

Table I. Nmr Parameters of Alkylarylhalonium Ions^a

| Ion | CH ₃ X ⁺ | CH ₃ | -CH ₂ - | CH ₃ CX ⁺ | Aromatic | ¹⁹ F ^b |
|-----------------------------------------------------------------------------------|--------------------------------|-----------------|--------------------|---------------------------------|----------|------------------------------|
| C ₆ H ₅ -Br ⁺ -CH ₃ | 4.45 | | | | 7.5-7.9 | |
| C ₆ H ₅ -I ⁺ -CH ₃ | 3.80 | | | | 7.7-8.3 | |
| 4-FC ₆ H ₄ -I ⁺ -CH ₃ | 3.80 | | | | 7.0-8.1 | 103.4 |
| 4-FC ₆ H ₄ -Br ⁺ -CH ₃ | 4.40 | | | | 7.3-8.1 | 103.7 |
| 4-CH ₃ C ₆ H ₄ -I ⁺ -CH ₃ | 3.75 | 2.40 | | | 7.3-8.0 | |
| 4-CH ₃ C ₆ H ₄ -Br ⁺ -CH ₃ | 4.35 | 2.40 | | | 7.4-7.9 | |
| C ₆ H ₅ -I ⁺ -C ₂ H ₅ | | | 4.70 | 1.95 | 7.6-8.1 | |
| 4-FC ₆ H ₄ -I ⁺ -C ₂ H ₅ | | | 4.75 | 1.92 | 7.2-8.2 | 104.2 |
| C ₆ H ₅ -Br ⁺ -C ₂ H ₅ | | | 5.30 | 1.90 | 7.7-8.2 | |
| 4-FC ₆ H ₄ -Br ⁺ -C ₂ H ₅ | | | 5.35 | 1.90 | 7.3-8.1 | 104.1 |

^a Proton chemical shifts are from TMS in external capillary tube. Spectra were recorded at -70° in SO₂ solution at 60 MHz. Relative peak areas were in agreement with expectation. ^b Fluorine chemical shifts are from CF₃CCl₃ in external capillary tube. The chemical shifts of 4-fluorobromobenzene and 4-fluoroiodobenzene in SO₂ solution are 114.8 and 113.9 ppm, respectively.

fluorobenzene and chlorobenzene are more reactive toward the resulting ⁺SO₂CH₃ than the unshared electron pairs on halogen. The fluorine atom in any case is too electronegative to form a fluoronium ion. When chlorobenzene is added to methyl fluoroantimonate in SO₂ClF, sulfinylmethylation does not occur while methylation occurs on the aromatic ring to give chlorotoluenes and chloroxylenes.

All of the methylarylhalonium ions observed are stable to -20° as shown by pmr. When a SO₂ solution of the methylphenylbromonium ion 1-Br is heated in a sealed tube to 0° , decomposition readily occurs to give a mixture of bromoxylenes. The $n \rightarrow \pi$ methyl rearrangement is irreversible indicating that the C-methylated products are thermodynamically more stable once formed. The SO₂ solution of the methylphenyliodonium ion 1-I is considerable more stable. However, after 15 hr at room temperature in a sealed tube, rearrangement had occurred. Rearrangement of the ethylphenylbromonium ion 2-Br occurs readily at -70° to give C-methylated products.

These results indicate the possibility that alkylarylhalonium ions may play an important role in Friedel-Crafts alkylation of halobenzenes. The fact that alkylarylhalonium ions can alkylate aromatics in an intermolecular reaction is demonstrated by the reaction of the methylphenylbromonium ion 1-Br with benzene at -78° to give toluene and xylenes. Furthermore, in the presence of excess bromobenzene, the methylphenylbromonium ion is unstable even at -78° due to reaction with the excess bromobenzene to give bromotoluenes and bromoxylenes. The strong ability to alkylate aromatics is an explanation for the fact that bromoxylenes and not bromotoluenes are formed in the decomposition of ion 1-Br. Any bromotoluenes that are formed under these conditions would be immediately alkylated by the excess methylphenylbromonium ion to give bromoxylenes.

