

References and Notes

- (1) M. Sakai, D. L. Harris, and S. Winstein, *J. Chem. Soc., Chem. Commun.*, 861 (1972).
- (2) The mechanistic details of Wolff-Kishner reactions of hydrazones and previous complications therein have been summarized excellently by H. H. Szmant, *Angew. Chem., Int. Ed. Engl.*, **7**, 120 (1968), and by H. House, "Modern Synthetic Methods", 2nd ed, W. A. Benjamin, Menlo Park, Calif., 1972, p 228-239.
- (3) M. J. Goldstein and R. Hoffmann, *J. Am. Chem. Soc.*, **93**, 6193 (1971), and references therein.
- (4) (a) These initial experiments were conducted by D. C. Sanders, Ph.D. Dissertation, The Ohio State University, 1972. (b) All subsequent research was carried out by T. V. Rajan Babu, Ph.D. Dissertation, The Ohio State University, 1976.
- (5) The method summarized is superior for preparing the indicated product.
- (6) (a) All new compounds are of proper analysis and mass, NMR, and IR spectra. (b) Deuterated derivatives were assigned by NMR and mass spectral methods. The proton contents at C₂-C₅, C₇-C₈, and C₉ in **9** and **10** were determined by NMR integration relative to that at C₁ and C₆.
- (7) Wolff-Kishner reaction of tricyclo[6.1.0.0^{4,9}]nona-2,6-dien-5-one (homosembullvalenone) with potassium hydroxide/hydrazine/diethylene glycol at reflux (210 °C) yields **5** (95%) presumably via kinetic capture of **4**,^{4b} **3** was not detected.
- (8) (a) The resistance of conversion of **3** to **2** is further revealed by the observation that reaction of **3** with lithium cyclohexylamide in cyclohexylamine-*N*-d₂ gives recovered triene with 89% deuterium on the monoene, 55% on the diene, and 0% at the C₉ positions. (b) A similar result has been reported by R. R. Boettcher, Ph.D. Dissertation, University of Wisconsin, Madison, Wis., 1970.
- (9) Prepared with ~80% deuterium incorporation by treatment of bicyclo[4.2.1]nona-2,4,7-trien-9-one hydrazone with excess deuterium oxide in methylene chloride.
- (10) T. A. Antkowiak, D. C. Sanders, G. B. Trimitsis, J. B. Press, and H. Shechter, *J. Am. Chem. Soc.*, **94**, 3366 (1972).
- (11) (a) It has been previously observed that Wolff-Kishner reduction of bicyclo[4.2.2]deca-2,4,9-trien-7-one by hydrazine/potassium hydroxide/ethylene glycol fails to produce bicyclo[4.2.2]deca-2,4,7-triene.^{11b} Under these conditions the decatrienone is converted to 2,3-diazatricyclo[6.3.1.0^{4,11}]dodeca-2,5,9-triene.^{11b} (b) J. B. Press and H. Shechter, *J. Org. Chem.*, **40**, 2446 (1975). (c) NOTE ADDED IN PROOF. After submittal of this manuscript, M. Kato, T. Chikamoto, and T. Miwa, *Bull. Chem. Soc. Jpn.*, **50** (5), 1082 (1977), reported that benzo[7,8]bicyclo[4.2.1.]nona-2,4,7-trien-9-one hydrazone reacts with potassium *tert*-butoxide/dimethyl sulfoxide to give 9,10-diazabenzocyclo[2,3]tricyclo[6.3.0.0^{4,11}]undeca-2,6,9-triene which pyrolyzes at 180°C or photolyzes with a high pressure lamp to yield benzo[6,7]tricyclo[6.1.0.0^{4,9}]nona-2,6-diene. These transformations are thus formally analogous to the conversions of **1** to **14** and then **5** in the present communication.
- (12) For related experiments and theory, see J. K. Stille and K. N. Sannes, *J. Am. Chem. Soc.*, **94**, 8489 (1972), and references therein.

