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Dipole-Stabilized Carbanions from a Methyl Thio Ester and a Methylamide

Sir:

Dipole-stabilized carbanions, species in which inductive stabilization of the negative charge on carbon is provided by an α heteroatom which is the positive end of a dipole, have been postulated as reaction intermediates in base-catalyzed hydrogen-deuterium exchanges,¹⁻¹³ base-promoted rearrangements,¹⁴ metalations,¹⁵⁻²¹ and decarboxylation.²² The permanent dipole of amine oxides provides a number of examples of such an effect, and, for a variety of functions,¹⁴⁻²¹ metalated species have been trapped by electrophiles in synthetically useful reactions. The formation and electrophilic trapping of a dipole-stabilized carbanion from dibenzylbenzamide reported by Fraser, *et al.*,¹⁹ is an important advance in the synthetic use of carboxamide-stabilized carbanions; however, these are, at present, less useful than analogous species from nitrosoamines.¹⁸

(1) P. Beak and J. Bonham, *J. Amer. Chem. Soc.*, **87**, 3365 (1965); the 2 anion of *N*-methyl-1,4-pyridone provides a case for the importance of inductive stabilization by the nitrogen of a vinylogous amide function.

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(3) H. U. Blank, I. Wempfen, and J. J. Fox, *ibid.*, **35**, 1131 (1970); J. A. Rabi and J. J. Fox, *J. Amer. Chem. Soc.*, **95**, 1628 (1973).

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(13) R. R. Fraser and Y. Y. Wigfield (*Tetrahedron Lett.*, 2515 (1971)) report that inductive stabilization is not a dominant factor for *N*-nitrosoamines and favor resonance stabilization of the anion in that case.

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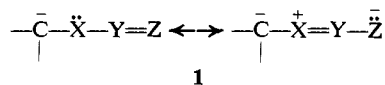
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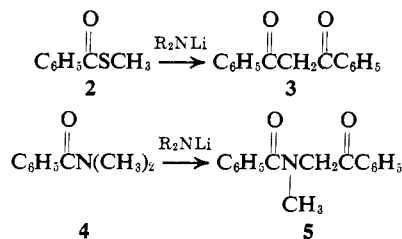
(22) P. Beak and R. Watson, *Tetrahedron*, **27**, 953 (1971); P. Beak and B. Siegel, unpublished work.

Although serious questions need to be raised about the contribution of inductive effects in each case,^{1,13,23,24} there are experimental indications that carbanion stabilization may be provided by a number of mesomeric dipoles as generalized in formula 1. The possible opera-



tion of such stabilization has been individually noted for carboxamides^{2,3,14,19} and a vinylogous carboxamide¹ (1, X—Y=Z = —N—C=O), nitrosoamines^{12,13,18} (1, X—Y=Z = —N—N=O), imidates which are part of polyazaheteroaromatic systems (1, X—Y=Z = —N—C=N—),^{10,11,16} isonitriles¹⁷ (1, X—Y=Z = —N=C:), and a vinylogous thio ester² (1, X—Y=Z = —S—C=O); this factor could be important for carbanions from isothiocyanates²⁰ (1, X—Y=Z = —N=C=S) and dithioimides²¹ (1, X—Y=Z = SC(S)=N—). We wish to draw attention to the formal correlation among carbanions stabilized by these different functions, to suggest that dipole-stabilized carbanions may be more accessible as reaction intermediates than previously suspected, and to provide two examples of novel reactions which appear to involve such species.

Reaction of methyl thiobenzoate (2) with lithium 2,2,6,6-tetramethylpiperidide²⁵ in tetrahydrofuran at ambient temperature gives a 64% yield²⁶ of dibenzoylmethane (3). Reaction of dimethylbenzamide (4) under the same conditions gives a 60% yield of methylphenacylamide (5).²⁷



These transformations can be reasonably postulated to involve initial formation of the dipole-stabilized carbanion 6. Conversion of 6 to products could follow at least two different routes: intramolecular rearrangement to give 7 which reacts with 2 or 4 to give 8, or direct reaction of 6 with 2 or 4 to give 8. The conversion of 8, X = S, to 3 could involve intramolecular rearrangement of 8 or reaction with another molecule of 2 and cleavage of the α sulfur-carbon bond induced by the thiolate.²⁸

The postulation of 6 (X = S) as a reaction intermediate appears to be the first suggestion that the thio ester function might act as a dipole-stabilizing function for a carbanion, although d-orbital effects may be impor-

(23) Inductive stabilization by different dipoles is generally noted as a possible contributor to anion stability: D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, Chapter 2.

(24) For an excellent review of α -heteroatom-substituted organometallic compounds, see D. J. Peterson, *Organometal. Chem. Rev., Sect. A*, **7**, 295 (1972).

(25) R. A. Olofson and C. M. Dougherty, *J. Amer. Chem. Soc.*, **95**, 582 (1973), and references cited therein.

(26) The crude yield is 84%, based on 3 mol of starting thio ester.

(27) The material is identical by melting point, mixture melting point, nmr, and ir spectral criteria with independently prepared material: D. G. Ott, F. N. Hayes, and V. N. Keir, *J. Amer. Chem. Soc.*, **78**, 1941 (1956).

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