Preparation of *β*-Oxoketene Dithioacetals by Isomerisation of *gem*-Diphenylthiocyclopropyl Ketones

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Ketene dithioacetals have received considerable attention in recent years as important intermediates in a wide variety of organic syntheses[1,2]. Several methods are reported for the preparation of ketene dithioacetals[1,3] and *α*-oxoketene dithioacetals[4]. However, these methods are not suitable for the synthesis of derivatives of ketene dithioacetals containing carbonyl groups in the *β*-position. We report that *β*-oxoketene diphenylthioacetals **2** may be prepared by acid-catalysed isomerisation of *gem*-diphenylthiocyclopropyl ketones **1**. It is observed that the products **2** are formed quantitatively if the reaction is carried out in the presence of catalytic amounts of *p*-toluenesulphonic acid in dry dichloromethane (Table 1).

When traces of moisture are present in the dichloromethane the yield decreases due to partial hydrolysis of the dithioacetals **2** to 4-oxoalkanethioate *S*-phenyl esters **3**. The latter compounds can be formed directly from ketones **1** by treatment with 90% aqueous formic acid (Table 2). In this case the reaction proceeds through the intermediate formation of ketene dithioacetals **2**, which can be detected by T.L.C.

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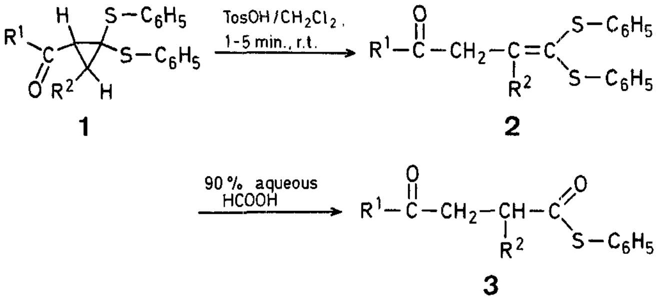

Table 1. β-Oxoketene Diphenylthioacetals **2**

Product No.	R^1	R^2	Yield[a] [%]	m.p. [°C]	Molecular Formula[c]	I.R. (CCl_4) ν_{CO} [cm^{-1}]	^{1}H-N.M.R. (CCl_4) δ [ppm]
2a	CH_3	H	85	63°	$C_{17}H_{16}OS_2$ (300.5)	1725	2.08 (s, 3 H); 3.48 (d, $J=7$ Hz, 2 H); 6.30 (t, $J=7$ Hz, 1 H); 7.14-7.32 (m, 10 H)
2b	C_2H_5	H	83	38-39°	$C_{18}H_{18}OS_2$ (314.5)	1725	1.00 (t, $J=7$ Hz, 3 H); 2.34 (q, $J=7$ Hz, 2 H); 3.45 (d, $J=7$ Hz, 2 H); 6.32 (t, $J=7$ Hz, 1 H); 7.11-7.28 (m, 10 H)
2c	n-C_3H_7	H	95[b]	oil	$C_{19}H_{20}OS_2$ (328.5)	1727	0.88 (t, $J=7$ Hz, 3 H); 1.44-1.72 (m, 2 H); 2.28 (t, $J=7$ Hz, 2 H); 3.42 (d, $J=7$ Hz, 2 H); 6.27 (t, $J=7$ Hz, 1 H); 7.12-7.38 (m, 10 H)
2d	n-C_4H_9	H	95[b]	oil	$C_{20}H_{22}OS_2$ (342.5)	1727	0.91 (t, $J=7$ Hz, 3 H); 1.10-1.70 (m, 4 H); 2.36 (t, $J=7$ Hz, 2 H); 3.47 (d, $J=7$ Hz, 2 H); 6.31 (t, $J=7$ Hz, 1 H); 7.10-7.45 (m, 10 H)
2e	C_6H_5	H	90	45-46°	$C_{22}H_{18}OS_2$ (362.5)	1690	4.04 (d, $J=7$ Hz, 2 H); 6.60 (t, $J=7$ Hz, 1 H); 7.10-7.43 (m, 13 H); 7.80-7.90 (m, 2 H)
2f	4-H_3C—C_6H_4	H	74	63-64°	$C_{23}H_{20}OS_2$ (376.5)	1690	2.31 (s, 3 H); 3.96 (d, $J=7$ Hz, 2 H); 6.48 (t, $J=7$ Hz, 1 H); 6.00-6.25 (m, 12 H); 7.20 (d, $J=8$ Hz, 2 H)
2g	CH_3	C_6H_5	94	68-70°	$C_{23}H_{20}OS_2$ (376.6)	1723	2.14 (s, 3 H); 3.98 (s, 2 H); 7.00-7.30 (m, 15 H)
2h	C_6H_5	C_6H_5	80	111-112°	$C_{28}H_{22}OS_2$ (438.6)	1684	3.52 (s, 2 H); 6.92-7.37 (m, 18 H); 7.60-7.70 (m, 2 H)

[a] Unless indicated otherwise, the yield is that of the recrystallised product.