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In Support of Anionic Hyperconjugation. The Versatile Methyl Group

Sir:

The direction of secondary isotope effects on the rates of solvolytic reactions proceeding through carbocationic transition states¹ and on gas phase equilibria involving stable carbocations² has been ascribed to hyperconjugation. In the language of perturbation molecular orbital theory,³ interaction of the highest filled, π symmetry, orbital on a methyl (CD₃) group with the vacant p function at C⁺ results not only in net energetic stabilization but also in significant charge reorganization. Specifically, electron density is removed from the methyl CH linkages, resulting in their weakening. The associated reduction in CH stretching force constants leads directly to the observed kinetic and thermodynamic preference for formation of the light cation.⁴

In this communication we present experimental and theoretical evidence in support of the notion that hyperconjugative factors are also operative in the interaction of anionic centers with alkyl substituents. Our data have led us to conclude that a methyl group attached to a center of negative charge may

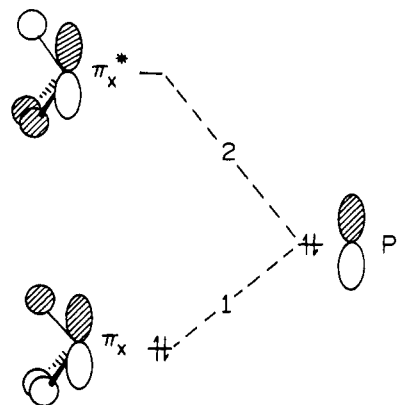
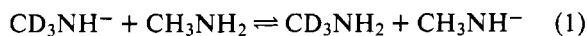


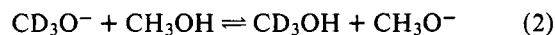
Figure 1. Interaction of a methyl group with the lone pair on an anionic center.

act as an electron acceptor. Furthermore, they indicate that the intrinsic electron-withdrawing ability of a methyl group is comparable with, if not greater than, its ability to donate charge in those instances where it is attached to an electron-deficient center.

We have determined by pulsed ion cyclotron resonance spectroscopy⁵ the free energies of the proton transfer equilibria 1, 2, and 3



$$\Delta G^\circ = -0.37 \pm 0.08 \text{ kcal/mol}^{6,7}$$

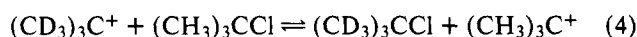


$$\Delta G^\circ = -0.50 \pm 0.10 \text{ kcal/mol}^6$$



$$\Delta G^\circ = -0.30 \pm 0.08 \text{ kcal/mol}^6$$

involving formation, in the gas phase, of the methylamino, methoxy, and thiomethoxy anions. In all three cases equilibrium lies to the right (i.e., favors the formation of the light ion), the same preference which has been observed thermodynamically² and kinetically¹ for processes leading to the buildup of positive charge adjacent to a methyl probe (e.g., reaction 4).²



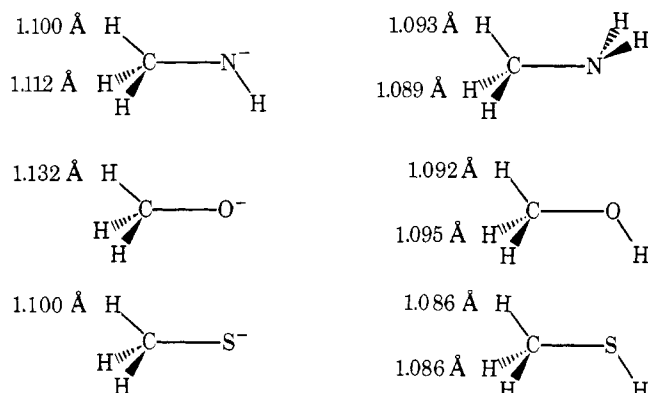
$$\Delta G^\circ (\text{per CD}_3) = -0.12 \pm 0.05 \text{ kcal/mol}^6$$

The preferences are also in the same direction, but of far greater magnitude, than secondary effects noted kinetically in solution for reactions leading through what are suspected to be anionic transition states.⁸

The observed isotope effects may be rationalized using the perturbation molecular orbital theory.³ Interaction of a methyl group with the lone pair on an anionic center to which it is attached through the σ system is describable in terms of stabilizing and destabilizing components (Figure 1). The four-electron term, 1, involving interaction of the methyl π orbital and the lone pair at the anion center, results in net energetic destabilization. Both functions are fully occupied, and little if any redistribution of electron density is to be expected. Significant charge reorganization is to be anticipated as a result of the stabilizing two-electron interaction, 2. Specifically, electron density is shifted away from the nonbonded lone pair at the anion center and directed into a CH antibonding orbital on methyl. As a result the CH bonds should weaken giving rise to the observed isotopic preference for formation of the light anion.

