Proximity Effects in *peri*-Substituted Naphthalenes. I. Some 8-Substituted 1-Hydroxymethyl- and 1-Chloromethylnaphthalenes[1]

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The methylene signals in the nmr spectra of a series of 8-substituted 1-hydroxymethyl- and 1-chloromethylnaphthalenes were analyzed. The greater deshielding observed for the chlorides over the alcohols is explained as due to differences in conformational preferences. Intramolecular hydrogen bonding in the alcohols may lead to greater populations of conformers in which the hydrogens are further removed from the naphthalene ring's maximum deshielding region than in the chlorides. Solvolysis of the chlorides in 80% aqueous acetone revealed a good Hammett σ_p plot when the unsubstituted compound was omitted from consideration. Steric acceleration can explain the faster rates for the substituted compounds.

The spatial proximity of substituents in naphthalene's 1 and 8 positions, the *peri* positions, is revealed by the appearance of several unique physical and chemical properties.[2] Our studies in *peri*-substituted naphthalenes have stemmed from similar studies accomplished and in progress on eclipsed groups in the norbornane system.[3] From a geometrical consideration *peri* substituents are much closer to one another than identical *ortho* substituents, and steric interactions and field effects should be more severe. Since such substituents are separated by three carbon atoms, they may be likened to *meta* substituents in their ability to transmit inductive and resonance effects between one another. However, imposition of one-third double bond character or less to the 8,9 and 9,1 bonds[4] should decrease the ability of the system to transmit such effects.

Relative magnitudes of proximity effects of *peri* substituents were to be studied by measurements of (a) pK_a values of 8-substituted 1-naphthoic acids, (b) frequency shifts in the infrared and shifts in the chemical shifts in the nmr spectrum associated with intramolecular and intermolecular hydrogen bonding in 8-substituted 1-hydroxymethylnaphthalenes, (c) chemical shift differences of the methylene hydrogens of the aforementioned alcohols and their corresponding chlorides, and (d) solvolysis rates of the chlorides. The present paper deals with the determination and evaluation of the latter two measurements.

The 8-substituted 1-hydroxymethylnaphthalenes were prepared by either lithium aluminum hydride or diborane reduction of the known corresponding acids. The desired chlorides were obtained *via* their alcohols by reaction either with thionyl chloride by the method of Kirner and Windus[5] or with gaseous hydrogen chloride by the method of Shoesmith and Rubli.[6]

Interpretation of Nmr Spectra.—The nmr spectra of the hydroxymethylnaphthalenes and chloromethylnaphthalenes were thoroughly analyzed in the region of the methylene hydrogen signals. The data are summarized in Table I. Normally the α-hydrogen signals of primary alcohols appear at lower fields than those of the corresponding chlorides.[7] When a phenyl substituent is present in the α position, both methylene signals undergo a paramagnetic shift presumably due to a combination of inductive and anisotropic effects. Still the methylene signal for the alcohol appears further downfield (line 7, Table I).

Fundamental to the meaningful interpretation of the relevancy of chemical shift positions of any aryl-substituted compound is that data be obtained in solutions sufficiently dilute so that further dilution does not alter the positions. In these dilute solutions intermolecular association of solute will be minimal, as will the mutual shielding of hydrogen nuclei by the induced ring current of the benzene ring of adjacent molecules.[8] The methylene signals for benzyl alcohol and benzyl chloride in 5 and 6% solutions in CCl_4 are reported to be 4.40 and 4.50 ppm, respectively,[9] a reversal of order in comparison with our data on these two compounds obtained at infinite dilution. Evidently greater association in benzyl alcohol is possible *via* intermolecular hydrogen bonding in which the methylene protons lie in the shielding cone of a neighboring benzene ring.

