The Diels–Alder adduct of anthracene and vinyl acetate[2] was hydrolyzed to the secondary alcohol, oxidized to the ketone[3] and converted with methylmagnesium iodide to the tertiary alcohol, m.p. 134–5°. Calcd. for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.46; H, 6.84. This with thionyl chloride gave Ia, m.p. 92–93°. Calcd. for $C_{17}H_{15}Cl$: C, 80.14; H, 5.93. Found: C, 80.15; H, 6.27. Ib was obtained via exchange of some of the ketonic precursor of Ia with deuterium oxide in boiling dioxane. Ic was made by the same route from anthracene-9,10-d_2, 1.79 atoms D per molecule, from reduction of anthrone.[4] N.m.r. spectra of Ia, Ib and the corresponding ketones were entirely consistent with these formulations and showed the deuterium compounds to be *ca.* 90% isotopically pure. Solvolysis of Ia in 60% aqueous dioxane produced olefin and unrearranged tertiary alcohol. The solvolysis rate constants measured conductometrically are given in the table.

TABLE

FIRST ORDER RATE CONSTANTS (10^{-5} SEC.$^{-1}$) FOR SOLVOLYSIS IN "60%" AQ. ETHANOL AT 45.00°

Each constant given is the average for one experiment of a number of integrated rate constants calculated for points taken over about three half lives. The point by point values drifted downward 1% or less during any run.

Compound			k		k_H/k_D
Ia	9.05	8.98	8.99^a	9.14^{a,b}	
Ib	7.80	7.88	7.92^a		1.14 ± 0.01
Ic	9.12	9.29^{a,b}			0.986 ± 0.01

[a] Taken after one additional recrystallization of previously used material. [b] Run in a second solvent batch.

These figures show that occurrence of the β-deuterium isotope effect depends not only on the position but also on the *orientation* of the isotopic bond. *This result is strikingly consistent with the previous suggestion that hyperconjugative intramolecular transmission of electronic charge is an essential factor in causing β-deuterium substituted compounds to give slower carbonium ion type reactions than their protium analogs.*[5] Theory predicts that hyperconjugation between the bridgehead deuterium atom in Ic and the carbonium ion center resulting from solvolytic loss of the chloride ion would be largely sterically prevented. In molecular orbital terms this is because the two orbitals which must overlap for hyperconjugation are mutually perpendicular. In valence-bond terms this is because contributing forms having double bonds at the bridgehead carbon atom would be too unstable to contribute significantly (Bredt's rule). Thus with Ic the normal isotope rate effect, observed with Ib and other β-deuterio tertiary chlorides,[5] is not found. Instead a very small "inverse" isotope effect, apparently due to an inductive interaction between the reaction center and the isotopic bond, appears. *It would seem that for the first time the inductive and hyperconjugative contributions to β-deuterium secondary isotope rate effects on a carbonium ion solvolysis reaction have been isolated for quantitative comparison.*

Acknowledgments.—The author appreciates the kind hospitality and assistance with this problem given him at University College, London, and at the École Nationale Supérieure de Chimie at Montpellier, France, during the tenure of his sabbatical leave. The author is indebted to Dr. F. Winternitz for the microanalyses and to Dr. Brian Figgis for the n.m.r. spectra.

CONTRIBUTION NO. 927
DEPARTMENT OF CHEMISTRY
INDIANA UNIVERSITY
BLOOMINGTON, INDIANA
V. J. SHINER, JR.

RECEIVED MARCH 11, 1960

---

(2) K. Alder and H. F. Rickert, *Ann.*, **543**, 1 (1939).

(3) S. Wawzonek and J. V. Hallum, *J. Org. Chem.*, **18**, 288 (1953).

(4) V. Gold and F. A. Long, THIS JOURNAL, **75**, 4543 (1953).

(5) For review of these results see V. J. Shiner, Jr., *Tetrahedron*, **5**, 243 (1959); E. S. Lewis, *ibid.*, **5**, 143 (1959).