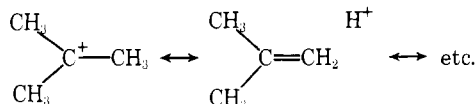
Ab initio molecular orbital calculations at the minimal basis STO-3G level^{9,10} concur with the conclusions of the simple

perturbation model. In particular, calculated CH bond lengths for the methylamino, methoxy, and thiomethoxy anions are significantly longer than those in the corresponding neutral precursors. Preliminary calculations using the split-valence-shell 4-31G basis representation¹¹ substantiate these conclusions.

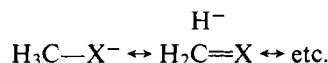


It is, of course, an oversimplification to ascribe the observed secondary β -deuterium isotope effects in these systems to changes in CH stretching force constants alone. Other factors (i.e., changes in bending force constants) no doubt contribute to the total, and need to be considered in any complete analysis. The preliminary results of theoretical studies, aimed at obtaining the energies of processes such as 1-3 from first principles, using complete quadratic force fields from ab initio molecular orbital calculations, suggest, however, that changes in CH stretching force constants are the primary cause behind the observed isotope effects.¹²

The connection between the results of the perturbation molecular orbital treatment and those of classical resonance theory should be noted. Just as the predicted CH bond lengthening (and CC bond shortening) in a species such as the *tert*-butyl cation may be ascribed to contributions of hyperconjugative resonance structures of the form



the calculated geometrical distortions (and observed equilibrium isotope effects) for the methylamino, methoxy, and thiomethoxy anions indicate the involvement of the corresponding negative hyperconjugative structures



Although resonance structures such as these have often been written in cases where F^- is detached¹³ (i.e., $\text{>C}^--\text{CF}_3 \leftrightarrow \text{>C}=\text{CF}_2 \text{F}^-$), the notion of negative hyperconjugation for simple alkyl substituents attached to anionic centers has not received support. This is probably due to the fact that, in solution, alkyl groups inevitably act to decrease rather than to increase acidity.¹⁴ This is not always the case in the gas phase, for here methylamine is a stronger acid than ammonia,¹⁵ and methanol a stronger acid than water.¹⁶ Methanethiol is, however, a weaker acid than hydrogen sulfide.¹⁷ It should be emphasized, therefore, that *relative acidity is not an appropriate measure of the importance of anionic hyperconjugation*. Other factors need to be considered, in particular, the extent of repulsive interactions between the methyl group and the anionic center. The magnitudes and directions of secondary isotope effects are, on the other hand, appropriate indicators, for they are a direct reflection of the changes in bonding which occur as a result of anion formation.¹⁸ For the systems considered here, these quantities suggest the importance of neg-

ative hyperconjugative structures involving hydrogen and, therefore, the ability of a methyl group to act as an electron acceptor. This observation, taken together with those on electron-deficient systems, indicates that the methyl substituent is capable of adopting to its immediate environment, serving to donate or to accept electronic charge depending on the needs of the moiety to which it is attached.

