Preparation of Cyclopropenone Acetals and Dithioacetals

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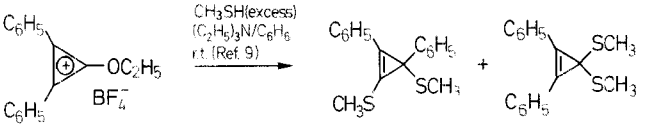
The title compounds are prepared in good yields from ethoxycyclopropenium fluoroborate and the corresponding alcohols, diols, or dithiols with added triethylamine. Cyclopropenone reacted with dithiols in the presence of trifluoroacetic acid to afford dithioacetals in lower yields, while diols were inert under similar reaction conditions.

Cyclopropenones have been of great interest because of their high degree of strain. Extensive studies dealing with the preparation of new cyclopropenes, as well as their thermal and photochemical ring-opening have been of continuing interest.[1] In this communication we report a convenient method for the preparation of the title compounds from cyclopropenone by a one-pot procedure. Only few papers have reported on cyclopropenone acetals as intermediates in the hydrolysis of oxocarbonium ions[2] or their use as three-carbon synthetic reagents.[3]

Unsubstituted cyclopropenone dimethylacetal[4] has been obtained by the cyclization of 1-bromo-3-chloro-2,2-dimethylpropane in 40–65% yield. Starting with 2,3-diphenyl-1-ethoxycyclopropenium fluoroborate (**2a**), diphenylcyclopropenone acetals are prepared by a substitution reaction with sodium methoxide[2a] or ethylene glycol disodium salt.[5]

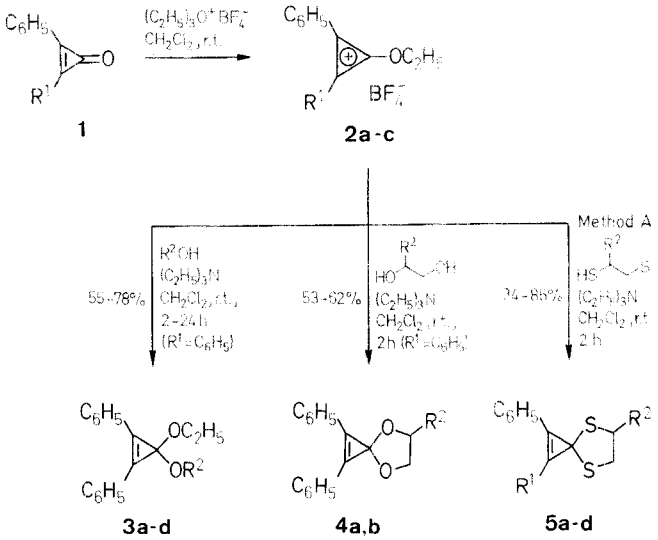
Salt **2a** is easily prepared from diphenylcyclopropenone (**1a**) and triethyloxonium fluoroborate (Meerwein reagent) and has been shown to be useful for the preparation of amino- or thio-substituted cyclopropenium salts,[6,7] fulvenes,[8] and heterocycles.[8] In the presence of triethylamine, **2a** readily reacted with alcohols to afford cyclopropenone acetals **3** in moderate yield (Table 1). In contrast, the reaction of **2a** with ethylene glycol gave spiro compounds **4** by elimination of ethanol. The results are shown in Table 1.

The reaction of equimolar amounts of thiols with **2a** affords monoalkylthiodiphenylcyclopropenium salts.[7] Treatment of **2a** with excess methanethiol in the presence of triethylamine gave a mixture of isomeric cyclopropenes, the separation of which was unsuccessful:[9]

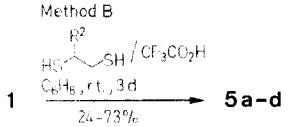


2a

A smooth reaction took place between **2a–c** and *vic*-dimercaptoalkanes in the presence of triethylamine to give cyclic dithioacetals **5** in moderate yields, as indicated in Table 2 (Method A). The structure of compounds **3**, **4**, and **5** are assigned



