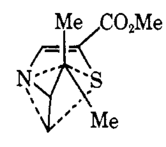
The monodeuterated aziridine **2** was heated in toluene for 4 days[1] to give **4** (30% after silica gel chromatography), which was converted into the sulfoxide[12] without loss of deuterium; the isotope was located at the 2α position of the sulfoxide by nmr spectroscopy [τ ($CDCl_3$) 7.70 (d, 0.73 H, $J_{2\beta,3}$ = 13.2 Hz, t, 0.27 H, $J_{2\alpha,2\beta}$ = $J_{2\beta,3}$ = 13.2 Hz, 2β-H), 7.00 (d of d, 0.27 H, $J_{2\alpha,2\beta}$ = 13.2, $J_{2\alpha,3}$ = 3.0 Hz, 2α-H)].

The isomerization of **2** to **4** illustrates that the 1,3-sulfur migration occurs so that the new carbon–sulfur bond is formed with retention of configuration. This result, although not excluding nonconcerted pathways, is consistent with a concerted reorganization, in which the aziridine reacts in its thermodynamically unfavorable conformation[9] *via* a transition state such as **16** or **17**. In the former event, **18** is an intermediate in the reaction, which represents an example of a [4.4]-dyotropic shift.[13]



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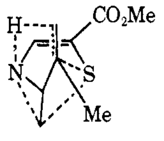

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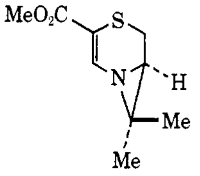

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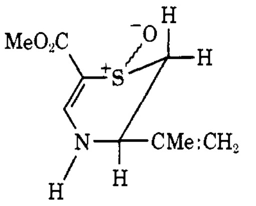
Acknowledgments. We thank Mr. P. Kelly for the mass spectral determinations, Dr. N. M. S. Hill for measuring the 90-MHz nmr spectra, and the Science Research Council for a research studentship (to J. K.).

(12) Oxidation of **3** by sodium periodate gave (89%) a single sulfoxide:[2] mp 154–156° dec; $[\alpha]_D$ +291° (EtOH); nmr τ ($CDCl_3$) 7.70 (t, 1 H, $J_{2\alpha,2\beta}$ = $J_{2\beta,3}$ = 13.2 Hz, 2β-H), 7.00 (d of d, 1 H, $J_{2\alpha,2\beta}$ = 13.2, $J_{2\alpha,3}$ = 3.0 Hz, 2α-H). The configurational and conformational features of 3-substituted-3,4-dihydro-6-methoxycarbonyl-2*H*-1,4-thiazine 1-oxides will be discussed elsewhere (J. Kitchin and R. J. Stoodley, *Tetrahedron*, submitted for publication). However, the magnitudes of the vicinal coupling constants of the sulfoxide of **3** indicate that the sofa conformer i is adopted in solution. For a discussion of the conformational properties of 3-substituted-3,4-dihydro-6-methoxycarbonyl-2*H*-1,4-thiazines see A. R. Dunn and R. J. Stoodley, *Tetrahedron*, **28**, 3315 (1972).



i

(13) M. Reetz, *Angew. Chem., Int. Ed. Engl.*, **11**, 129 (1972).

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Conversion of Amides to Thiol Acids and Isothiocyanates. A Novel Method for Breaking of the Amide Bond

Sir:

Of all the derivatives of the carboxylic group, an amide bond is the hardest to break hydrolytically. In many instances extreme conditions, such as heating with very concentrated acids or bases, have to be employed.

We have discovered a new method of breaking primary or secondary amides under anhydrous conditions and at room temperature. The products are a thiol acid and an isothiocyanate, which can be easily converted to an amine. Tertiary amides are stable under those conditions, and indeed the solvent of choice is a 1:1 mixture of *N,N*-dimethylacetamide and benzene. The amide is first converted to the corresponding anion by sodium hydride, carbon disulfide is added, and the reaction is finished after 90 min at room temperature, even in the case of aromatic amides, which are notoriously hard to hydrolyze by the usual methods.

