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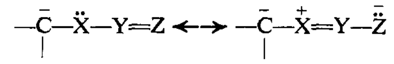
Dipole-Stabilized Carbanions from a Methyl Thio Ester and a Methylamide

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]

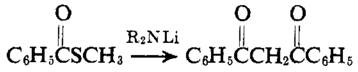
Although serious questions need to be raised about the contribution of inductive effects in each case,[1,13,23,24] there are experimental indications that carbanion stabilization may be provided by a number of mesomeric dipoles as generalized in formula **1**. The possible operation of such stabilization has been individually noted for carboxamides[2,3,14,19] and a vinylogous carboxamide[1] (**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] isonitriles[17] (**1**, X—Y=Z = -N=C:), and a vinylogous thio ester[2] (**1**, X—Y=Z = -S—C=O); this factor could be important for carbanions from isothiocyanates[20] (**1**, X—Y=Z = -N=C=S) and dithioimidates[21] (**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.



$$-\underset{|}{\overset{-}{C}}-\ddot{X}-Y{=}Z \longleftrightarrow -\underset{|}{\overset{-}{C}}-\overset{+}{X}{=}Y-\overset{=}{Z}$$

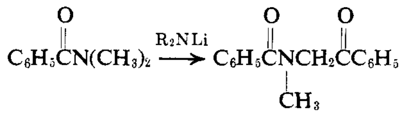
1

Reaction of methyl thiobenzoate (**2**) with lithium 2,2,6,6-tetramethylpiperidide[25] in tetrahydrofuran at ambient temperature gives a 64% yield[26] of dibenzoylmethane (**3**). Reaction of dimethylbenzamide (**4**) under the same conditions gives a 60% yield of methylphenacylbenzamide (**5**).[27]



$$C_6H_5\overset{O}{\overset{\|}{C}}SCH_3 \xrightarrow{R_2NLi} C_6H_5\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}C_6H_5$$

2 **3**



$$C_6H_5\overset{O}{\overset{\|}{C}}N(CH_3)_2 \xrightarrow{R_2NLi} C_6H_5\overset{O}{\overset{\|}{C}}\underset{\underset{CH_3}{|}}{N}CH_2\overset{O}{\overset{\|}{C}}C_6H_5$$

4 **5**

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-

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(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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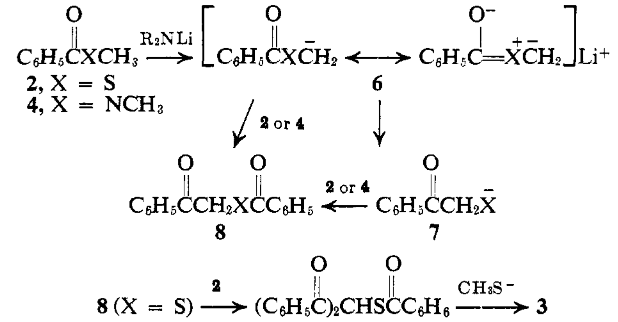

tant and a similar effect has been noted for a vinylogous thio ester.[2] Carbanion 6 (X = NCH_3) appears to be the first carboxamide-stabilized species[1-3,14,19] which is not also a vinylic or benzylic anion. It is clear that the actual amount of inductive stabilization provided by the dipole is a matter of conjecture and, in fact, a homoenolate ion[29] could be postulated as an alternative to **6**, although analogous species are not reasonable for many of the precedents.[1-22] The proposal of **6** raises a number of intriguing mechanistic and structural questions, which are under investigation.

Acknowledgement. We are grateful to Professors R. R. Fraser and R. A. Olofson for preprints and cogent discussion and to the National Institutes of Health for support of this work.

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*Book Reviews**

Analysis and Simulation of Biochemical Systems. Volume 25 of the Proceedings of FEBS. Organized by H. C. HEMKER and B. HESS. North Holland/American Elsevier, New York, N. Y. 1972. vi + 460 pp. $25.75.

The Eighth Meeting of FEBS, held in Amsterdam in August, 1972, gave rise to the 31 papers reproduced in this volume. They are largely concerned with models for enzyme systems and are organized in six groups: Thermodynamics, Mathematics, Enzymology (General), Spatially Structural Systems, Studies on Specific Enzymes, and Computation of Structure. They are photographically reproduced from the authors' typescripts, in the interest of prompt appearance, but they include many figures and, of course, references. All are in English. The publishers are to be commended for providing an index.

