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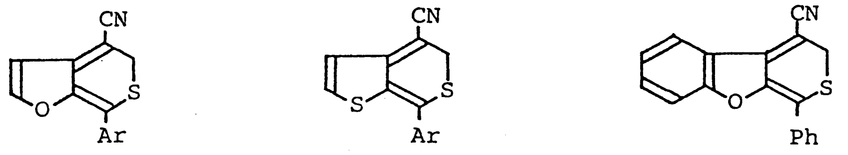
Syntheses of 3-Cyano-2H-thiin S-Imides and Ylides and Their Base-Promoted Rearrangement

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 ^{1}H-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



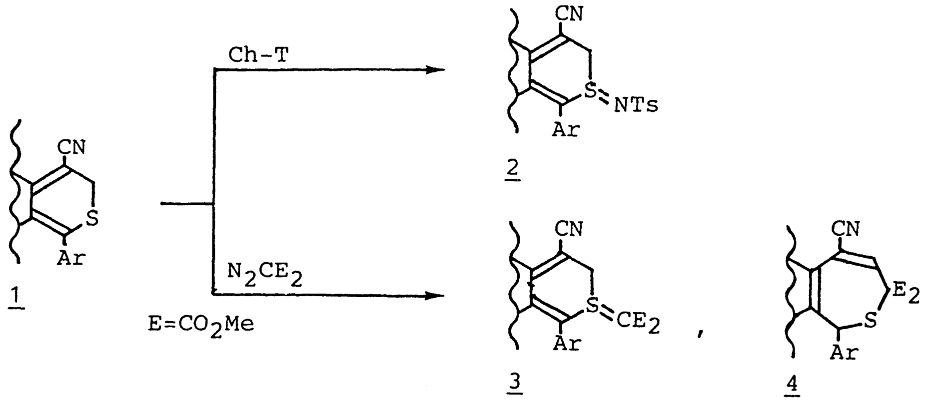
1a,b a:Ar=Ph
b:Ar=p-MeOC$_6$H$_4$

1c,d c:Ar=Ph
d:Ar=p-MeOC$_6$H$_4$

1e

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 ^{1}H-NMR and ^{13}C-NMR spectra of 3 and 4 showed the presence of CH_2 or =CH- and >CH- moieties in addition to the aromatic group, being in accordance with the proposed structure (Table 1).



Scheme 2.

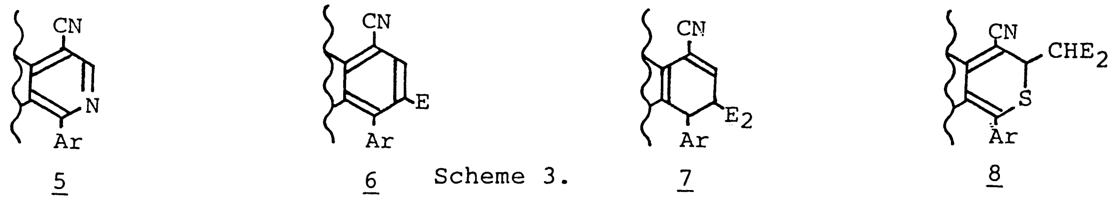
Table 1. Reaction of 2H-thiin derivatives 1 with chloramine-T and dimethyl diazomalonate

2H-	Product	Yield	Mp	Product	Yield	^{1}H-NMR, δ			Mp
thiin		%	°C		%	CH_2	>CH	=CH	°C
1a	2a	64	136-137	4a	42	——	5.81	6.01	125-126
1b	2b	78	147-148	3b	76	3.54	——	——	111-112
1c	2c	33	115-120	4c	41	——	5.62	a)	167-168
1d	2d	88	125-127	4d	24	——	5.79	7.77	205-206
1e	2e	87	174-176	3e	35	3.69	——	——	149-152

a) Superimposed on Ar-H.

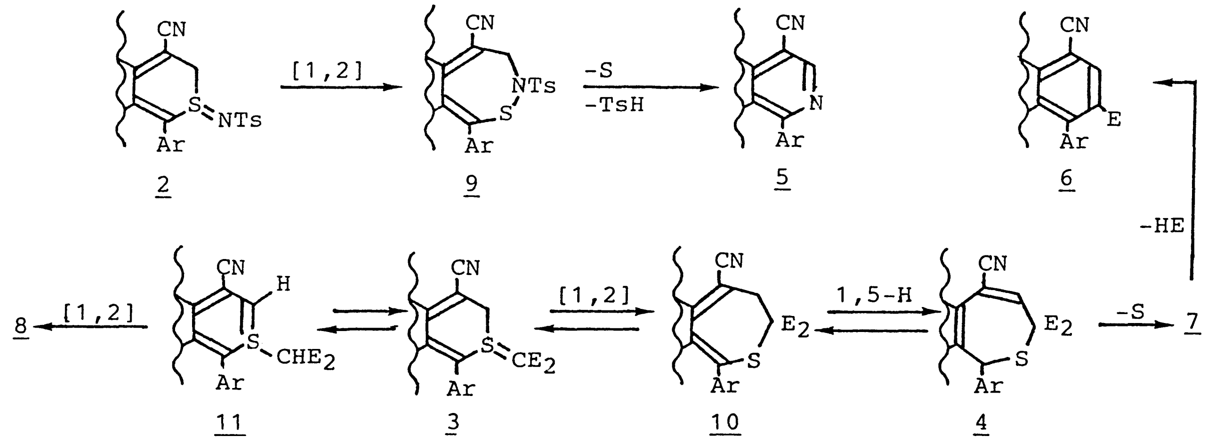
It is known that certain cyclic sulfilimines undergo the Stevens rearrangement or ring expansion reaction by the action of triethylamine[4] or DBU.[5] We, therefore, examined the reaction of sulfilimines 2 with these amines. Although the use of triethylamine was not effective in the reaction, treatment 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).



Scheme 3.

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 11 8) giving 8 takes place competitively with the ring expansion Stevens-type rearrangement.10)



Scheme 4.

Table 2. Reaction of 2, 3, and 4 with DBU[a)]

Compd	Product	Yield	^{1}H-NMR, δ	Mp	Compd	Product	Yield	^{1}H-NMR, δ			Mp
		%	=CH	°C			%	=CH	>CH	CHE$_2$	°C
2a	5a	20	8.76	159-160	4a	7a	64	5.74	5.71	——	113-114
2b	5b	24	8.71	192-193	3b	8b	34	——	3.85	4.50	142-143
2c	5c	50	8.85	165-166	4c	6c	61[b)]	8.29	——	——	121-122
2d	5d	51	8.82	184-186	4d	6d	39	8.24	——	——	128-129
2e	5e	22	8.68	165-166	3e	6e	41	8.06	——	——	128-129

a) 12% equiv. DBU/0 °C/15 h. b) 36% equiv. DBU/0 °C/7 h.

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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. Et$_3$N or 24% equiv. DBU).

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