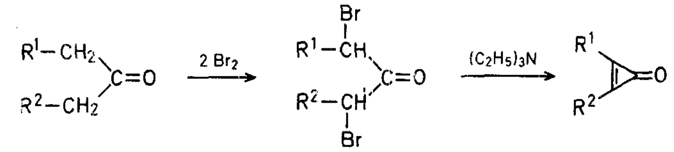
Synthesis of Cyclopropenethiones or 3,3-Bis[acylthio]cyclopropenes from Cyclopropenones and Thiocarboxylic Acids

Hiroshi Yoshida*, Mikito Nakajima, Tsuyoshi Ogata

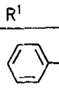
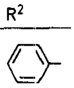
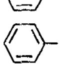
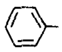
Department of Synthetic Chemistry, Faculty of Engineering, Shizuoka University, Hamamatsu 432, Japan

The chemistry of cyclopropenone and its derivatives has attracted considerable attention in the last two decades. In continuation of our studies on cyclopropenones[1] 3, we now report on their reactions with thiocarboxylic acids to give cyclopropenthiones 4 or 3,3-bis[acylthio]cyclopropenes 5.

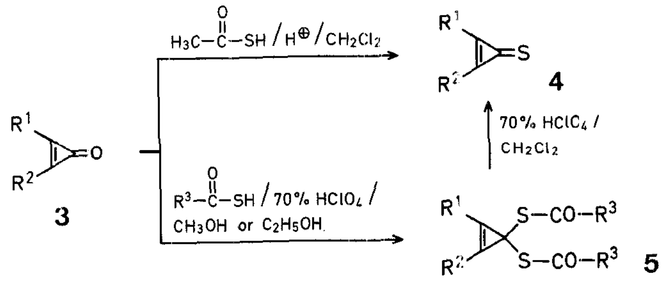
The starting cyclopropenones 3 were prepared by a modification of the Favorskii reaction[2] as shown below.



1 2 3

1-4	R1	R2
a		
b		H_3C
c		C_2H_5
d	4-H_3C—C_6H_4	H_3C
e	4-H_3CO—C_6H_4	H_3C

We first investigated the reaction of 3a with thioacetic acid in dichloromethane under acid catalysis and obtained the cyclopropenethione 4a. Best results (84% yield of 4a) were achieved using tetrafluoroboric acid at 25 °C in 1 h. Other catalysts tested include: sulfuric acid, 25 °C/1 h to give 77% yield; perchloric acid, 25 °C/1 h, 80% yield; trifluoroacetic acid, 25 °C/24 h, 65% yield; trifluoroacetic acid, reflux/1 h, 83% yield. In the absence of a catalyst no reaction had occurred after 24 h at 25 °C. A series of products 4a-e were prepared under these optimum conditions (Table 1).



0039-7881/81/0132-0036 $ 03.00

Table 1. Cyclopropenethiones **4a-e**

Product	Yield [%]	m.p. [°C] (solvent)	Molecular formula[a]	^{1}H-N.M.R. (CDCl$_3$) δ [ppm]	M.S. m/e (M$^{+\cdot}$)
4a	84	127–128° (cyclohexane)[b]	$C_{15}H_{10}S$ (222.2)	7.4–8.3 (m, H_{arom})	222
4b	82	127.5–129° (cyclohexane)[c]	$C_{10}H_8S$ (160.2)	2.67 (s, CH_3); 7.4–8.3 (m, H_{arom})	160
4c	84	55–56° (cyclohexane)	$C_{11}H_{10}S$ (174.2)	1.49 (t, $J=7.5$ Hz, CH_3); 3.03 (q, CH_2); 7.1–8.2 (m, H_{arom})	174
4d	90	117–119° (cyclohexane)	$C_{11}H_{10}S$ (174.2)	2.47 (s, H_3C—C_6H_4); 2.65 (s, H_3C—C=); 7.2–8.2 (m, H_{arom})	174
4e	87	173–175° (benzene/cyclohexane)	$C_{11}H_{10}OS$ (190.2)	2.64 (s, H_3C—C=); 4.00 (s, H_3CO); 7.9–8.2 (m, H_{arom})	190

[a] Satisfactory microanalyses obtained (C ±0.19, H ±0.12).

[b] Lit.[3,5] m.p. 125–126 °C, Lit.[4] m.p. 130–131 °C, Lit.[6] m.p. 122 °C.

[c] Lit.[7] m.p. 124 °C.