A NEW SYNTHESIS OF ALIPHATIC AND AROMATIC THIOAMIDES FROM NITRILES

Sir:

Previously available methods for the preparation of thioamides from nitriles involve heating the nitrile in alcoholic solution in the presence of an alkali-metal hydrogen sulfide[1] or an ammonium[2] or substituted ammonium[1] sulfide. The formation of aliphatic thioamides under these conditions requires the use of high pressures in an autoclave,[3] and the method is facile only with aromatic nitriles containing electron-withdrawing substituents.[1] However, reduction can take place even under mild conditions, and the formation of *p*-aminothiobenzamide from *p*-nitrobenzonitrile is illustrative.[4,5] The use of a mixture of triethylamine and pyridine as a catalyst for the direct addition of hydrogen sulfide to nitriles is useful only for aromatic nitriles and has little value for the preparation of aliphatic thioamides.[6] Thioacids have found limited application as a source of hydrogen sulfide for this conversion.[7,8]

We wish to report a new and general synthesis of thioamides from nitriles which utilizes thioacetamide as a source of hydrogen sulfide under acidic conditions. The thioamides are formed in good yield in a high state of purity, and the method is equally applicable to aliphatic nitriles, and aromatic nitriles containing either electron-releasing, electron-withdrawing or potentially reducible substituents. One equivalent of the nitrile is heated on a steam-bath for 15–30 minutes with two equivalents of thioacetamide in dimethyl-

Nitrile	Thioamide	Yield, %	M.p., °C.	Ref.
p-$O_2NC_6H_4CN$	*p*-$O_2NC_6H_4CSNH_2$	83	158.5–159.5	7
p-$CH_3OC_6H_4CN$	*p*-$CH_3OC_6H_4CSNH_2$	87	148.5–149.5	6,9
$CH_2(CN)_2$	$CH_2(CSNH_2)_2$	63	211–212 d.	10
$NC(CH_2)_4CN$	$H_2NCS(CH_2)_4CSNH_2$	78	178.5–179.5 d.	3,11,12

---

(1) K. Kindler and F. Burghard, *Ann.*, **431**, 201 (1923).

(2) S. Gabriel and P. Heymann, *Ber.*, **23**, 157 (1890).

(3) H. Erlenmeyer and K. Degen, *Helv. Chim. Acta*, **29**, 1080 (1946).

(4) C. Engler, *Ann.*, **149**, 297 (1869).

(5) A. W. Hofmann, *Ber.*, **1**, 194 (1868).

(6) A. E. S. Fairfull, J. L. Lowe and D. A. Peak, *J. Chem. Soc.*, 742 (1952).

(7) S. Ishikawa, *Sci. Pap. Inst. Phys. Chem. Res., Tokyo*, **7**, 293 (1928).

(8) A. Albert, *Ber.*, **48**, 470 (1915).

(9) P. Rehländer, *ibid.*, **27**, 2154 (1894).

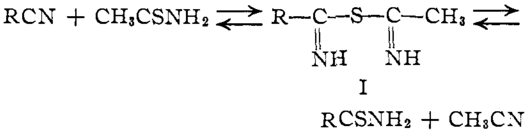
(10) H. Lehr, W. Guex and H. Erlenmeyer, *Helv. Chim. Acta*, **27**, 970 (1944).

(11) H. Erlenmeyer and G. Bischoff, *ibid.*, **27**, 412 (1944).

(12) W. E. Hanford and P. L. Salzberg, *C. A.*, **36**, P5482^4 (1942).

formamide saturated with dry hydrogen chloride. The reaction mixture is reduced to one-fourth its volume by distillation under water aspirator pressure and aqueous sodium bicarbonate is added to neutralize excess acid. Filtration and cooling of the hot aqueous filtrate yields the thioamide. The conversions listed are illustrative.

We consider that the reaction involves the establishment of an equilibrium, essentially as given by equation (i), which is displaced irreversibly to the right by removal of the low-boiling acetonitrile.



$$\mathrm{RCN} + \mathrm{CH_3CSNH_2} \rightleftarrows \underset{\mathrm{I}}{\mathrm{R{-}}\underset{\mathrm{NH}}{\underset{\|}{\mathrm{C}}}\mathrm{{-}S{-}}\underset{\mathrm{NH}}{\underset{\|}{\mathrm{C}}}\mathrm{{-}CH_3}} \rightleftarrows \mathrm{RCSNH_2} + \mathrm{CH_3CN} \quad \text{(i)}$$

Further applications of this reaction are under investigation.

FRICK CHEMICAL LABORATORY
PRINCETON UNIVERSITY
PRINCETON, NEW JERSEY
EDWARD C. TAYLOR
JOHN A. ZOLTEWICZ

RECEIVED MARCH 31, 1960

BOOK REVIEWS

Annual Review of Physical Chemistry. Volume 10. H. EYRING, Editor, University of Utah, C. J. CHRISTENSEN, Associate Editor, University of Utah, and H. S. JOHNSTON, Associate Editor, University of California. Annual Reviews, Inc., Grant Avenue, Palo Alto, California. 1959. vii + 537 pp. 16 + 23 cm. Price, $7.00 (U.S.A.); $7.50 (elsewhere).