Alkylarylhalonium ions were shown to be good general alkylating agents not only for π , but also for n bases. Dimethyl ether, for example, when added to a SO₂ solution of the methylphenylbromonium ion 1-Br is methylated to the trimethyloxonium ion, trimethylamine is methylated to the tetramethylammonium ion, and methyl bromide is methylated to the dimethylbromonium ion. The fact that 1-Br reacts with methyl bromide to give dimethylbromonium ion irreversibly shows that methyl bromide has a greater affinity for the incipient methyl cation than bromobenzene.

The fact that one gets increasing amounts of the ortho alkylated isomer going through the series from fluorobenzene to iodobenzene in Friedel-Crafts alkylations has been generally explained by an intramolecular rearrangement of the intermediate alkylarylhalonium ions. However, if alkylarylhalonium ions are involved in alkylation reactions, the present results indicate that the preferred reaction pathway would proceed *via* an intermolecular methyl transfer and not an intramolecular rearrangement. Nevertheless the results do not discount the fact that Friedel-Crafts reactions carried out under the usual conditions may proceed by direct attack of the alkyl halide-Lewis acid complex on the aromatic ring.

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Strong Conformational Consequences of Hyperconjugation

Sir:

It is in ionic species that hyperconjugation comes to the fore.¹⁻⁴ We show here that in the cations XCH₂-CH₂⁺ or anions XCH₂-CH₂⁻ there may be large barriers to internal rotation due to hyperconjugation. *If X is more electronegative than H, then the cation will prefer conformation B, while the anion favors A. If X is less electronegative than H, then the cation favors A while the anion prefers B.*⁵ The magnitude of these preferences

(1) The molecular orbital representation of hyperconjugation was introduced by R. S. Mulliken, *J. Chem. Phys.*, **1**, 492 (1933); **3**, 520 (1935); **7**, 339 (1939).

(2) Proceedings of the Conference on Hyperconjugation, *Tetrahedron*, **5**, 105 (1959).

(3) M. J. S. Dewar and H. M. Schmeising, *ibid.*, **6**, 166 (1959); M. J. S. Dewar, "Hyperconjugation," Ronald Press, New York, N. Y., 1962.

(4) For reviews of anionic fluorine hyperconjugation, see (a) D. Holtz, *Progr. Phys. Org. Chem.*, **8**, 1 (1971), and (b) W. A. Sheppard and C. M. Sharts, "Organic Fluorine Chemistry," W. A. Benjamin, New York, N. Y., 1969, p 18 ff.

(5) Idealized geometries, locally tetrahedral at XCH₂, trigonal planar at CH₂, are here assumed also for the anion. Distortions from these are discussed below.

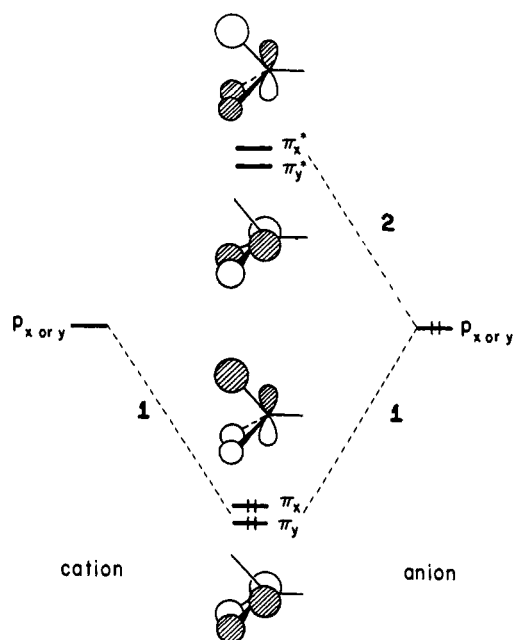


Figure 1. The π -type orbitals of a methyl group. In conformation A the adjacent p orbital is p_x ; in conformation B, it is p_y . Interaction 1 is the stabilizing cation interaction, while in the anion both 1 and 2 must be considered.



depends on the electronegativity of X but the range of the effect, as will be seen below, is impressively large.

