis[2d] of the solvolytic reactivity of systems 1-5 (X = *p*-OMe, H, *p*-CF_3) utilized the 3-methyl-2-butyl system 1, as the "no NGP" model for cyclopropyl derivatives 2 and 3, while the *endo*-isomer 4 served as the "no NGP" model for *exo*-5. We feel that a more consistent



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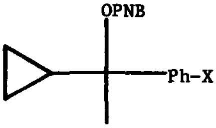

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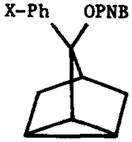

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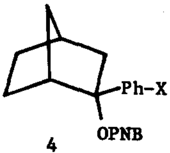

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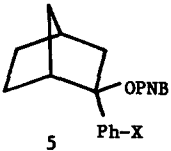

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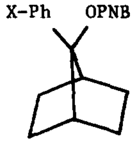
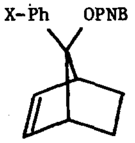
and meaningful correlation is achieved when the same model, 1, is applied to all systems, 2-5. When this is done (see Table 1) one finds a similar pattern of change in relative reactivity with changing substitution in 4 and 5 as previously noted for 2 and 3 (ie. increasing electron supply with increasing electron demand). If one accepts the applicability of the Gassman-Fentiman method[1] to cyclopropyl derivatives 2 and 3, and given that the magnitude of reactivity is not large in 4 and 5, then one is hard put to escape the apparent conclusion of 1,6-sigma participation in the *exo*-2-norbornyl derivatives 5. Further consideration of the data in Table I suggests the feasibility of 1,7-sigma participation in the *endo*-isomer 4.[4] If the latter were in fact operative, one would expect the *exo*:*endo* rate ratios to remain relatively constant within the 2-aryl-2-norbornyl series as previously noted.[2c] This constancy of the *exo*:*endo* rate ratios led to the earlier conclusion[2] of no sigma participation in 4 or 5 while the present analysis, if correct, would appear to indicate the exact opposite!

TABLE I. RELATIVE REACTIVITIES OF p-NITROBENZOATES 1-5 IN 80% ACETONE AT 25°.

Substituent (X)	1	2	3	4	5	*exo*-5/*endo*-4
p-OMe	1.0	505	2.36	0.62	175	284
p-H	1.0	25,000	38.40	5.57	795	143
p-CF_3	1.0	285,000	270.00	16.70	3120	188
mm'-$(CF_3)_2$	1.0	1,210,000	682.00	....	....	....

By direct comparison with their respective model systems one can examine the relative magnitude of the anisyl leveling effect in the cyclopropyl, 2,[2c] and the 7-aryl-7-norbornenyl, 6,[1a] systems. For example, from the data given below it is apparent that a 10^4 rate enhancement by the double bond in the p-trifluoromethyl derivative 6 (X = *p*-CF_3) is essentially "leveled" by the *p*-anisyl group in 6 (X = *p*-OMe), whereas a similar reactivity factor of 10^5 for cyclopropyl derivative 2 (X = *p*-CF_3) is reduced by a factor of only 550 (see Table I) for the identical substituent change. Obviously, all parameters controlling reactivity are not equal nor do the reactive centers experience substituent-reactivity changes in the same manner.





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X		k_{rel}	
p-OMe	1.0		3.4
p-CF_3	1.0		3.45×10^4

From the above analysis it seems clear that from one system to another the magnitude of NGP is not identically controlled by aryl substitution, *ie*. the 3×10^{10} "leveling" effect ascribed[1a] to the 4-methoxyphenyl substituent in the 7-norbornenyl system should not be a general value applicable to other systems. When making *a priori* assignments as to the leveling effect of various substituents on NGP one must not only consider the magnitude of the participation, but also the vertical *vs*. nonvertical nature (with subsequent conformational requirements) of such participation.[5] Thus in the 7-norbornenyl system the neighboring group effect is transmitted by a through space interaction which is enhanced by movement of the C-7 bridge plane towards the participating olefinic group (nonvertical stabilization). In the case of **2** and **3** and perhaps **4** and **5**, the situation is different in that direct through bond interaction with the reactive center is possible (vertical stabilization).[6] To the extent that NGP is kinetically significant in such sigma "conjugated" systems aryl substitution should serve to compliment charge delocalization without the abruptness observed on the 7-norbornenyl system. Such systems would therefore be expected to exhibit greater reactivity over a larger range of aryl substituents than a "no participation" model as is indeed found for systems **2** and **5** relative to **1**.