The expected lower field methylene chemical shift for the alcohol is observed with the simple 1-substituted naphthalene compounds (line 1, Table I). However, when the 8 position is substituted the reverse is generally true. This reversal is attributed to changes in the conformational preferences between the alcohols and their chlorides. For 1-chloromethylnaphthalene potential-energy functions governing internal rotation have been estimated from van der Waals interaction data[10] and the equation of Hill.[11] The potential (E_v) minimum was calculated to be 70–80°. The 60° rotomer (**1**) for the chloride is depicted below.

The negative $\Delta\delta$'s in Table I for the 8-substituted compounds may be explained as follows. If the population of conformations approaching **2**, the 180°

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[1] Grateful acknowledgement is made to the National Science Foundation for a research grant (NSF-GP-1574) which supported a large portion of this work.

[2] For a recent review of naphthalene *peri* interactions see V. Balasubramaniyan, *Chem. Rev.*, **66**, 567 (1966).

[3] D. C. Kleinfelter, *J. Org. Chem.*, **32**, 3526 (1967), and references therein.

[4] *Cf.* D. W. J. Cruickshank, *Acta Cryst.*, **10**, 504 (1957).

[5] W. R. Kirner and W. Windus, "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1943, p 136.

[6] J. B. Shoesmith and H. Rubli, *J. Chem. Soc.*, 3098 (1927).

[7] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Ltd., London, 1959, p 54.

[8] A. A. Bothner-By and R. E. Glick, *J. Chem. Phys.*, **26**, 1651 (1957).

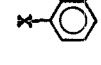
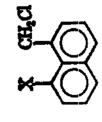
[9] G. V. D. Tiers, "Tables of τ-Values for a Variety of Organic Structures," Minnesota Mining and Manufacturing Co., St. Paul, Minn, 1958.

[10] R. J. W. Le Févre, B. J. Orr, and G. L. D. Ritchie, *J. Chem. Soc.*, 3619 (1965).

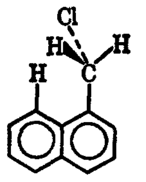
[11] T. L. Hill, *J. Chem. Phys.*, **16**, 399 (1948). For a recent discussion of the evaluation of potential-energy functions employing the van der Waals curve in analytical form, see E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformation Analysis," Interscience Publishers, New York, N. Y., 1965, p 450.

Table I

Nmr Spectral Data for Some 1-Hydroxymethylnaphthalenes and 1-Chloromethylnaphthalenes[a]

	Registry no.	δ(CCl_4)	δ($CHCl_3$)		Registry no.	δ(CCl_4)	δ($CHCl_3$)	Δδ(CCl_4)[b]
X = H	4780-79-4	5.04	5.18	X = H	86-52-2	5.00	5.08	+0.04
X = OCH_3	19190-42-2	4.94	5.08	X = OCH_3	19190-47-7	5.26	5.33	−0.32
X = Br	14938-58-0	5.40	5.51	X = Br	19190-48-8	5.52	5.59	−0.12
X = Cl	10446-06-7	5.37	5.47	X = Cl	19190-49-9	5.47	5.53	−0.10
X = CH_3	10336-29-5	5.09	5.23	X = CH_3	15675-12-4	5.14	5.23	−0.05
X = NO_2	19190-46-6	4.86	5.00	X = NO_2	19190-51-3	4.90	4.98	−0.04
Benzyl alcohol	100-51-6	4.60	4.70	Benzyl chloride	100-44-7	4.53	4.61	+0.07
o-Methoxybenzyl alcohol	612-16-8	4.58	4.72	*o*-Methoxybenzyl chloride	7035-02-1	4.57	4.67	+0.01