The orbitals of a CH_3 group are well known.^{1,6} For interaction with a neighboring p orbital, the significant levels are those of local e symmetry or π_x , π_y , π_x^* , π_y^* of Figure 1. In the cation, where the $-\text{CH}_2$ p orbital is empty, interaction 1 (with π_x in conformation A, π_y in B) is stabilizing and dominant. In the anion, where the p orbital is occupied, a balance must be struck between interaction 1, now closed shell, four electron, destabilizing,⁷ and stabilizing interaction 2 (with π_x^* in A, π_y^* in B).^{4a} It is difficult to decide which interaction will dominate. For $\text{CH}_3-\text{CH}_2^+$ or planar $\text{CH}_3-\text{CH}_2^-$ there is no essential differential between interaction with π_x and with π_y . The barrier to internal rotation is sixfold and tiny.⁸⁻¹⁰

Now replace the CH_3 hydrogen in the xz plane by a group $-\text{X}$. To a first approximation π_y and π_y^* are

(6) Recent discussions include B. M. Gimarc, *J. Amer. Chem. Soc.*, **93**, 593 (1971), and P. H. Owens and A. Streitwieser, Jr., *Tetrahedron*, **27**, 4471 (1971).

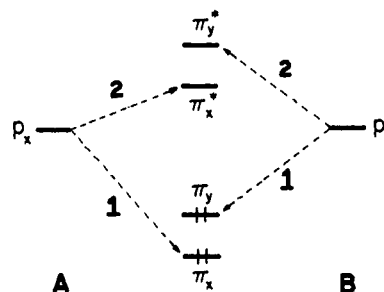
(7) L. Salem, *J. Amer. Chem. Soc.*, **90**, 543 (1968); K. Müller, *Helv. Chim. Acta*, **53**, 1112 (1970), and references cited therein.

(8) (a) W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 808 (1971); (b) R. Sustmann, J. E. Williams, M. J. S. Dewar, L. C. Allen, and P. v. R. Schleyer, *ibid.*, **91**, 5350 (1969); (c) J. E. Williams, V. Buss, L. C. Allen, P. v. R. Schleyer, W. A. Lathan, W. J. Hehre, and J. A. Pople, *ibid.*, **92**, 2141 (1970); (d) J. E. Williams, V. Buss, and L. C. Allen, *ibid.*, **93**, 6867 (1971). (e) The CH_3CH_2^- result is from unpublished work by W. J. Hehre.

(9) (a) G. V. Pfeiffer and J. G. Jewett, *J. Amer. Chem. Soc.*, **92**, 2143 (1970); (b) L. J. Massa, S. Ehrenson, and M. Wolfsberg, *Int. J. Quantum Chem.*, **4**, 625 (1970); (c) L. J. Massa, S. Ehrenson, M. Wolfsberg, and C. A. Frishberg, *Chem. Phys. Lett.*, **11**, 196 (1971).

(10) Clearly there is an inductive component to cation stabilization,^{8d} However, the conformational preferences are largely set by the relative hyperconjugating abilities discussed here.

unaffected. Two changes take place in π_x and π_x^* . If X is more electronegative than H, both π_x and π_x^* move to lower energy; if X is less electronegative, then they move to higher energy. Moreover the degree of localization of these orbitals increases. If X is more electronegative then π_x becomes more localized on X, π_x^* on C. If X is electropositive π_x becomes less localized on X, π_x^* less on C.¹¹ Conformations A and B are now differentiated, as shown below for the case of X more electronegative than H.



