

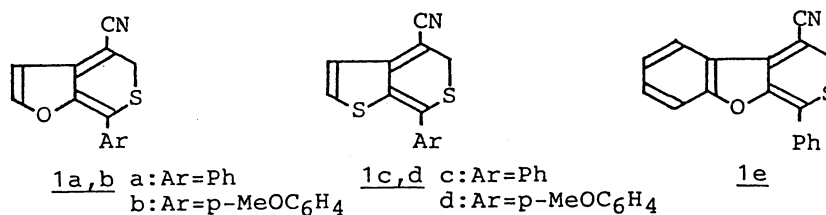
Syntheses of 3-Cyano-2H-thiin S-Imides and Ylides
and Their Base-Promoted Rearrangement

Shinichi MOTOKI,* Narushi TAKAHASHI, Kazuhiro EGUCHI, and Takao SAITO
Department of Chemistry, Faculty of Science,
Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162

The reaction of 3-cyano-2H-thiin derivatives with chloramine salt or diazomalonate gave the corresponding sulfilimines or sulfonium ylides and dihydrothiepin derivatives. These products rearranged by the action of DBU eventually to afford pyridine derivatives or benzofuran and benzothiophene derivatives.

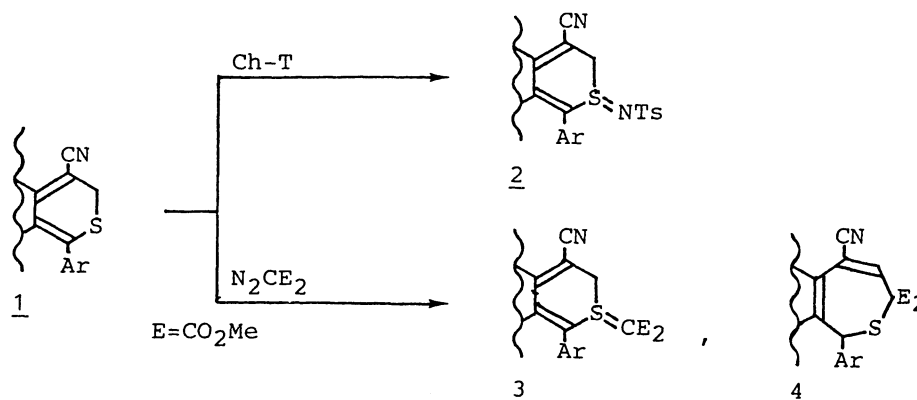
Previously we found some interesting results in the oxidation of 3-cyano-2H-thiin derivatives 1 with mCPBA.¹⁾ The products obtained were not the expected sulfoxide but were found to be 2-alkoxy-2H-thiins and ring contracted thiophene derivatives. As this unusual result has led to the suggestion that a similar reaction would take place with the corresponding sulfilimines 2 and sulfonium ylides 3, reactions of 1 with chloramine salt and with diazomalonate have been examined.

To 1 (1 mmol) in dry dichloromethane was added a dry methanol solution of chloramine-T anhydride (1.2 mmol), and the mixture was stirred at room temperature for 2 days. Sulfilimines 2²⁾ were obtained as stable yellow to orange crystals (Table 1). In the ¹H-NMR spectra, signals of the methylene protons adjacent to the sulfur atom shifted to a lower field than those of 1 ($\Delta\delta=1.88-1.23$). The reaction of 1 with dimethyl diazomalonate was carried out by



Scheme 1.

the following procedure. To a mixture of 1 (1 mmol) and rhodium acetate dimer (5 mg) in refluxing benzene (10 ml) was added a benzene solution of dimethyl diazomalonate (1.2 mmol) dropwise over 20-60 min.³⁾ An ylide 3 or dihydrothiepin 4 was isolated in a moderate yield (Table 1). The product 4 was undoubtedly formed by the Stevens rearrangement of the ylide 3 followed by 1,5-H shift during the reaction. The ¹H-NMR and ¹³C-NMR spectra of 3 and 4 showed the presence of CH₂ or =CH- and >CH- moieties in addition to the aromatic group, being in accordance with the proposed structure (Table 1).



Scheme 2.