[a] Chemical shifts (δ) are for very dilute solutions in which no shifts in δ upon further dilution were observed, and are presumed correct to ±0.01 ppm. [b] Δδ is the difference between the δ for the alcohol and the corresponding chloride in CCl_4; negative values imply the alcohol signal is upfield from the chloride.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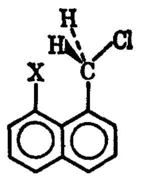
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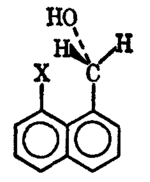
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rotomer, is preferred for the 8-substituted 1-chloromethylnaphthalenes, then the methylene hydrogens reside more within a region of high anisotropic deshielding, *i.e.*, near the plane of the naphthalene ring at the fusion point. Conversely, if conformations approaching **3** are preferred for the 8-substituted 1-hydroxymethylnaphthalenes, then the methylene hydrogens, on the average, are further removed from the region of highest anisotropic deshielding. The α- and β-proton resonances for naphthalene are known to be 7.80 and 7.44 ppm, respectively.[12] Extension to the α- and β-methyl derivatives gives methyl resonances of 2.64 and 2.48 ppm.[13–16] The methylene signal of α-hydroxymethylnaphthalene of 5.04 ppm in CCl_4, corresponds to a downfield shift of 0.26 ppm relative to the β isomer.[17] All these differences may be largely attributed to the exertion of greater anisotropic deshielding at the α position.

Conformations approaching **3** would be preferred for those alcohols in which significant intramolecular hydrogen bonding to the 8 substitutent occurs. The greatest Δδ is observed for the 8-methoxy compound in which ir and nmr data have revealed the predominance of OH···O bonding.[18] In the 8-halogen compound OH···X bonding is less prevalent and the Δδ is correspondingly less.

In order to substantiate the assignments of preferred conformations from the nmr work and because such assignments are presumed important to the solvolytic study (*vide infra*), E_v calculations on the 8-substituted 1-chloromethylnaphthalenes have been performed. In these calculations an arbitrary value of 2.50 Å (an average value for the C_4–C_5 and C_1–C_8 distances in 3-bromo-1,8-dimethylnaphthalene of 2.44 and 2.56 Å, respectively[19]) was chosen as the mean C_8–X, C_1–CH_2 interplanar distance. Serious steric interactions between *peri* substituents would cause in-plane and out-of-plane deformations[20] and would magnify this value. Assuming the *o*-methyl group is held in the "anti" orientation, the C···O interaction for the 8-methoxy compound is calculated to be only *ca.* 0.6 kcal/mol. Therefore, the calculated E_v minima at *ca.* 110 and 180° should be significant. The 0.8-kcal difference between these minima for 1-chloromethylnaphthalene is decreased to 0.3 kcal for the 8-methoxy derivative.[21] Such calculations are only qualitatively significant for the more bulky 8 substituents in that appreciable distortions of the *peri* groups will be involved. Cal-

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(12) D. C. F. Garbutt, K. G. R. Pachler, and J. R. Parrish, *J. Chem. Soc.*, 2324 (1965).

(13) F. Fu-Hsie, R. J. Kurland, and B. J. Mair, *Anal. Chem.*, **36**, 843 (1964).

(14) B. A. Nagasampagi, R. C. Pandey, V. S. Pansare, J. R. Prahlad, and S. Dev, *Tetrahedron Lett.*, No. 8, 411 (1964).

(15) C. MacLean and E. L. Mackor, *Mol. Phys.*, **3**, 223 (1960).

(16) C. Reid, *J. Mol. Spectrosc.* **1**, 18 (1957).

(17) D. C. Kleinfelter, unpublished observation.

(18) D. C. Kleinfelter, P. H. Chen, and L. Joris, to be published.

(19) M. D. Jameson and B. R. Penfold, *J. Chem. Soc.*, 528 (1965).

(20) Reference 2, p 568.

(21) The absolute values for 110 and 180° are 1.7 and 2.0 kcal/mol, respectively.