[b] By ^{1}H-N.M.R. analysis.

[c] The microanalyses were in satisfactory agreement with the calculated values (C ±0.30, H ±0.15, S ±0.25).

Table 2. *S*-Phenyl 4-Oxoalkanethioates **3a-e, h**

Product	Yield[a] [%]	m.p. [°C]	Molecular formula[b]	I.R. (CCl_4) ν_{CO} [cm^{-1}]	^{1}H-N.M.R. (CCl_4) δ [ppm]
3a	50	31-33°	$C_{11}H_{12}O_2S$ (208.3)	1717	2.05 (s, 3 H); 2.5-2.9 (m, 4 H); 7.33 (s, 5 H)
3b	78	oil	$C_{12}H_{14}O_2S$ (222.3)	1705, 1722	0.97 (t, $J=7$ Hz, 3 H); 2.32 (q, $J=7$ Hz, 2 H); 2.5-2.9 (m, 4 H); 7.27 (s, 5 H)
3c	72	oil	$C_{13}H_{16}O_2S$ (236.3)	1690, 1720	0.90 (t, $J=7$ Hz, 3 H); 1.3-1.8 (m, 2 H); 2.33 (t, $J=7$ Hz, 2 H); 2.5-3.0 (m, 4 H); 7.32 (s, 5 H)
3d	75	oil	$C_{14}H_{18}O_2S$ (250.4)	1692, 1722	0.87 (t, $J=7$ Hz, 3 H); 1.2-1.6 (m, 4 H); 2.30 (t, $J=7$ Hz, 2 H); 2.5-2.9 (m, 4 H); 7.30 (s, 5 H)
3e	75	61-62°	$C_{16}H_{14}O_2S$ (270.4)	1690, 1714	2.9-3.3 (m, 4 H); 7.3-7.4 (m, 8 H); 7.8-8.0 (m, 2 H)
3h	79	77-78°	$C_{22}H_{18}O_2S$ (346.5)	1694, 1715	3.14 (dd, $J=18$ Hz, $J=5$ Hz, 1 H); 3.88 (dd, $J=18$ Hz, $J=9$ Hz, 1 H); 4.52 (dd, $J=9$ Hz, $J=5$ Hz, 1 H); 7.1-7.4 (m, 13 H); 7.8-7.9 (m, 2 H)

[a] Yield of isolated product.

[b] The microanalyses were in satisfactory agreement with the calculated values (C ±0.15, H ±0.20, S ±0.20).

The transformations described above can be recommended as synthetic methods for the preparation of ketene dithioacetals **2** and thioesters **3**, because the starting material diphenylthioacetals **1** can be obtained easily from *gem*-dichlorocyclopropyl ketones and sodium thiophenolate[5].

β-Oxoketene Dithioacetals 2; General Procedure:

To a stirred solution of **1**[5] (10 mmol) in dichloromethane (50 ml; dried by distillation over phosphorus pentoxide), some crystals of *p*-toluenesulphonic acid are added and the resultant mixture is stirred at room temperature for 1-5 min. The solution is shaken with saturated sodium hydrogen carbonate solution (50 ml). The organic layer is separated and the aqueous layer is extracted with ether (2 × 50 ml). The combined organic layers are dried with anhydrous sodium sulphate and the solvent is removed by distillation in vacuo. The residual oil is identified as **2** by ^{1}H-N.M.R. (10% solution in CCl_4) and recrystallised from 2-propanol (Table 1).

S-Phenyl 4-Oxooctanethioate (3d); Typical Procedure:

A mixture of **1d** (3.4 g, 10 mmol) and 90% aqueous formic acid (50 ml) is stirred at room temperature for 3 h. Then water (50 ml) is added and the resulting mixture is extracted with hexane (3 × 30 ml). The combined extracts are shaken with saturated sodium hydrogen carbonate solution (50 ml) and dried with anhydrous sodium sulphate. The solvent is removed in vacuo to yield the crude **3d**, which is purified by column chromatography on silica gel with hexane as eluent.

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