Table 2. 3,3-Bis[acylthio]cyclopropenes **5**

Substrate **3** used	R^3 in R^3—COSH	Reaction solvent	Yield [%]	m.p. [°C]	Molecular formula[a]	^{1}H-N.M.R. (CDCl$_3$) δ [ppm]	I.R. (KBr) ν [cm^{-1}]
3a	H_3C	C_2H_5OH	75	131–133°	$C_{19}H_{16}O_2S_2$ (340.2)	2.25 (s, 6H, CH_3); 7.2–8.1 (m, 10H_{arom})	1660
3a	t-C_4H_9	CH_3OH	44	145–149°	$C_{25}H_{28}O_2S_2$ (424.5)	1.19 (s, 18H, t-C_4H_9); 7.4–8.2 (m, 10H_{arom})	1670
3a	C_6H_5	C_2H_5OH	77	139–140.5°	$C_{29}H_{20}O_2S_2$ (464.5)	7.2–8.3 (m, 20H_{arom})	1640
3a	$C_6H_5CH_2$	C_2H_5OH	49	95.5–99°	$C_{31}H_{24}O_2S_2$ (492.5)	3.78 (s, 4H, CH_2); 7.0–8.2 (m, 20H_{arom})	1670
3a	4-H_3CO—C_6H_4	C_2H_5OH	99	141–142.5°	$C_{31}H_{24}O_4S_2$ (524.5)	3.80 (s, 6H, CH_3); 6.8–8.4 (m, 18H_{arom})	1640
3d	C_6H_5	C_2H_5OH	83	103–105°	$C_{22}H_{20}O_2S_2$ (380.4)	2.31 (s, 3H, H_3C—C_6H_4); 2.50 (s, 3H, H_3C—C=); 7.5–7.9 (m, 14H_{arom})	1640
3b	4-H_3CO—C_6H_4	CH_3OH	70	118–119°	$C_{26}H_{22}O_4S_2$ (462.4)	2.60 (s, 3H, H_3C—C=); 3.82 (s, 6H, H_3CO); 6.7–8.0 (m, 13H_{arom})	1640

[a] Satisfactory microanalyses obtained (C ±0.19, H ±0.15).

Diphenylcyclopropenethione (**4a**) was previously obtained by three methods:

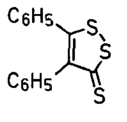
(1) Reaction of **3a** with diphosphorus pentasulfide[3] [this reaction was also reported in one case to give 4,5-diphenyl-3-thioxo-3*H*-1,2-dithiole[4] (**A**)];

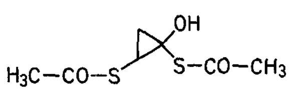
(2) reaction of **3a** with hydrogen sulfide in the presence of hydrochloric acid[5]; and

(3) reaction of **3a** with a chlorinating reagent and subsequent treatment with thioacetic acid[6] (product **4b** was prepared in 16% yield only by this method[7]).

It was also reported that *N*-, *O*-, and *C*-nucleophiles (amine, hydroxide, alkoxide, Grignard reagent) react with the carbonyl C-atom of **3a** to give ring-opened products[2]. Thus, we also studied the reactions of **3** with thiocarboxylic acids in methanol or ethanol instead of dichloromethane. Reaction of a mixture of **3**, thiocarboxylic acid (≥2 mol) and 70% perchloric acid in methanol or ethanol at room temperature resulted in a crystalline mass of **5** within a few minutes. The solubility of the product **5** in the alcohol used influences the reaction: in methanol **3b** reacts with the acids where $R^3=t$-C_4H_9 or 4-H_3CO—C_6H_4 to give products **5** whereas in ethanol the corresponding products **4** are obtained. Finally, reaction of **5a** ($R^3=CH_3$) with 70% perchloric acid in dichloromethane resulted in the formation of **4a** in 91% yield. Further studies are in progress.

3,3-Bis[acetylthio]-1,2-diphenylcyclopropene (**5a**, $R^3=CH_3$) was previously isolated as a byproduct from the reaction of dichlorodiphenylcyclopropene with thioacetic acid but no physical data were reported[6]. It was also reported that cyclopropenone itself (**3**; $R^1=R^2=H$) reacts with thioacetic acid to give the 1:2-addition product **B** but no precise details were given[8].


A


B

Cyclopropenethiones 4; General Procedure:

A mixture of the cyclopropenone **3** (10 mmol), thioacetic acid (30 mmol), and an acid (1 ml) in dichloromethane (30 ml) is stirred vigorously at room temperature until the propenone **3** has completely reacted. The reaction mixture is then poured into water (20 ml). The organic layer is separated, dried with sodium sulfate, and evaporated under reduced pressure to give a crystalline mass. Recrystallization from an appropriate solvent yields the corresponding cyclopropenethione **4** (Table 1).

3,3-Bis[acylthio]cyclopropenes 5; General Procedure:

To a solution of cyclopropenone **3** (2 mmol) and the thiocarboxylic acid (4.8 mmol) in ethanol or methanol (3 ml) is added 70% perchloric acid (0.2 ml) in one portion and the mixture is stirred well at room temperature. Within a few minutes a crystalline mass of **5** has appeared, and one hour later the crystals were separated, and washed well with cold ethanol, and dried in vacuo (Table 2).

Received: February 19, 1980
(Revised form: August 21, 1980)

---

[1] H. Yoshida, S. Sogame, in preparation.

[2] K. T. Potts, J. S. Baum, *Chem. Rev.* **74**, 189 (1974).

[3] Y. Kitahara, M. Funamizu, *Bull. Chem. Soc. Jpn.* **37**, 1897 (1964).

[4] G. Laban, J. Fabian, R. Mayer, *Z. Chem.* **1968**, 414.

[5] P. Metzner, J. Vialle, *Bull. Soc. Chim. Fr.* **1972**, 3138.

[6] J. W. Lown, T. W. Maloney, *J. Org. Chem.* **35**, 1716 (1970).

[7] S. S. Dehmlow, E. V. Dehmlow, *Z. Naturforsch.* [b] **30**, 404 (1975).

[8] R. Breslow, M. Oda, J. Pecosaro, *Tetrahedron Lett.* **1972**, 4415.