TABLE II

SOLVOLYTIC DATA OF 8-SUBSTITUTED 1-CHLOROMETHYLNAPHTHALENES IN 80% AQUEOUS ACETONE

Substituent	$k_1 \times 10^6$ sec^{-1} [a] (75.0 ± 0.1°)	$k_1 \times 10^5$ sec^{-1} [a]	ΔH^*, kcal mol^{-1} (75.0°)	ΔS^*, eu (75.0°)	Rate relative to H (75.0°)
H	5.08	4.65 (100°)	22.2	−21.2	1.00
Cl	3.23	3.53 (100°)	23.8	−15.4	0.645
Br	4.38	3.65 (100°)	21.9	−22.5	0.862
OCH_3	30.0	11.5 (90°)	21.9	−16.9	5.91
CH_3	108	56.9 (95°)	20.5	−18.2	21.3
NO_2	0.525 [b]	0.625 (100°)	24.3	−17.7	0.104

[a] Average value from two runs. [b] Estimated from 85.0 and 100.0° by graphic method.

culations on these compounds indicate the lower energy minima now lie at *ca.* 180°, with the energy difference between them and the other minima at *ca.* 105° to be 11 kcal/mol and greater. Hence, bulky substituents alter the populations of the preferred conformations.

Some further comments should be made concerning the chemical shifts of the 8-substituted compounds relative to the unsubstituted parent compounds. The methylene signals for the 8-bromo and 8-chloro compounds are considerably downfield from those of the parent compounds. The methyl group signals for *o*-chloro- and *o*-bromotoluenes[22] do not significantly differ from that in toluene itself. Evidently the change in geometry to the *peri* positions permits the halogens to exert their anisotropic deshielding effect[23] due to the closer proximity of the halogen to the methylene hydrogens. Again, some of the greater downfield shifts for the 8-halo-1-chloromethylnaphthalenes relative to the alcohols may be due to the greater contributions of conformation **2** in which the maximum anisotropic effect of the halogen substituent may be experienced. A deshielding electrostatic effect of oxygen on the methylene hydrogens may be more important in 8-methoxy-1-chloromethylnaphthalene, relative to the corresponding alcohol. The methylene signal positions for *o*-methoxybenzyl alcohol and its chloride are approximately the same.

That the methylene signals for the 8-methyl compounds are downfield relative to the unsubstituted compounds is not surprising in light of known data on the methylnaphthalenes. The values for 1-methylnaphthalene and 1,8-dimethylnaphthalene are 2.64 and 2.82 ppm, respectively.[13] This lower field shift of sterically hindered protons has been explained by Tiers[24] as being due to net electron displacement away from hydrogen nuclei induced by repulsive interactions with neighboring groups in the molecule.

Finally, the methylene signals of the 8-nitro compounds are upfield from those of the unsubstituted parent compounds. Such behavior has been noted previously by Wells.[25] Presumably the nitro group is twisted considerably from the plane of the naphthalene nucleus by rotation about the C–N bond. The plane of the nitro group may actually be nearly perpendicular to the naphthalene plane, which would cause a change over to the methylene hydrogens lying in the diamagnetic shielding region of the anisotropic grouping.

It is interesting to note that there is practically a constant chemical shift difference of 0.12 ± 0.02 and 0.08 ± 0.01 ppm between the methylene signals in CCl_4 *vs.* $CHCl_3$ (or $CDCl_3$) for the hydroxymethylnaphthalenes and their corresponding chloromethylnaphthalenes. Hydrogen bonding with chloroform would presumably be more important in the alcohols than in the chlorides. Chloroform is apparently not significantly affecting the conformational preference of the compounds even where intramolecular hydrogen bonding is involved.

Solvolysis of the 1-Chloromethylnaphthalenes.—The 1-chloromethylnaphthalenes were solvolyzed at two different temperatures in 80% aqueous acetone. First-order rate constants at each temperature and energies and entropies of activation at 75.0° are summarized in Table II. Among structural features which could presumably affect the solvolysis rates are polar effects, steric effects, resonance effects, and neighboring group participation. As mentioned previously resonance effects should be minimal since the 8 substituents may be likened to *meta* substituents.