Two questions remain from the above analysis: 1) to what extent, if any, is participation by the 1,7 carbon-carbon bond important in the ionization of *endo*-2-norbornyl derivatives; [7] 2) what criteria are essential to application of the substituent leveling concept to the question of sigma participation in a variety of carbon systems? Each of these questions merits serious experimental testing before accepting conclusions based on the premise of presumptive fact.

Acknowledgement. We wish to thank Professor Paul Gassman and Professor Paul v. R. Schleyer for their helpful discussion and critical comments.

References.

1. (a) P. G. Gassman and A. F. Fentiman, Jr., *J. Amer. Chem. Soc.*, **92**, 2549 (1970); (b) *Idem.*, *ibid.*, **92**, 2551 (1970).

2. (a) H. C. Brown and K. Takaeuchi, *ibid.*, **90**, 2691 (1968); (b) *Idem.*, *ibid.*, **90**, 2693 (1968); (c) E. N. Peters and H. C. Brown, *ibid.*, **95**, 2397 (1973); (d) H. C. Brown, *Accounts Chem. Res.*, **6**, 377 (1973).

3. The term participation as used in this report is meant to encompass both vertical stabilization (hyperconjugation) as well as nonvertical stabilization (bridging).

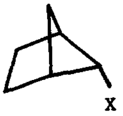
4. The α-CH_3/H rate ratio for the *endo*-2-norbornyl system is estimated to be *ca.* 10^4-10^5.[4b] A similar "normal" α-CH_3/H value has been found for the *exo*-2-norbornyl system;[4c] however, as Schleyer[4c] has recently pointed out such values are well below the newly proposed limiting value of 10^8 and appear to indicate accelerated pathways for solvolysis of the secondary systems. Solvent assistance, while considered unreasonable in the *exo*-2-norbornyl case, is

clearly a distinct possibility in the *endo*-isomer; however, recent observations[4d] of essential constancy of the *exo*-*endo* rate ratio for 2-norbornyl tosylates with change in solvent nucleophilicity (acetic to formic to trifluoroacetic acid) militates against this pathway. Thus, 1,7 sigma participation is clearly implicated. See footnote 7 for further discussion of this point; (b) H. C. Brown and F. J. Chloupek, *J. Amer. Chem. Soc.*, **85**, 2322 (1963); H. C. Brown and M. H. Rei, *ibid.*, **86**, 5004, 5008 (1964); (c) See P. v. R. Schleyer, *ibid.*, **92**, 2540 (1970); (d) Unpublished results cited in Ref. 2d.

5. Similar reasoning has been used in a report on the solvolysis of 8-vinyl-*exo*-8-bicyclo[3.2.1]-octyl-3,5-dinitrobenzoate; G. D. Sargent and T. J. Mason, *J. Amer. Chem. Soc.*, **96**, 1063 (1974).

6. (a) These arguments do not exclude the possibility of non-vertical (bridging) participation in the ionization of *exo*-2-norbornyl tosylate. Indeed the stability of the derived bridged ion would appear to be the major factor responsible for the high *exo*-*endo* rate ratio in the unsubstituted 2-norbornyl system whereas the evidence against bridged structures for 2-aryl-2-norbornyl cations[6b] points to a leveling of the non-vertical component for 1,6 participation by the 2-aryl substituent. Finally, it should be recognized that *exo*-*endo* rate ratio comparisons between the 2-aryl-2-norbornyl derivatives and the 2-norbornyl parent are complicated by enhanced steric consideration in the tertiary systems.[6c] (b) D. G. Farnum and A. D. Wolf, *J. Amer. Chem. Soc.*, **96**, 5166 (1974); (c) G. D. Sargent, in "Carbonium Ions," Vol. III, G. A. Olah and P. v. R. Schleyer, Eds., Wiley-Interscience, New York, 1972, p 1173.

7. If one considers the immediate homologous neighbors of **ii**, namely the *endo*-5-bicyclo[2.1.1]-hexyl (**i**)[7b] and *endo*-2-bicyclo[3.2.1]octyl derivative (**iii**),[7c] it appears unreasonable to continue to ignore the possibility of sigma participation in **ii** when recent investigation established the extensive level of vertical or non-vertical stabilization in the ionization of **i** and **iii**. (b) K. B. Wiberg, R. A. Fenoglio, V. Z. Williams, Jr., and R. W. Ubersax, *J. Amer. Chem. Soc.*, **92**, 568 (1970); (c) H. L. Goering and G. N. Fickes, *ibid.*, **90**, 2848 (1968).



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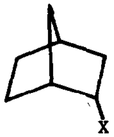

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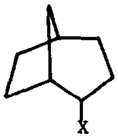

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