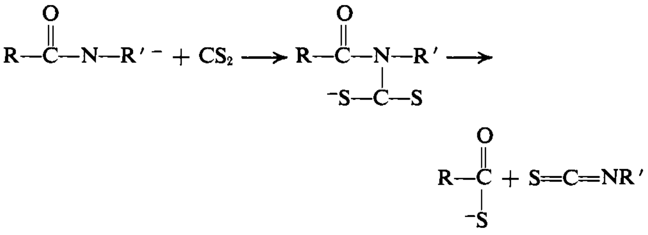
The reaction can be represented as follows. In the case of primary amide

$$RCONH_2 \xrightarrow{NaH} RCONH^- \xrightarrow[NaH]{CS_2} RCOS^- + NCS^-$$

In the case of a secondary amide

$$RCONHR' \xrightarrow{NaH} RCONR'^- \xrightarrow{CS_2} RCOS^- + S{=}C{=}NR'$$

We propose the following mechanism



$$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}N{-}R'^- + CS_2 \longrightarrow R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\underset{\underset{\displaystyle ^-S{-}C{-}S}{|}}{N}{-}R' \longrightarrow R{-}\underset{\underset{\displaystyle ^-S}{|}}{\overset{\overset{\displaystyle O}{\|}}{C}} + S{=}C{=}NR'$$

Similar mechanisms were proposed for the conversion of imides by carbon disulfide to thio ketones[1,2] known in the aromatic series. A similar reaction in the aliphatic series was carried out recently by one of the authors (I. S.) in the laboratory of Professor D. M. R. Barton

$$[(CH_3)_3C]_2C{=}NH \xrightarrow[2.\ CS_2]{1.\ MeLi} [(CH_3)_3C]_2C{=}S$$

The thiol acids obtained from our reaction can be easily isolated in good yields. In case of very volatile thiol acids it may be convenient to oxidize them *in situ* to the less volatile diacyl disulfides. The isothiocyanates can be easily isolated in the aromatic series, but more generally they are either hydrolyzed *in situ* to the corresponding amines, or isolated as thioureas after reaction with aniline. The primary and secondary amides which reacted are given in Tables I and II.

Table I. Primary Amides, $RCONH_2$

R	Yield of RCOSH, %
C_6H_5	80
$C_6H_5CH_2$	65
1-Naphthyl	70
CH_3	65[a]

[a] Isolated diacetyl disulfide, bp 110° (20 mm).

The general procedure for secondary amides is as follows. To a suspension of 2.5 g (50 mmol) of sodium hydride (53% suspension in mineral oil) in 40 ml of *dry* dimethylacetamide and 40 ml of dry benzene, 50 mmol

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(1) R. Ahmed and W. Lwowski, *Tetrahedron Lett.*, 3611 (1969).
(2) H. B. Williams, R. N. Yarborough, K. L. Crochet, and D. W. Wells, *Tetrahedron*, **26**, 817 (1970).

Table II. Secondary Amides, RCONHR′

R	R′	Yield of RCOSH	Yield of R′N=C=S
C_6H_5	C_6H_5	85	93[c]
C_6H_5	1-Naphthyl	91	95[d]
$C_6H_5CH_2$	*p*-$CH_3C_6H_4$	61	65[e]
$C_6H_5CH_2$	CH_3CH_2	70	*f*
CH_3	C_6H_5	85[a]	90[c]
CH_3	1-Naphthyl	85[a]	71
$CH_3(CH_2)_{10}$	CH_3	40	*f*
5-Norbornene-2-carboxylic acid 5-Norbornenyl (?)	1-Naphthyl	60[b]	65

[a] Isolated diacetyl disulfide, bp 110° (20 mm). [b] The thiol acid polymerizes rapidly in air presumably by addition of the –SH group to the double bond. [c] Isolated as thiocarbanilide, mp 154°. [d] Isolated after hydrolysis with hydrochloric acid as 1-naphthylamine hydrochloride. [e] Isolated as *N*-phenyl-*N*′-*p*-tolylthiourea, mp 141°. [f] Not isolated.

of the amide is added. After the evolution of hydrogen is finished, the mixture is cooled in ice and water, and with stirring 5.9 g (75 mmol, 50% excess) of carbon disulfide is added slowly. The mixture is stirred at room temperature for 20 min (if the isothiocyanate is to be trapped as a thiourea the excess of carbon disulfide has to be removed by evaporation *in vacuo* at this stage). The reaction is decomposed by addition of 40 ml of ice water followed by 40 ml of concentrated hydrochloric acid, the benzene is separated and the aqueous phase extracted with benzene. From the benzene the thiol acid is extracted by 5% sodium hydroxide.

For the primary amide a double amount of sodium hydride is employed. Thiocyanate anion was shown to be present in the aqueous solution. From all the new compounds adequate analyses were obtained. Experiments on the application of this reaction to the breaking of the amide bond in amino acid derivatives and peptides are in progress.