Winstein and coworkers[26] have aptly demonstrated the importance of methoxy-assisted ionization (MeO participation) in the solvolyses of *o*-anisyl substituted tosylates in which the methoxy group is in a position proximate to the reaction sites. The hydrolysis rates of a number of –OCOR substituted benzyl and benzhydryl bromides have been determined.[27] Only in *o*-carbophenoxybenzydryl bromide was participation considered to be an important factor. Bender.[28] in his review of nucleophilic reactions of carboxylic acid derivatives, states that sterically favorable intramolecular reactions proceed more rapidly than the corresponding intermolecular processes, but that the intramolecular nucleophile must be a powerful one compared to external nucleophiles, and the potential interacting groups must be able to adopt the proper steric orientation.

Only in the 8-methoxy-1-chloromethylnaphthalene could the nonbonded p electrons of the 8 substitutent lie near to the *trans–anti*-parallel arrangement of the attacking intramolecular nucleophile. The p electrons of the other potential intramolecular nucleophiles would lie too far above the *peri* carbon atom for participation to occur. Even in the 8-methoxy derivative little significant participation might be anticipated, in that the geometry of the resonance stabilized oxonium ion

(22) Spectra No.'s 13M and 161M, The Sadtler Standard Spectra, N. M. R., Sadtler Research Laboratories, Inc., Philadelphia, Pa., 1966.

(23) J. W. Emsley, J. Feeney, and L. H. Sutcliff, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. I, Pergamon Press, London, 1965, p 136.

(24) G. V. D. Tiers, *J. Amer. Chem. Soc.*, **78**, 2914 (1956); see also H. J. Bernstein and W. G. Schneider, *J. Chem. Phys.*, **24**, 468 (1956).

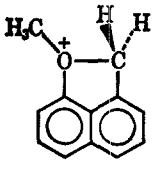
(25) P. R. Wells, *Aust. J. Chem.* **17**, 967 (1964).

(26) R. Heck, J. Corse, E. Grunwald, and S. Winstein, *J. Amer. Chem. Soc.*, **79**, 3278 (1957); S. Winstein, E. Allred, R. Heck, and R. Glick, *Tetrahedron*, **3**, 1 (1957), and numerous subsequent papers by S. Winstein and coworkers.

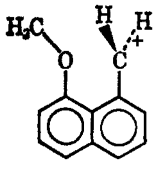
(27) A. Singh, L. J. Andrews, and R. M. Keefer, *J. Amer. Chem. Soc.*, **84**, 1179 (1962).

(28) M. L. Bender, *Chem. Rev.*, **60**, 53 (1960).

intermediate (**4a**) would be such that the vacant p orbital of contributor **4b** would lie perpendicular to the adjacent π cloud, and benzylic type resonance, known to be very important in this system,[29] would be precluded. One might not expect the contribution of **4a** to be sufficient to outweigh benzylic-type resonance.



4a



4b

As to the question of the importance of polar effects in evaluating the factors influencing the solvolysis rates, whether such polar effects be of an inductive type transmitted through the bonding system or of a field type through space, the test is the classical Hammett $\sigma\rho$ treatment. In Figure 1 the logarithms of the rate constants have been plotted *vs.* the σ *meta* substituent constants. If one ignores the value for H, one obtains an excellent correlation according to Jaffé's standard.[30] Two explanations for the correlation may be suggested. (1) Polar effects operate in the expected manner, similar to those one would expect for *meta*-substituted benzyl chlorides, and steric acceleration contributes nearly an equal amount to increase the solvolysis rates regardless of the nature of the *peri* substituent. (2) There exists a collaboration of changing factors which fortuitously results in the Hammett correlation.

Steric acceleration has been invoked to explain results in other systems[31] and may offer an alternative explanation for the enhanced solvolysis rates of the *ortho*-substituted α-phenylalkyl chlorides previously attributed to polar effects of the methyl groups outweighting steric inhibition to resonance.[32] A substituent with a large E_s value[33a] could cause not only the ground state energy to be raised but also the transition state energy, with the latter increase resulting from the *peri* substituent causing steric inhibition to resonance stabilization of the developing positive charge in the transition state. The first explanation requires that for a substituent with a small E_s value, *e.g.*, methoxy, steric contributions to the energies of the ground and transition states may not be raised so much, but the difference between the contributions (steric acceleration) remains the same as for a substituent with a larger E_s value. Hence, for the solvolysis reactions the *peri* substituent might be likened to a torque that maintains a constant energy difference between ground and transition states attributable to steric factors.

