Acylthiocyclopropenium Ions

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Synopsis. On treatment with a mixture of thiocarboxylic acid and perchloric acid in acetic anhydride, cyclopropenone gave acylthiocyclopropenium perchlorate in a good yield. Bis(acylthio)cyclopropene also yielded the salt under similar reaction conditions. The salt was stable under nitrogen at low temperatures, but was easily hydrolyzed to yield the corresponding cyclopropenethione.

The chemistry of cyclopropenone and their derivatives has attracted considerable attention in the past two decades.[1] Cyclopropenium ions substituted with tris(alkylthio), triamino, or triaryl groups have been isolated as stable crystals.

In a previous paper[2] the present authors have shown the reaction of cyclopropenones, **1**, with thiocarboxylic acids in the presence of strong acids. The reaction in dichloromethane yields the corresponding cyclopropenethiones, **4**, in good yields, while the reaction in ethanol gives bis(acylthio)cyclopropenes, **2**. In this communication we will show two easy routes for the preparation of acylthiocyclopropenium ions, **3**, which are believed to be intermediates for the reaction of **1** with thiocarboxylic acid to yield **4**.

Although it has been reported that unsubstituted cyclopropenone yields a 1 : 2 addition product, **5**, by a reaction with thioacetic acid, no precise study has been made.[3]

No reaction was observed between **1a** and thioacetic acid without a strong acid. When a mixture of **1a**, thioacetic acid, and 70% perchloric acid in acetic anhydride was allowed to stand at room temperature, colorless needles appeared within a few minutes. One hour later crystals were collected. Similarly, the treatment of **1b** with a mixture of thiocarboxylic acids and perchloric acid in acetic anhydride yielded the crystalline products. The structure of the products was confirmed to be **3** on the basis of their ^{13}C- and ^{1}H-NMR and IR spectra, molecular-weight determination, and the subsequent acid hydrolysis.

The ^{13}C chemical shifts for some **3** ions, together with the cyclopropene derivatives, are given in Fig. 1. The assignments were made by considering the signal multiplicities from off-resonance decoupling experiments or from coupled spectra, line intensities, and chemical shifts in comparison with substituted cyclopropenium ions. The chemical shifts for ring carbons of trimethyl-, tris(*t*-butylthio)-, and triphenylcyclopropenium ions are observed at δ 179.3, 156.1, and 155.4 (154.0)[4] ppm respectively.[1] The ^{13}C chemical shifts for carbonium ions are interpreted in terms of the charge densities.[5] Figure 1 indicates that positive charges on the carbons of the cyclopropenium ions would be furnished in this order with respect to the substituents: Me>MeS>Acylthio≥Ph.

The reaction of **2** with perchloric acid in acetic anhydride also yielded **3**. The results are collected in Table 1.