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*Book Reviews**

Determination of Organic Structures by Physical Methods. Volumes 3 and 4. Edited by F. C. NACHOD (Sterling-Winthrop Research Institute) and J. J. ZUCKERMAN (SUNY Albany). Academic Press, New York, N. Y. 1971. Volume 3: xv + 472 pp. $22.50. Volume 4: xiii + 381 pp. $19.50.

The editors refer to the first two volumes of this series, which appeared earlier, as dealing with methods that "are now considered classic." These two volumes, and another yet to appear, are intended to bring the coverage up to date by including newer methods.

Volume 3 contains chapters on Photoelectron Spectroscopy (Brundle and Robin), X-Ray Diffraction (Stewart and Hall), Optical Rotatory Dispersion and Circular Dichroism (Crabbé), Thermochemistry (Wiberg), Mass Spectrometry (Williams), Electron-Spin Resonance (Russel), and Configuration and Conformation by NMR (Anet and Anet). Volume 4 covers Applications of High-Field NMR (Naegele), Pulsed NMR Methods (Boden), Nuclear Magnetic Double Resonance (McFarlane), ^{15}N NMR (Lichter), NMR Spectra of the Heavier Elements (Wells), ^{13}C NMR (Pregosin and Randall), and ^{31}P NMR (Van Wazer). Each chapter is a good review and includes introduction, theory, methods, and applications, plus extensive references. The contributing authors are obviously well chosen. Each volume has its own author and subject indexes.

Organic Functional Group Preparations. Volume III. By S. R. SANDLER (The Borden Chemical Co.) and W. KARO. Academic Press, New York, N. Y. 1972. xiii + 496 pp. $24.50.

Thirteen functional groups are covered in this volume: acetals and ketals; anhydrides; monoalkyl sulfates; sulfenic acids and derivatives; isocyanides; amidines; imides; imidates; nitrones; hydroxylamines; oximes; hydroxamic acids; and thiohydroxamic acids. As in earlier volumes, each chapter contains succinct procedures for a large number of representative examples. The selection of preparative reactions to discuss and exemplify is conservative, in that only well-established methods have been chosen. Other methods are then simply listed. Everything is well documented, and each chapter has about a hundred references. One can always differ with the selections made by the authors, but mistakes seem to be few. One minor one occurs in the chapter on hydroxylamines, wherein the reaction of Grignard reagents, RMgX, with alkyl nitrates, $RONO_2$, is stated to give the mixed compound, RR′NOH, instead of that derived only from the alkyl of the Grignard reagent: R_2NOH. The coverage extends through 1971.

The Purines—Theory and Experiment. Volume IV of the Jerusalem Symposia on Quantum Chemistry and Biochemistry. Edited by E. D. BERGMANN (The Hebrew University) and B. PULLMAN (Université de Paris). Academic Press, New York, N. Y. The Israel Academy of Sciences, Jerusalem. 1972. iv + 614 pp. $29.00.

The proceedings of an international symposium, held in April 1971, are collected in this volume. They consist of the texts of the papers, averaging about ten pages each, and including tables, figures, references, and the discussions on the floor (mercifully edited). The entire text is in English.

New Journals

Synthesis. International Journal of Methods in Synthetic Organic Chemistry. Edited by G. SCHILL, G. SOSNOVSKY, and H. J. ZIEGLER. Academic Press, New York, N. Y. Vol. 1, No. 1, Jan 1972. $42.00 plus postage per year.

Includes reviews, communications, and abstracts.

Bibliographies of Chemists. Edited by H. B. LEWIS and N. KHARASCH. Gordon and Breach, Science Publishers, Inc., New York, N. Y. Vol. 1, No. 1, 1971. $36.00 per volume.

Contains chronological lists of publications, including titles of articles, of selected leading chemists from universities and industry.

Polymeric Materials, International Journal of. Edited by H. S. KAUFMAN. Gordon and Breach, Science Publishers, Inc., New York, N. Y. Vol. 1, No. 1, 1971. $47.00 per volume to libraries; $17.00 per volume to individuals.

Devoted to papers concerned with the relation of chemical structure, origin, and properties to engineering properties.

Environmental Analytical Chemistry. Edited by R. W. FREI. Gordon and Breach, Science Publishers, Inc., New York, N. Y. Vol. 1, No. 1, 1972. $41.50 per volume to libraries; $14.50 per volume to individuals.

Separation and Purification Methods. Edited by E. S. PERRY

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* Unsigned book reviews are by the Book Review Editor.