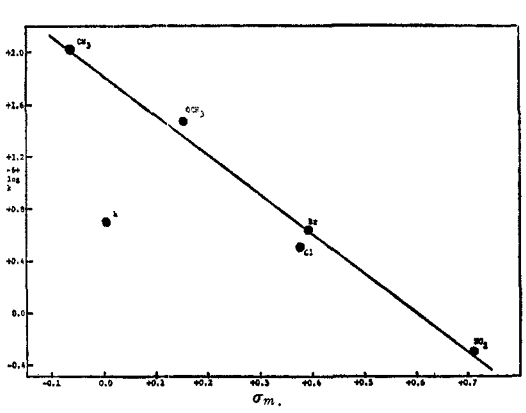


Figure 1.—Hammett plot for 1-chloromethylnaphthalenes (75°): $\rho = -3.01$; $r = 0.995$; $s = 0.0107$.

In considering the second explanation, which the authors tentatively favor, the E_s values for methyl and bromine are identical (0.00) so that these two substituents could be expected to contribute equally to steric acceleration in any case. The E_s value for the nitro group (−0.75) suggests a greater steric interaction. However, if the plane of the nitro group approaches a position perpendicular to the naphthalene ring, as suggested by the nmr data, then its effective size will be decreased[33b] and may approximate that of bromine and methyl. The E_s value for chlorine (+0.18) suggests a smaller contribution towards steric acceleration. This contribution seems to be substantiated by the fact that the 8-chloro compound solvolyzes more slowly than the 8-bromo analog, and the reverse would be expected from σ *meta* substituent constants. Finally, the E_s value for methoxy (+0.99) suggests a significantly smaller steric acceleration role and thereby a deviation from the Hammett plot, which deviation was not observed. For methoxy the smaller steric effect could be counterbalanced by rate enhancement due to some methoxy-assisted ionization. Further rate studies are planned to elucidate the roles of the *peri* substituents.

Solvolyses of benzyl systems have been referred to as "limiting" or borderline systems between S_N1 and S_N2 types of mechanisms; therefore, we feel that some defense must be offered for largely S_N1 character for our solvolyses. An excellent analysis of the solvolysis reaction including borderline system evaluations may be found elsewhere.[34]

In a variety of solvent systems 1-chloromethylnaphthalene solvolyses at least twice as fact as benzyl chloride.[29] The enhancement of reactivity is associated with the increased opportunity for delocalization of positive charge in the carbonium ion of the naphthalene system. The magnitude of the reaction constant, ρ, has been proposed as a measure of the change in electronic charge on the benzenoid system between the ground and transition states.[35] The larger the ρ value, the greater is the positive charge on the system at the transition state. A plot of log k_1 for the benzyl chlorides *vs.* log k_1 for the benzyl tosylates has given a good straight line showing the correspondence in behavior between the two systems, although the ρ is less for the chlorides.[36] Since a ρ of *ca.* −2.20 has been obtained for the benzyl tosylates in *ca.* 50% aqueous acetone at 25.3°, and since the tosylates presumably involve a more complete breaking of the old bond in the transition state (*i.e.*, greater carbonium ion character), our ρ of −3.01 certainly suggests a large degree of positive charge in the transition state for the chloride solvolyses.

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[29] A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 177.

[30] H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

[31] Reference 29, p 92.

[32] G. Baddeley and J. Chadwick, *J. Chem. Soc.*, 368 (1951).

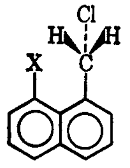
[33] (a) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., N. Y., 1956, Chapter 13, p 598; (b) ref 33a, p 651.

[34] See ref 29.

[35] C. G. Swain and W. P. Langsdorf, *J. Amer. Chem. Soc.*, **73**, 2813 (1951).