1 **2a-c** **3a-d** **4a,b** **5a-d**



5a-d

2	R^1
a	C_6H_5
b	CH_3
c	C_2H_5

3	R^2
a	C_2H_5
b	*i*-C_3H_7
c	C_6H_5
d	*p*-$CH_3C_6H_4$

4	R^2
a	H
b	CH_3

5	R^1	R^2	5	R^1	R^2
a	C_6H_5	H	c	CH_3	H
b	C_6H_5	CH_3	d	C_2H_5	H

Table 1. Diphenylcyclopropenone Acetals **3** and **4** Prepared

Product	Yield (%)	m.p. (°C)	Molecular Formula[a] or Lit. m.p. (°C)	IR (KBr)[b] (cm^{-1})	^{1}H-NMR ($CDCl_3$/TMS)[c] δ (ppm)	MS[d] (*m/z*)
3a	55	67–68	67–68[2a]	1850	1.20 (t, 6H, J = 7.5 Hz, CH_3); 3.75 (q, 4H, J = 7.5 Hz, CH_2); 7.2–7.9 (m, 10H$_{arom}$)	280 (M^+)
3b	60	80–82	$C_{20}H_{22}O_2$ (294.4)	1840	1.15 (d, 6H, J = 8 Hz, $CH(CH_3)_2$); 1.20 (t, 3H, J = 8 Hz, CH_2CH_3); 3.70 (q, 2H, J = 8 Hz, CH_2); 7.3–8.1 (m, 10H$_{arom}$)	294 (M^+)
3c	60	88–90	$C_{23}H_{20}O_2$ (328.4)	1850	1.20 (t, 3H, J = 7.5 Hz, CH_3); 3.85 (q, 2H, J = 7.5 Hz, CH_2); 6.8–8.2 (m, 15H$_{arom}$)	253 ($M^+ - C_6H_5$)
3d	78	83–84	$C_{24}H_{22}O_2$ (342.4)	1850	1.22 (t, 3H, J = 8 Hz, CH_2CH_3); 2.28 (s, 3H, $C_6H_4CH_3$); 3.92 (q, 2H, J = 8 Hz, CH_2); 6.8–8.1 (m, H$_{arom}$)	253 ($M^+ - C_6H_4CH_3$)
4a	62	85–86	84.5–85.2[5]	1770[e]	4.15 (s, 4H, CH_2CH_2); 7.2–7.9 (m, 10H$_{arom}$)[e]	250 (M^+)
4b	53	93–96	$C_{18}H_{16}O_2$ (264.3)	1770	1.46 (d, 3H, J = 8 Hz, CH_3); 3.6–4.8 (m, 3H, $CHCH_2$); 7.1–8.0 (m, 10H$_{arom}$)	264 (M^+)

[a] Satisfactory microanalyses obtained: C ±0.2, H ±0.2.
[b] Recorded on a JASCO A-3 spectrophotometer.
[c] Recorded on a Hitachi–Perkin Elmer R-24 (60 MHz) spectrometer.
[d] Recorded on a Hitachi RMU-7 M mass spectrometer at 40 eV.
[e] Lit.[5] IR: ν = 1770 cm^{-1}; ^{1}H-NMR ($CDCl_3$/TMS): δ = 4.15 (s, 4H); 7.25–8.5 ppm (m, 10H).

Table 2. Substituted Cyclopropenone Cyclic Dithioacetals **5** Prepared

Product	Yield (%)		m.p. (°C)	Molecular Formula[a]	^{1}H-NMR ($CDCl_3$/TMS) δ (ppm)	MS (*m/z*)
	Method A	Method B				
5a	85	73	135–137	$C_{17}H_{14}S_2$ (282.4)	3.65 (s, 4H, CH_2CH_2); 7.1–8.0 (m, 10H$_{arom}$)	282 (M^+)
5b	34	24	114–116	$C_{18}H_{16}S_2$ (296.5)	1.75 (d, 3H, J = 8 Hz, CH_3); 3.1–3.8 (m, 2H, CH_2); 3.9–4.5 (m, 1H, CH); 7.3–8.1 (m, 10H$_{arom}$)	296 (M^+)
5c	67	58	93–98	$C_{12}H_{12}S_2$ (220.4)	2.35 (s, 3H, CH_3); 3.50 (s, 4H, CH_2CH_2); 7.2–7.8 (m, 5H$_{arom}$)	220 (M^+)
5d	83	47	53–54	$C_{13}H_{14}S_2$ (234.4)	1.35 (t, 3H, J = 7 Hz, CH_3); 2.75 (q, 2H, J = 7 Hz, CH_2); 3.50 (s, 4H, CH_2CH_2); 7.2–7.8 (m, 5H$_{arom}$)	234 (M^+)

[a] Satisfactory microanalyses obtained: C ±0.22, H ±0.13.

on the basis of their ^{1}H-NMR spectra. IR spectra of **3** and **4** showed moderately strong absorption bands at 1800 cm^{-1} due to the cyclopropene ring. In contrast, compounds **5** gave no such absorption. The ^{13}C-NMR spectrum of **5a** ($CDCl_3$/TMS): δ = 39.2 (t, CH_2); 46.0 (s, C-3); 118.2 (s, C-1); 126.4 (s); 128.2 (d); 128.9 (d); 131.8 ppm (d)] clearly suggests the dithioacetal structure.

It is well known that ketones react with alcohols in the presence of strong acid to afford ketals. The reaction of **1a** with ethylene glycol in the presence of trifluoroacetic acid did not give acetal **4a**. Similar reaction with ethanedithiol, however, did give dithioacetals in moderate yield (Method B). The results are summarized in Table 2.

Substituted Cyclopropenone Acetals and Dithioacetals; General Procedures:

Method A: Ethylation Procedure: A mixture of substituted cyclopropenone **1** (2 mmol) and triethyloxonium fluoroborate (10, 2.2 mmol) in dry dichloromethane (3 ml) is stirred at room temperature for 1 h. To the resulting solution is added a dichloromethane solution of the alcohol, diol or dithiol (2.4 mmol) and triethylamine (3 mmol). After 2 h the precipitated amine salt is filtered (aromatic alcohols, 24 h later), the filtrate is condensed; recrystallization from hexane or ethanol affords crystalline **3**, **4**, or **5**, respectively.

Method B; Acidic Conditions: A mixture of cyclopropenone **1** (2 mmol), alkane-thiol (2.2 mmol), and trifluoroacetic acid (2.5 mmol) in benzene (3 ml) was allowed stand at room temperature. The reaction was monitored by TLC until the complete disappearance of **1** (3d). The mixture was washed with water and dried over sodium sulfate. Removal of the solvent and recrystallization from ethanol gave compound **5**.

Received: 1 May 1986
(Revised form: 6 October 1986)

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