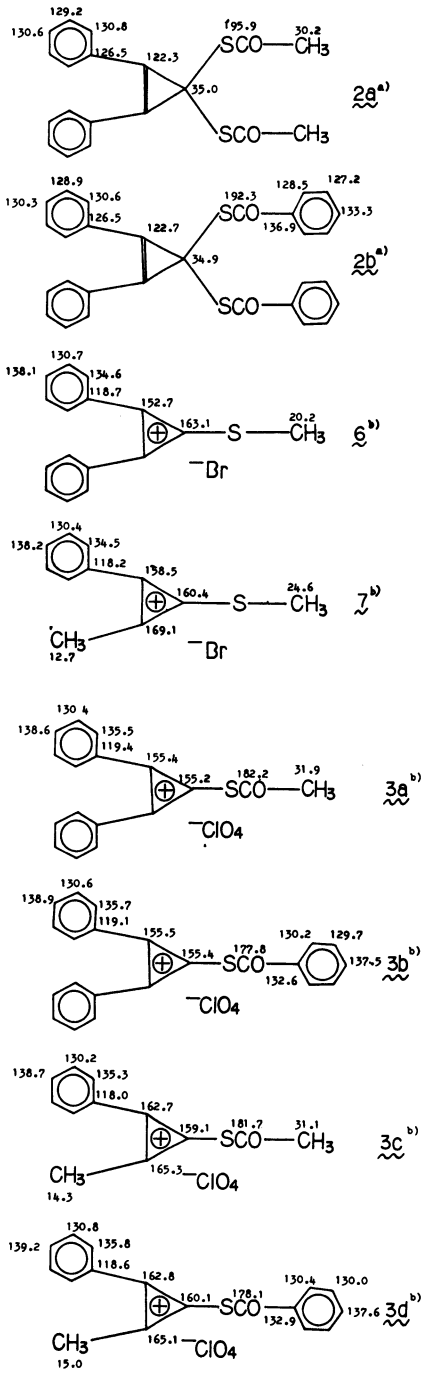


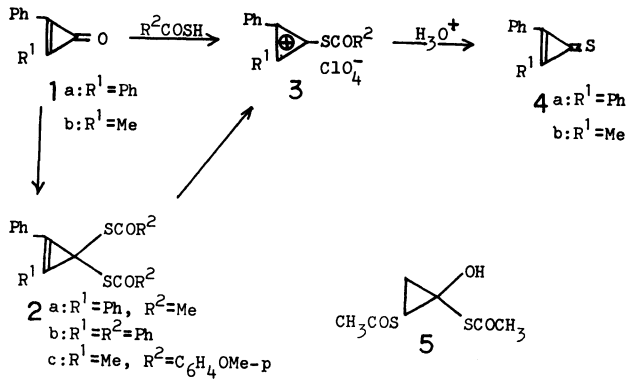
Fig. 1. Selected ^{13}C-NMR data.
a) Solvent: $CDCl_3$, b) solvent: $CDCl_3$–CF_3CO_2H (1 : 0.1—0.3 v/v).

Although the **3** salts were stable under nitrogen at low temperatures, the **3** were easily hydrolyzed under acidic

Table 1. Physioal properties of 3

	R^1	R^2	Mp θ_m/°C	Yield/% (from)	NMR[a)]	IR ν/cm^{-1}(Nujol)
3a	Ph	Me	132—142	94(**1a**) 91(**2a**)	2.90(s,3H,Me), 7.8—8.5(m,10H,Ph)	1910,1650
3b	Ph	Ph	150—153.5	65(**1a**) 75(**2b**)	7.6—8.4(m,15H,Ph)	1720,1600
3c	Me	Me	84.5—85.5	62(**1b**)	2.81(s,3H,MeCO), 3.25(s,3H,MeC=C), 7.6—8.2(m,5H,Ph)	1790,1590
3d	Me	Ph	107—109	73(**1b**)	3.33(s,3H,MeC=C), 7.6—8.4(m,10H,Ph)	1750,1600
3e	Me	*p*-$MeOC_6H_4$	126—129.5	62(**2c**)	3.32(s,3H,MeC=C), 3.95(s,3H,MeO), 7.0—8.3(m,9H,Arom)	1720,1600

a) In $CDCl_3$–CF_3CO_2H (10 : 1 v/v).



conditions at room temperature to yield the corresponding cyclopropenethione, **4**, in fairly good yields.

Experimental

General. The ^{13}C FT NMR spectra were recorded on a JEOL JNM FX-60 spectrometer (15.04 MHz), and ^1H-NMR spectra, on a Hitachi Perkin Elmer R-24 (60 MHz). The IR spectra were recorded on a JASCO A-3 spectrometer.

Preparation of 3 from 1. To a solution of perchloric acid (70%, 1.1 mmol) in acetic anhydride (3 cm^3), we added **1** (1 mmol) to give a clear solution. Thiocarboxylic acid (1.1 mmol) was then added to the mixture, and the stirring was continued at room temperature. The colorless needles which appeared in the reaction mixture within 5 min were collected after 1 h, washed with dry benzene, and dried *in vacuo*.

Preparation of 3 from 2. To a solution of perchloric acid (70%, 1.1 mmol) in acetic anhydride (3 mmol), we added **2** (1 mmol) at room temperature, and then we stirred the mixture well. The colorless needles which appeared were collected and treated as above.

Hydrolysis of 3. To a cold mixture of 2 mol dm^{-3} hydrochloric acid and dichloromethane (10 cm^3 each), we added **3** (1 mmol). The reaction mixture was stirred well for 30 min, and the organic layer was separated. The condensation of the solution and recrystallization gave **4** in good yields: **4a** from **3a** in a 96% yield and from **3b** in a 90% yield, and **4b** from **3c** in a 89% yield respectively. The structures of **4a** and **4b** were confirmed by a comparison of their mp's and ^1H-NMR spectra with those of authentic samples.[2)]

Molecular-weight Determination. The molecular weights of **3** were determined as follws: an exactly weighed amount of **3** (*ca.* 200 mg) was dissolved in dry ethanol (5 cm^3). To the solution under nitrogen we added an excess amount of potassium hydroxide in ethanol (5% solution). The resulting mixture was stirred well for 20 min. The precipitated potassium perchlorate (the solubility in ethanol: 0.008% at 21 °C) was collected in a glass-sintered filter, washed with dry ethanol and benzene under nitrogen, dried at 100 °C, and weighed. The observed (calcd) molecular weights for **3a—e** were **3a**: 360 (365), **3b**: 442 (427), **3c**: 316 (303), **3d**: 352 (365), and 373 (395). Studies of the elemental and mass spectroscopic analyses of **3a—e** were unsuccessful because of the decomposition of the samples.

References

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