Preparation of α,β-Unsaturated Ketene Diphenylthioacetals by the Dehydration of *gem*-Diphenylthiocyclopropylcarbinols

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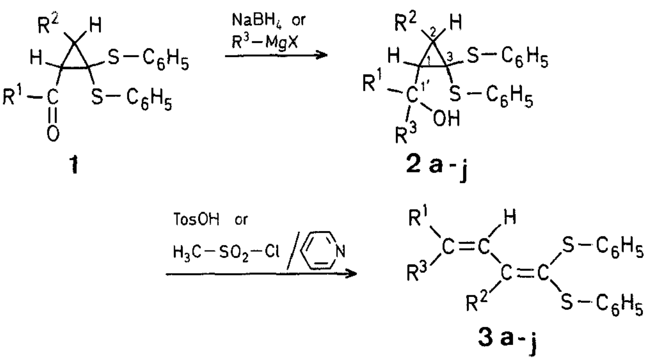
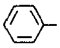
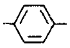
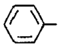
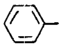
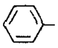
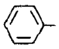
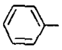
α,β-Unsaturated ketene dithioacetals are widely used in organic synthesis[1-5]. Attention to these compounds is focussed mainly on their ability to act as synthetic equivalents of *α,β*-unsaturated acyl anions[1-3]. Among all known methods of synthesis of *α,β*-unsaturated ketene dithioacetals, Peterson olefination[1,6] and enethiolization with subsequent alkylation of unsaturated dithioesters[2,3] are most widely used.

In the present work we describe a new and convenient method to obtain *α,β*-unsaturated ketene diphenylthioacetals **3** by the dehydration of *gem*-diphenylthiocyclopropylcarbinols **2**.

The starting materials **2** were prepared from the easily available *gem*-diphenylthiocyclopropyl ketones **1**[7,8] by treatment with sodium borohydride or organomagnesium compounds (Table 1). Reduction of ketones **1** with sodium borohydride gave a mixture of two diastereomeric alcohols **2**. In the case of alcohol **2e** ($R^1 = R^2 = C_6H_5$; $R^3 = H$) both the diastereomers (1*R*,1′*R*; 1*R*,1′*S*) were isolated by fractional crystallization. The diastereomer which was formed as major product, gave a signal for the methine proton ($R^3 = H$) in its ^{1}H-N.M.R. spectrum in the form of a doublet with a coupling constant of $J = 9$ Hz; while the diastereomer which was formed as minor product gave a doublet with $J = 7$ Hz. By analogy with the spectral data of diastereomeric secondary dichlorocyclopropylcarbinols[9], we could conclude that the major product from the reduction of the ketone **1e** has the (*R**,*S**)-configuration.



2,3	R^1	R^2	R^3	2,3	R^1	R^2	R^3
a		H	H	f	CH_3	H	CH_3
b	H_3C– 	H	H	g		H	
c	O_2N– 	H	H	h	C_2H_5	H	H
d		CH_3	H	i	*n*-C_3H_7	H	H
e			H	j	*n*-C_4H_9	H	H

Secondary benzylic **2a–e** and tertiary alcohols **2f**, **g** were dehydrated by refluxing in dichloromethane in the presence of catalytic amounts of *p*-toluenesulphonic acid. Dehydration of secondary *gem*-diphenylthiocyclopropylcarbinols **2h–j** (R^1 = alkyl) took place very slowly in these conditions; dienes **3h–j** might be obtained by refluxing the corresponding alcohols in benzene with methanesulphonyl chloride as dehydrating agent in the presence of pyridine. In the case of compounds **2a–e**, **h–j** the dehydration proceeds stereospecifically and only one geometrical isomer is formed. The magnitudes