Table 1. Reaction of 2H-thiin derivatives 1 with chloramine-T and dimethyl diazomalonate

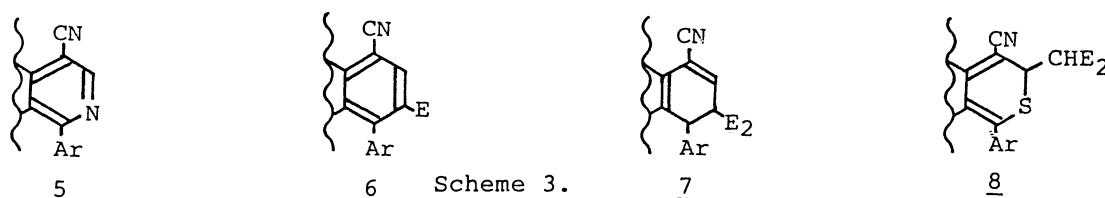
2H-thiin	Product	Yield %	Mp °C	Product	Yield %	¹ H-NMR, δ			Mp °C
						CH ₂	>CH	=CH	
<u>1a</u>	<u>2a</u>	64	136-137	<u>4a</u>	42	—	5.81	6.01	125-126
<u>1b</u>	<u>2b</u>	78	147-148	<u>3b</u>	76	3.54	—	—	111-112
<u>1c</u>	<u>2c</u>	33	115-120	<u>4c</u>	41	—	5.62	a)	167-168
<u>1d</u>	<u>2d</u>	88	125-127	<u>4d</u>	24	—	5.79	7.77	205-206
<u>1e</u>	<u>2e</u>	87	174-176	<u>3e</u>	35	3.69	—	—	149-152

a) Superimposed on Ar-H.

It is known that certain cyclic sulfilimines undergo the Stevens rearrangement or ring expansion reaction by the action of triethylamine⁴⁾ or DBU.⁵⁾ We, therefore, examined the reaction of sulfilimines 2 with these amines. Although the use of triethylamine was not effective in the reaction, treatment

with DBU (12% equiv.) afforded the pyridine derivatives 5 at 0 °C for 15 h in dichloromethane. The structure of 5 was determined by means of NMR spectroscopy and elementary analyses (Table 2).

Treatment of the ylide 3e and dihydrothiepins 4c and 4d with DBU under the same reaction conditions also gave the aromatized products, viz., dibenzofuran 6e and benzothiophene derivatives 6c and 6d, respectively. However, the compounds 4a and 3b produced a dihydrobenzofuran derivative 7a and a rearranged product 8b, respectively (Table 2).



Although there are many papers reporting the rearrangement reaction of sulfilimines⁶⁾ and sulfonium ylides,^{7,8)} the reaction including sulfur replacement of the thiin ring-member by exocyclic nitrogen or carbon atom leading to aromatized compounds such as 5 and 6 is little explored⁹⁾ and interesting. The products formation is rationalized as follows: the sulfilimines 2 and the sulfonium ylides 3 first rearrange in a [1,2]sigmatropic fashion to the seven-membered ring intermediates 9 and 10 (4), which undergo successive elimination of Ts-H/HE and sulfur giving 5 and 6, respectively (Scheme 4). Aromatization of 9 and 10 (4) by the elimination must be the driving force for these reactions. The Stevens-type [1,2]sigmatropic rearrangement of the thiabenzene 11⁸⁾ giving 8 takes place competitively with the ring expansion Stevens-type rearrangement.¹⁰⁾