In the cation we need compare interaction 1 in A vs. B. p_y is closer in energy to π_y in B than p_x is to π_x in A. Moreover π_y is more localized on C than is π_x . Application of the simplest perturbation theoretic argument on both counts, smaller energy separation and greater overlap, favors B over A. In the anion interaction 1 is repulsive and, in a negative fashion, favors A over B. The attractive mixing 2 reinforces this effect. Thus the effect of substitution is the same whether 1 or 2 dominates. The conclusion stated in the introduction follows directly; a similar interaction diagram derives the converse argument for X less electronegative. *Ab initio* calculations show just how large this effect is. Table I lists computed barriers $E(\text{B}) - E(\text{A})$ for X = F and X = BH_2 .¹²⁻¹⁴

Table I. Calculated Barriers, $E(\text{B}) - E(\text{A})$, kcal/mol, for Two XCH_2-CH_2 Species

| | Cation | Radical | Anion |
|----------------------------------------|--------|---------|-------|
| $(\text{BH}_2)\text{CH}_2-\text{CH}_2$ | +10.4 | +0.3 | -6.2 |
| FCH_2-CH_2 | -8.4 | 0.0 | +9.2 |

Geometrical distortions from the idealized geometries are being studied. They no doubt occur. We emphasize that on theoretical grounds there is no dichotomy between participation with and without bridging. The hyperconjugative interaction will *always* be accompanied by geometrical adjustment, but the extent of that deformation may be small or large. Our calculations support in part the important recent

(11) The arguments may be found, among other sources, in E. Heilbronner and H. Bock, "Das HMO Modell und seine Anwendung," Verlag Chemie, Weinheim Bergstr., Germany, 1968, p 168 ff.

(12) Our calculations have used an STO-3G basis with standard geometries. The BH_2 group was fixed in the BCC plane in order to minimize 1,3 interaction. Details of the calculations for the cations, including barriers for X = OH, CH_3 , CN, and CCH, are given in ref 13.

(13) L. Radom, J. A. Pople, and P. v. R. Schleyer, submitted for publication in *J. Amer. Chem. Soc.*

(14) (a) Similar conclusions on $\text{FCH}_2-\text{CH}_2^+$ are reported by D. T. Clark and D. M. J. Lilley, *Chem. Commun.*, 603 (1970); D. T. Clark, *Proc. Int. Congr. Pure Appl. Chem.*, **1**, 31 (1971). (b) Compare also extended Hückel calculations on $\text{BrCH}_2-\text{CH}_2^+$ by G. Heublein and P. Hallpap, *J. Prakt. Chem.*, **312**, 245 (1970), and (c) CNDO/2 calculations on pyramidal $\text{FCH}_2-\text{CH}_2^-$ by D. Holtz, A. Streitwieser, and R. G. Jesaitis, *Tetrahedron Lett.*, 4529 (1969).

conclusions of Traylor and coworkers on σ - π conjugation in cations.^{15,16} Several ancillary points follow.

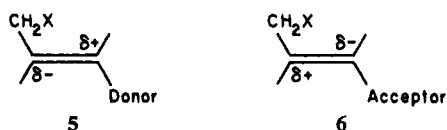
1. An argument equivalent to that given above is that a polar C-X bond is at its C end a better π acceptor than C-H, provided that X is more electronegative than H; that bond, however, is a better π donor if X is less electronegative than H. Increased π -bonding opportunities follow.



2. The anions $XCH_2-CH_2^-$ certainly pyramidalize at the carbanion end. Sizable V_1 and V_3 torsional terms then enter, but our argument accounts for the magnitude and sign of the twofold barrier component, V_2 .¹⁸ While the reliability of the numerical results for the anions remains to be established, it is the trend, opposite to that in the cations, which we stress.¹⁹

3. In the geometries we have studied, the conformationally dominating factor appears to be the hyperconjugative aptitude discussed above, rather than a direct 1,3 interaction of substituent lone pairs or vacant orbitals with $-CH_2^+$ or $-CH_2^-$. The 1,3 through-space interaction, significant in that it may lead to bridging as a consequence, appears to be important only in the unstable A conformations of $FCH_2-CH_2^+$ and $BH_2CH_2-CH_2^-$.

4. The arguments constructed here obviously can be extended to $YCX_2-CZ_2^+$ species, where the X-Y electronegativity difference is determinative. It also plays an important role in setting the equilibrium conformations of YCX_2-NZZ' , YCX_2-OZ , $NXY-OZ$,^{18,20,21} and other unsymmetrical neutral molecules, as well as ligands such as PX_2Y . Attenuated traces of this effect should influence the conformations of propylenes 5 and 6 substituted by π donors or acceptors.²²



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(15) T. G. Traylor, W. Hanstein, H. J. Berwin, N. A. Clinton, and R. S. Brown, *J. Amer. Chem. Soc.*, **93**, 5715 (1971), and references cited therein.