References and Notes

- (1) For reviews, see (a) V. J. Shiner, *ACS Monogr.*, no. 167, 90 (1970); (b) D. E. Sunko and S. Borcic, *ibid.*, no. 167, 160 (1970).
- (2) J. L. Devlin, III, J. F. Wolf, J. L. M. Abboud, R. W. Taft, and W. J. Hehre, *J. Am. Chem. Soc.*, in press.
- (3) For discussions of the application of the perturbation molecular orbital theory to the structures and stabilities of carbocations, see (a) W. J. Hehre, *Acc. Chem. Res.*, **8**, 369 (1975); (b) R. Hoffmann, L. Radom, J. A. Pople, P. v. R. Schleyer, W. J. Hehre, and L. Salem, *J. Am. Chem. Soc.*, **94**, 6221 (1972); (c) W. L. Jorgensen and L. Salem, "The Organic Chemists Book of Orbitals", Academic Press, New York, N.Y., 1973.
- (4) J. Bigeleisen and M. G. Mayer, *J. Chem. Phys.*, **15**, 261 (1947).
- (5) Trapped ion cyclotron resonance spectroscopy. Method: (a) R. T. McIver, Jr., *Rev. Sci. Instrum.*, **41**, 555 (1970); (b) J. D. Baldeschwieler and S. S. Woodgate, *Acc. Chem. Res.*, **4**, 114 (1971); (c) R. T. McIver, Jr., and R. C. Dunbar, *Int. J. Mass Spectrom. Ion Phys.*, **7**, 471 (1971). Application to the determination of equilibrium isotope effects: ref 2 and (d) J. F. Wolf, J. L. Devlin, III, R. W. Taft, M. Wolfsberg, and W. J. Hehre, *J. Am. Chem. Soc.*, **98**, 287 (1976).
- (6) Errors quoted correspond to two standard deviations.
- (7) It should be mentioned that the possibility exists for the deuterium label in the methylamino anion to scramble onto the nitrogen. Although we have no evidence for this at present, rapid scrambling has been noted in a number of instances involving carbocations (e.g., isopropyl).
- (8) (a) A. Streitwieser, Jr., and D. E. Van Sickle, *J. Am. Chem. Soc.*, **84**, 254 (1962), and references therein. For a review, see (b) E. A. Halevi, *Prog. Phys. Org. Chem.*, **1**, 109 (1963).
- (9) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969). All calculations have been performed using the Gaussian 70 series of computer programs: W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, program no. 236, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.
- (10) Little is known experimentally about the structures of anions with which to test the predictions of the ab initio calculations regarding their geometries. The small amount of experimental structural data which is available appears to be adequately reproduced by molecular orbital calculations at the minimal basis set STO-3G level, and better so by computations using the split-valence-shell 4-31G method. (For a review, see (a) L. Radom, *Aust. J. Chem.*, **29**, 1635 (1976).) More importantly, the theoretical methods employed in the present study have been shown to be capable of reproducing the known geometrical structures for a wide variety of neutral species. (For reviews, see (b) W. A. Lathan, W. J. Hehre, L. A. Curtiss, J. B. Lisle, and J. A. Pople, *Prog. Phys. Org. Chem.*, **11**, 175 (1974); (c) W. J. Hehre, *Acc. Chem. Res.*, **9**, 399 (1976); (d) J. A. Pople in "Modern Theoretical Chemistry", H. F. Schaefer, Ed., Plenum Press, New York, N.Y., in press.) Hence, some degree of confidence may be put in their findings in situations where experimental data are unavailable.
- (11) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971).
- (12) D. J. DeFrees, E. A. Peter, D. Hassner, M. Wolfsberg, and W. J. Hehre, research in progress.
- (13) (a) D. Holtz, *Prog. Phys. Org. Chem.*, **8**, 1 (1971); (b) W. A. Sheppard and C. M. Sharts, "Organic Fluorine Chemistry", W. A. Benjamin, New York, N.Y., 1969, p 18 ff; (c) D. J. Cram, "Fundamentals of Carbanion Chemistry", Academic Press, New York, N.Y., 1965, p 68 ff.
- (14) For example, see (a) J. Hine and M. Hine, *J. Am. Chem. Soc.*, **74**, 5266 (1952); (b) M. M. Kreevoy, B. E. Eighinger, F. E. Stary, E. A. Katz, and J. H. Sellstedt, *J. Org. Chem.*, **29**, 1641 (1964).
- (15) (a) J. I. Brauman and L. K. Blair, *J. Am. Chem. Soc.*, **93**, 3911 (1971); (b) G. I. Mackay, R. S. Hemsworth, and D. K. Bohme, *Can. J. Chem.*, **54**, 1624 (1976).
- (16) (a) J. I. Brauman and L. K. Blair, *J. Am. Chem. Soc.*, **92**, 5986 (1970); (b) D. K. Bohme, E. Lee-Ruff, and L. B. Young, *ibid.*, **93**, 4608 (1971); (c) J. S. Miller and R. T. McIver, Jr., *ibid.*, **96**, 4323 (1974).
- (17) J. E. Bartmess and R. T. McIver, Jr., *J. Am. Chem. Soc.*, **99**, 4163 (1977).
- (18) A referee has commented that there exists substantial evidence in favor of the notion that CD bonds act as though they were better electron donors than CH linkages. Such an inductive influence would act in the same direction as the proposed hyperconjugative effect (i.e., favor formation of the isotopically light anion), although would by itself not be likely to account for the large magnitudes of the isotopic preferences noted.
- (19) (a) University of California Regents Intern Fellow, 1974-1978; (b) Alfred P. Sloan Fellow, 1973-1976; (c) Alfred P. Sloan Fellow, 1974-1976. This work has been supported in part by grants from the National Science Foundation and by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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