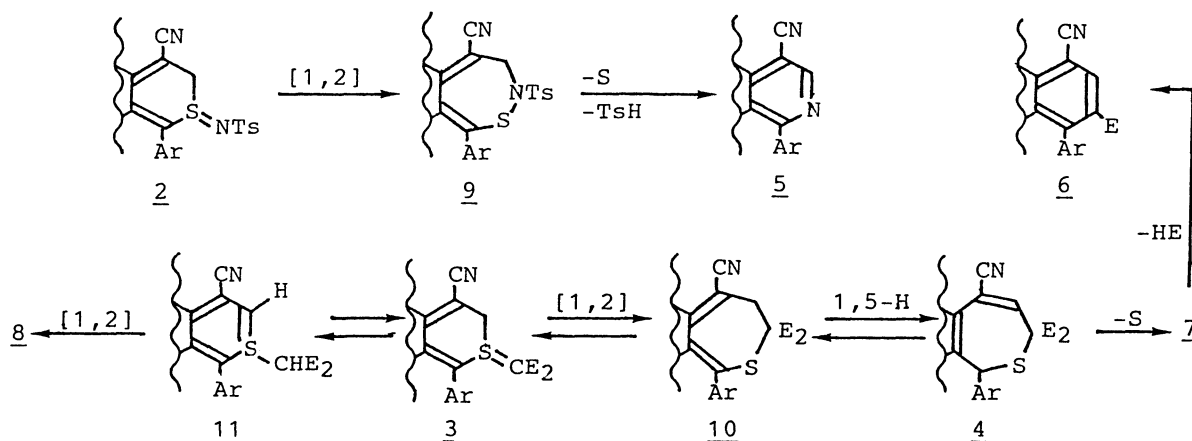


Table 2. Reaction of 2, 3, and 4 with DBU^{a)}

Compd	Product	Yield %	¹ H-NMR, δ =CH	Mp °C	Compd	Product	Yield %	¹ H-NMR, δ =CH >CH CHE ₂	Mp °C
<u>2a</u>	<u>5a</u>	20	8.76	159-160	<u>4a</u>	<u>7a</u>	64	5.74 5.71 —	113-114
<u>2b</u>	<u>5b</u>	24	8.71	192-193	<u>3b</u>	<u>8b</u>	34	— 3.85 4.50	142-143
<u>2c</u>	<u>5c</u>	50	8.85	165-166	<u>4c</u>	<u>6c</u>	61 ^{b)}	8.29 — —	121-122
<u>2d</u>	<u>5d</u>	51	8.82	184-186	<u>4d</u>	<u>6d</u>	39	8.24 — —	128-129
<u>2e</u>	<u>5e</u>	22	8.68	165-166	<u>3e</u>	<u>6e</u>	41	8.06 — —	128-129

a) 12% equiv. DBU/0 °C/15 h.

b) 36% equiv. DBU/0 °C/7 h.

We thank Miss Kayoko Nakamura, Miss Mayumi Suzuki, and Mr. Shuji Kakizawa for their technical assistance.

References

- 1) H. Ohmura and S. Motoki, Chem. Lett., 1984, 1973.
- 2) The IR spectra of 2 showed strong absorptions of $\nu_{S=N}$ in the region of 920-1040 cm⁻¹.
- 3) R. J. Gillespie, J. Murray-Rust, P. Murray-Rust, and A. E. A. Porter, J. Chem. Soc., Chem. Commun., 1978, 83; R. J. Gillespie, A. E. A. Porter, and W. E. W. Willmott, *ibid.*, 1978, 85.
- 4) Y. Tamura, S. M. Bayomi, C. Mukai, M. Ikeda, M. Murase, and M. Kise, Tetrahedron Lett., 21, 533 (1980).
- 5) Y. Tamura, C. Mukai, Y. Nishizawa, and M. Ikeda, J. Org. Chem., 44, 3296 (1979).
- 6) S. Oae, "Yuki Iō Kagaku, Gosei Hanno Hen," p.220; "Yuki Iō Kagaku, Hanno Kiko Hen," p.405, Kagaku Dojin, Kyoto (1982); S. Oae and N. Furukawa, "Sulfilimines and Related Derivatives," ACS Monograph 179, Washington, D. C. (1983).
- 7) Y. Ohara and K. Akiba, Kagaku No Ryoiki, 33, 843 (1979); W. Ando, Acc. Chem. Res., 10, 179 (1977); B. M. Trost and L. S. Melvin, "Sulfur Ylides," Academic Press, New York (1975), p.108.
- 8) M. Hori and T. Kataoka, Yuki Gosei Kagaku Kyokai Shi, 45, 232 (1987); L. Benati, P. C. Montevicchi, and P. Spagnolo, J. Chem. Soc., Perkin Trans. 1, 1982, 917.
- 9) Several examples are known that sulfur extrusion from a seven-membered heterocycle occurs in cases where the ring contraction leads to an aromatized ring: H. C. Van Der Plas, "Ring Transformations of Heterocycles," Academic Press, New York (1973), Vol. 2, Chap. 5.
- 10) Each reaction step between 4 and 11 might be reversible because 4c gave 8c (52%) or a mixture of 6c (25%) and 8c (20%) depending on the base used (36% equiv. Et₃N or 24% equiv. DBU).

(Received December 1, 1988)