[36] J. K. Kochi and G. S. Hammond, *ibid.*, **75**, 3445 (1953).

In addition, the steric difficulty in accomplishing an SN2-type displacement on the *peri* substituted 1-chloromethylnaphthalenes argues strongly in favor of the SN1 mechanism. The lowest energy conformer (**2a,** except for methoxy) should be an unreactive one for an SN2-type displacement since the *peri* substituent would block the approach of the nucleophile to the carbinyl C atom. Therefore, the lone possibility for SN2 displacement would be **5,** a conformer in which one of the hydrogen atoms would have to pass by the *peri* substituent in order to fulfill the inversion requirement of this reaction type. Presumably such a passage would involve severe atomic repulsions and a high activation energy relative to the unsubstituted "parent" compound.



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Obviously there would be considerable steric strain in a planar carbonium ion intermediate for the *peri*-substituted compounds; however, a fairly large ρ is observed. As pointed out by Streitwieser,[37] the π overlap between two p orbitals is roughly proportional to the cosine of the angle between them, and hence, a carbonium ion may be twisted rather severely from the plane of an attached aromatic ring and still be able to distribute a considerable amount of positive charge to the ring.

In our system steric acceleration is invoked to explain the facilitation of the conversion of an sp^3 hybridized ground state carbon to an sp^2 hybridized intermediate. It is interesting that the counterpart, the conversion of an sp^2 hybridized ground state carbon to a tetrahedral sp^3 hydridized intermediate as in the saponification of *peri*-substituted esters,[38] is retarded. These may be general occurrences in such sterically hindered systems.

Experimental Section

Melting points were determined in soft capillary tubes using a Mel-Temp apparatus (Laboratory Devices, Cambridge, Mass.) and are uncorrected. A Varian A-60 nmr spectrometer, calibrated with tetramethylsilane ($\delta = 0$) and chloroform ($\delta = 436.5$ cps), was used for the nmr determinations. Chemical shifts are presumed correct to ±0.01 ppm. Microanalyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn., and by Weiler and Strauss Microanalytical Laboratory, Oxford, England.

Naphthoic Acids.—Methods of preparation of these acids appear in the literature. The α-naphthoic acid was a commercial sample,[39] the 8-methyl-1-naphthoic acid was prepared by the method of Cason and Wordie,[40] and 8-nitro-1-naphthoic acid was prepared by the method of Ekstrand.[41] The 8-bromo-, 8-chloro-, and 8-methoxy-1-naphthoic acids were prepared by the procedure of Rule and Barnett.[42]

Hydroxymethylnaphthalenes.—Lithium aluminum hydride reduction in the standard manner[43] was employed for reduction of α-naphthoic acid and 8-methyl-1-naphthoic acid. With the remaining acids the externally generated diborane reduction in diglyme of Brown and Subba Rao[44] was used. The percentage yields, physical constants, recrystallizing solvents, and analytical data (where appropriate) for these alcohols are as follows: 1-hydroxymethylnaphthalene (81%, mp 60–62°[45] from ether–ligroin); 8-chloro-1-hydroxymethylnaphthalene [92%, mp 81.5–83° from methanol (*Anal.* Calcd for $C_{11}H_9OCl$: C, 68.58; H, 4.71; Cl, 18.41. Found: C, 68.36; H, 4.60; Cl, 18.13)]; 8-bromo-1-hydroxymethylnaphthalene [92%, mp 88–89° from methanol[46] (*Anal.* Calcd for $C_{11}H_9OBr$: C, 55.72; H, 3.82; Br, 33.71. Found: C, 55.38; H, 3.73; Br, 33.72)]; 8-methoxy-1-hydroxymethylnaphthalenes [82%, mp 88–89° from ethanol–water (*Anal.* Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.32; H, 6.42)]; 8-methyl-1-hydroxymethylnaphthalene [74%, mp 93–94.5° from ether–ligroin (*Anal.* Calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.02. Found: C, 83.67; H, 7.04)]; 8-nitro-1-hydroxymethylnaphthalene [38%, mp 72–73° from ether–ligroin (*Anal.* Calcd for $C_{11}H_9O_3N$: C, 65.02; H, 4.46; N, 6.89. Found: C, 64.84; H, 4.61; N, 6.70)].