Cellular Antigens. Edited by ALOIS NOWOTNY. Springer Verlag, New York, N. Y. 1972. xi + 329 pp. $26.00.

The thirty lectures and summaries of a conference held in Philadelphia in 1971 are collected in this book. They demonstrate the intense interest in determining the structure and chemical nature of antigens as a basis for understanding their biological function. The papers are nicely reproduced, with illustrations, figures, tables, and references, together with subject and author indexes.

Compendium of Organic Synthetic Methods. By I. T. HARRISON and S. HARRISON (Syntex Research). Wiley-Interscience, New York, N. Y. 1971. xv + 529 pp. $11.95.

The title of this volume inevitably invites comparison with other recent works in which synthetic organic chemistry is treated. In format it resembles "Annual Reports in Organic Synthesis," in that there is no discursive text but only equations with succinct notations of conditions and yields. This allows a very large amount of information to be presented in uncluttered, easily scanned form.

The material is organized into fourteen chapters by functional group (*e.g.*, "Olefins," "Ethers and Epoxides," etc.). Within each chapter the content is divided into sections according to starting material (*e.g.*, "Olefins from Aldehydes"). References for each method are given adjacent to the equation, which saves time; they are given in condensed form, without authors' names (*e.g.*, "JACS (1946) **68,** 1085"). Important reviews are also noted. The literature coverage extends into 1970, with emphasis on recent works, and the sources are eclectic. The logical arrangement of the material obviates need for an index.

This book is essentially complementary to such works as Buehler and Pearson's "Survey of Organic Syntheses" and Fieser and Fieser's "Reagents for Organic Synthesis." It is a very usable volume and a bargain at just over 2¢ a page; it deserves a wide sale.

Drugs and Society. Edited by VICTOR SNIECKUS (University of Waterloo). Department of Chemistry, University of Waterloo, N2L 3G1, Canada. 1973. 39 pp. $1.00.

The four lectures composing a symposium held in 1972 are given in full in this booklet, together with biographies of the lecturers and transcripts of the discussions. The subjects are: Plant Hallucinogens (R. E. Schultes); Non-Medical Use of Drugs (H. Kalant); Recreational Drugs and the Law (A. C. Whealy); and Combat of Narcotic Abuse (I. J. Pachter). The articles provide excellent orientation to chemists who are increasingly being asked about these subjects regardless of their personal specialties.

From Plasma to Planet. Nobel Symposium 21. Edited by AINA ELVIUS. Wiley-Interscience, New York, N. Y. 1972. 389 pp. $25.00.

This book embodies the proceedings of an international invited symposium held in 1971 to bring together cosmogonists and space-research scientists. The twenty-four papers are concerned with matter in cosmic space, particularly plasma, from the viewpoint of possible origins of the planets. There runs through the Symposium the implied general acceptance of condensation of plasma as a major phenomenon in the origin of the Solar System; it will be interesting to see how this view stands the test of time, since so many other seemingly satisfactory hypotheses have eventually had to be discarded.

Not all the papers are by any means chemical; they range from "Atomic and Molecular Reactions in Space" to "Semantics," but in general make fascinating reading. Much space is given to reproducing the discussions following the papers; it is a pity that a little bit could not have been spared for an index.

Handbook of Chromatography. Volumes I and II. Edited by GUNTER ZWEIG (Syracuse University Research Corporation) and JOSEPH SHERMA (Lafayette College). CRC Press, Cleveland, Ohio. 1972. Vol. I: 784 pp. $36.50. Vol. II: 343 pp. $21.50.

The first volume of this work consists of a collection of 549 tables of R_f values for gas, liquid-column, paper, and thin-layer chromatography. These tables are organized in a consistent form, and present clearly the absorbent and the developing agent, with references to the literature sources conveniently located beneath each table. Some tables are quite short, but some, such as those on Steroids and Derivatives, are extensive.

The last 125 pp of Volume I is a compound index, by which it is intended that one can quickly locate the tables in which a given substance is listed. It is an alphabetical index, and the compilers appear to have used the names as published by the original investigators, without attempt at standardization. This is a serious drawback to the use of this work, for it has led the compilers unthinkingly to scatter the entries for a single compound under different names,

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* Unsigned book reviews are by the Book Review Editor.