(16) Though experimental evidence (ref 17) points toward conformational preferences in $XCH_2-CH_2^-$ radicals as well, our calculations show only a small effect in the idealized geometry.

(17) (a) P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **93**, 846 (1971); T. Kawamura and J. K. Kochi, *ibid.*, **94**, 648 (1972); *J. Organometal. Chem.*, **30**, C8 (1971); T. Kawamura, D. J. Edge, and J. K. Kochi, *J. Amer. Chem. Soc.*, **94**, 1752 (1972); (b) A. R. Lyons and M. C. R. Symons, *Chem. Commun.*, 1068 (1971); *J. Amer. Chem. Soc.*, **93**, 7330 (1971).

(18) For a detailed analysis of torsional barriers, see L. Radom, W. J. Hehre, and J. A. Pople, *ibid.*, **94**, 2371 (1972).

(19) There is some disagreement on the role of fluorine hyperconjugation over our work and that of ref 4 and 14c.

(20) X, Y, Z, and Z' are substituents of different electronegativity.

(21) See also S. Wolfe, A. Rauk, L. M. Tel, and I. G. Csizmadia, *J. Chem. Soc. B*, 136 (1971).

(22) See, *inter alia*, R. D. Bach and P. A. Scherr, *J. Amer. Chem. Soc.*, **94**, 220 (1972), and references cited therein; J. M. J. Tronchet and Br. Baehler, *Helv. Chim. Acta*, **54**, 546 (1971).

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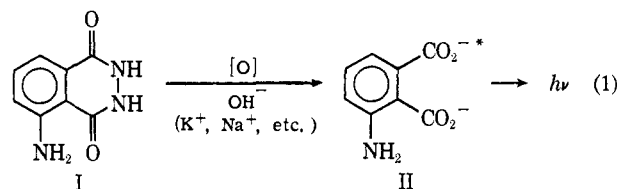
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Differences between Excited States Produced Chemically and Photochemically. Ion Pairs of Excited States

Sir:

Electronically excited states produced chemically, as in chemi- and bioluminescence, usually are identical with the corresponding states arrived at through light absorption.¹⁻³ Thus, in the chemiluminescence of luminol (I), 3-aminophthalate ion (II) is formed in an excited singlet state (eq 1), and the chemiluminescence



spectrum under most conditions is identical with the fluorescence spectrum of the aminophthalate ion.^{2,4} In aqueous dimethyl sulfoxide, however, the chemiluminescence and fluorescence spectra differ.⁴ We have verified and extended this observation and now show that the presence of the counterion (sodium in the earlier work⁴) is the causative factor.

The Water Effect. The chemiluminescence of luminol and the fluorescence of aminophthalate peak at 425 nm in water are independent of the base concentration

(1) (a) K. D. Gundermann, "Chemilumineszenz Organischer Verbindungen," Springer-Verlag, Berlin, 1968; (b) K. D. Gundermann, *Angew. Chem., Int. Ed. Engl.*, **4**, 566 (1965); (c) F. McCapra, *Pure Appl. Chem.*, **24**, 611 (1970).

(2) E. H. White and D. F. Roswell, *Accounts Chem. Res.*, **3**, 54 (1970).

(3) (a) E. H. White, E. Rapaport, H. H. Seliger, and T. Hopkins, *Bioorg. Chem.*, **1**, 92 (1971); (b) E. H. White and M. J. C. Harding, *Photochem. Photobiol.*, **4**, 1129 (1965); (c) C. C. Wei and E. H. White, *Tetrahedron Lett.*, 3559 (1971).

(4) (a) E. H. White, O. Zafriou, H. H. Kägi, and J. H. M. Hill, *J. Amer. Chem. Soc.*, **86**, 940 (1964); (b) E. H. White and M. M. Bursley, *ibid.*, **86**, 941 (1964).