The scientist who wishes to keep informed of progress in areas related to his special interests finds the annual reviews almost indispensable. He will appreciate especially those chapters in which special topics have been selected on which intensive and fruitful research has been done, and where the author has given enough detail to make the review read intelligibly. This year the reviewers have been well selected on an international basis and have contributed excellent chapters. When the field is too broad and the literature grows at a very rapid pace, a special section has been selected for review. Such are the chapters on Block and Graft Copolymers or Trapped Energetic Radicals. High Temperature Chemistry, Proteins and Synthetic Polypeptides and Electronic Spectra of Organic Compounds are also subjects not covered in recent years. There are also chapters on subjects covered in recent years which still deserve attention such as Thermodynamical Properties of Substances, Reaction Kinetics, Properties of Surfaces, Ion Exchange, Solutions, Molecular Structure and Nuclear and Paramagnetic Resonance.

The authors deserve an expression of appreciation for their efforts. Over 4700 references are quoted in the 19 chapters. This volume follows the high standard which has been established by previous issues of this series.

DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY
LAFAYETTE, IND.
THOS. DE VRIES

Scientific Russian. A Concise Description of the Structural Elements of Scientific and Technical Russian. By GEORGE E. CONDOYANNIS, Associate Professor of Modern Languages, Saint Peter's College. John Wiley and Sons, Inc., 440 Fourth Avenue, New York 16, N. Y. 1959. xii + 225 pp. 13 × 17 cm. Price, $3.50.

The author describes this book as a "reading-aim textbook." Suitable for class or individual study, this information-packed little volume is designed to provide the beginner "a reading knowledge of Russian adequate to cope with technical articles and books in his field." The approach is to emphasize the basic structure of the language, so that, armed with a dictionary and some linguistic intuition, the student will be prepared to make his way through forms and constructions *via* an "analytic rather than synthetic" approach.

There are twelve chapters, dealing with the basic elements of language from the author's viewpoint. These chapters treat the noun–adjective system, the verb system, pronouns, word building, numbers, and later chapters go into greater detail on nouns, adjectives and verbs than in the initial chapters. There are seventeen tables (aspects, declensions, endings, etc.); and four word lists (high frequency words, noun and adjective endings, verb prefixes, and troublesome words). From the fifth lesson on, there are reading exercises consisting of connected passages from Russian textbooks and articles. These are fairly representative of the physical sciences, slanted if at all toward chemistry.

Some novel features of the book deserve mention. One of these is the extensive use of tables for displaying grammatical relationships. This should appeal to scientists and engineers. Another is the general manner of construction of the chapters—as reference sources rather than as lessons. Lastly, the physical form of the book is pleasantly different; it is looseleaf, with a spiral plastic binder; lies flat when open; and best of all can accompany its owner to the library in his pocket.

GENERAL ENGINEERING LABORATORY
GENERAL ELECTRIC COMPANY
SCHENECTADY 5, NEW YORK
JOHN F. FLAGG

International Tables for X-Ray Crystallography. Volume II. Mathematical Tables. Edited by JOHN S. KASPER and KATHLEEN LONSDALE (General Editor). The Kynoch Press, Birmingham, England. 1959. xviii + 444 pp. 21 × 28.5 cm.

Those concerned with problems of crystallography and related subjects will welcome the appearance of the 2nd volume of the "International Tables." This compilation summarizes information primarily of a mathematical nature, providing tables, functions, formulas and geometrical diagrams of particular value in various phases of a crystal structure determination. Essentially none of the material is of the kind which might require future revision because of more refined measurements. Hence this volume, as its predecessor, will be a valuable reference work for many years.

The first part of the book (Section 2) is a comprehensive compilation (nearly a hundred pages) of fundamental mathematics, bringing together material on algebra, trigonometry and geometry, calculus, vectors and tensors, Fourier theory and statistics. This treatment is not intended to be introductory but rather provides a convenient summary of relationships and principles, from these varied branches of mathematics, which are of particular importance to problems of crystallography.

Section 3 presents features of crystal geometry. General relationships, valid for all crystal systems, are summarized, followed by special characteristics of each crystal system, conveniently arranged for consultation for any particular case. Tables of quadratic forms required for deducing interplanar spacings and for indexing powder patterns are provided.