Chloromethylnaphthalenes.—For the preparation of 1-chloromethylnaphthalene and 8-methoxy-1-chloromethylnaphthalene the method of Shoesmith and Rubli[6] involving passage of hydrogen chloride gas into benzene solution was employed. The remaining chlorides were obtained by addition of a thionyl chloride solution to the alcohol dissolved in chloroform.[5] The percentage yields, physical constants, recrystallizing solvents, and analytical data (where appropriate) for these chlorides are as follows: 1-chloromethylnaphthalene [45%, bp 137–139° (5.0 mm)[47]]; 8-chloro-1-chloromethylnaphthalene [86%, mp 47–48° from ligroin (*Anal.* Calcd for $C_{11}H_8Cl_2$: C, 62.58; H, 3.82; Cl, 33.59. Found: C, 62.39; H, 3.66; Cl, 33.36)]; 8-bromo-1-chloromethylnaphthalene [55%, mp 64–66° from ligroin (*Anal.* Calcd for $C_{11}H_8BrCl$: C, 51.70; H, 3.15; Cl, 13.88. Found: C, 51.58; H, 3.20; Cl, 13.65)]; 8-methoxy-1-chloromethylnaphthalene [55%, mp 46–47.5° from ligroin (*Anal.* Calcd for $C_{12}H_{11}ClO$: C, 69.73; H, 5.37; Cl, 17.16. Found: C, 69.93; H, 5.32; Cl, 16.95)]; 8-methyl-1-chloromethylnaphthalene [75%, mp 62.5–63.5° from ether–ligroin (*Anal.* Calcd for $C_{12}H_{11}Cl$: C, 75.59; H, 5.81; Cl, 18.60. Found: C, 75.37; H, 5.78; Cl, 18.90)]; 8-nitro-1-chloromethylnaphthalene [60%, mp 102–103.5° from ether–ligroin (*Anal.* Calcd for $C_{11}H_8O_2ClN$: C, 59.60; H, 3.64; Cl, 16.00; N, 6.32. Found: C, 59.87; H, 3.76; Cl, 15.72; N, 6.52)].

Solvolysis Procedure.—Approximately 0.15–0.20 g of the chloromethylnaphthalene weighed to the nearest 0.00002 g was diluted to 50.0 ml with 80% aqueous acetone, divided into nine 10-ml vials, and heated in a temperature bath maintained constant to ±1°. At appropriate time intervals the sample vials were removed from the temperature bath and swirled in an ice bath to stop the reaction. Exactly 5.00 ml of solution was pipeted into an erlenmeyer flask, and *ca.* 5 ml of 80% aqueous acetone was added to this solution. Titration of the hydrochloric acid that formed was accomplished with a standard sodium hydroxide solution to a blue lacmoid[48] end point (pH 4.4, red; pH 6.2, blue). The reaction solutions often became colored (amber to deep yellow) when solvolyzed longer than one or two half-lives. Hence, calculated infinity titers were used for calculating rate constants. Data for the solvolysis of 8-methyl-1-chloromethylnaphthalene, a typical example, are as follows: sample weight, 0.16855 g; base normality 0.01906; calcd infinity titer, 4.638 ml; 600 sec, 0.498 ml, 1.10 ($k_1 \times 10^4$ sec^{-1}); 1200 sec, 0.760 ml, 1.10; 2400 sec, 1.218 ml, 1.07; 3600 sec, 1.638 ml, 1.08; 5400 sec, 2.130 ml, 1.05; 7200 sec, 2.557 ml, 1.05; 10800 sec, 3.210 ml, 1.05; mean $k_1 \times 10^4$, 1.07 ± 0.02; average for two runs, 1.08 ± 0.02.

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