Table 1. *gem*-Diphenylthiocyclopropylcarbinols **2** prepared

Product No.	Yield [%]	m.p.[a] [°C]	Molecular formula[b]	^{1}H-N.M.R. (CCl_4) δ [ppm]
2a	86	84–85°	$C_{22}H_{20}OS_2$ (364.5)	1.05 (dd, J=6 Hz, J=7 Hz, 1H); 1.43 (dd, J=6 Hz, J=9 Hz, 1H); 1.8–2.3 (m, 2H); 4.56 (d, J=9 Hz, 1H); 7.1–7.5 (m, 15H)
2b	90[c]	oil	$C_{23}H_{22}OS_2$ (378.6)	1.05 (dd, J=6 Hz, J=7 Hz, 1H); 1.39 (dd, J=6 Hz, J=9 Hz, 1H); 1.7–2.2 (m, 2H); 2.30 (s, 3H); 4.53 (d, J=9 Hz, 1H); 6.8–7.6 (m, 14H)
2c	90[c]	oil	$C_{22}H_{19}NO_3S_2$ (409.5)	1.23 (dd, J=6 Hz, J=7 Hz, 1H); 1.44 (dd, J=6 Hz, J=9 Hz, 1H); 1.8–2.5 (m, 2H); 4.64 (d, J=9 Hz, 1H); 7.0–7.6 (m, 12H); 7.9–8.1 (m, 2H)
2d	85	78–79°	$C_{23}H_{22}OS_2$ (378.6)	1.0–1.7 (m, 5H); 1.88 (s, 1H); 4.58 (d, J=9 Hz, 1H); 6.9–7.6 (m, 15H)
2e	93[d]	150°[e]	$C_{28}H_{24}OS_2$ (440.6)	2.3–2.7 (m, 2H); 2.93 (d, J=9 Hz, 1H); 4.84 (d, J=7 Hz, 1H); 6.9–7.6 (m, 20H)
		78–80°		2.2–2.7 (m, 3H); 4.83 (d, J=9 Hz, 1H); 6.5–7.6 (m, 20H)
2f	60	31–32°	$C_{18}H_{20}OS_2$ (316.5)	1.18 (s, 6H); 1.4–1.9 (m, 3H); 2.65 (s, 1H); 7.1–7.6 (m, 10H)
2g	91	92–93°	$C_{28}H_{24}OS_2$ (440.6)	1.52 (dd, J=6 Hz, J=9 Hz, 1H); 1.95 (dd, J=6 Hz, J=7 Hz, 1H); 2.48 (dd, J=7 Hz, J=9 Hz, 1H); 3.78 (s, 1H); 7.0–7.6 (m, 20H)
2h	90[c]	oil	$C_{18}H_{20}OS_2$ (316.5)	0.90 (t, J=7 Hz, 3H); 1.3–1.9 (m, 5H); 2.02 (s, 1H); 3.2–3.6 (m, 1H); 7.1–7.4 (m, 10H)
2i	90[c]	oil	$C_{19}H_{22}OS_2$ (330.5)	0.92 (t, J=7 Hz, 3H); 1.2–2.0 (m, 8H); 3.3–3.7 (m, 1H); 7.1–7.5 (m, 10H)
2j	90[c]	oil	$C_{20}H_{24}OS_2$ (344.6)	0.87 (t, J=7 Hz, 3H); 1.1–2.0 (m, 10H); 3.2–3.7 (m, 1H); 7.0–7.6 (m, 10H)

[a] Melting points of stereoisomers (*R**,*S**)-**2**.
[b] All compounds gave satisfactory microanalyses: C ±0.35, H ±0.3.
[c] By ^{1}H-N.M.R. analysis.
[d] Yield of the mixture of (*R**,*S**)-**2e** and (*R**,*R**)-**2e** in the ratio 10 : 1.
[e] Melting point of (*R**,*R**)-**2e**.

Table 2. α,β-Unsaturated Ketene Diphenylthioacetals **3** prepared

Product No.	Yield [%]	m.p. [°C]	Molecular Formula[a]	^{1}H-N.M.R. (CCl_4) δ [ppm]	U.V. (C_2H_5OH) λ_{max} [nm] ($\log\varepsilon$)
3a	70	64–66°	$C_{22}H_{18}S_2$ (346.5)	6.60 (d, J=16 Hz, 1H); 6.77 (d, J=10 Hz, 1H); 7.1–7.6 (m, 16H)	344 (4.76)
3b	90	54–55°	$C_{23}H_{20}S_2$ (360.6)	2.30 (s, 3H); 6.48 (d, J=16 Hz, 1H); 6.73 (d, J=10 Hz, 1H); 7.0–7.5 (m, 15H)	346 (4.77)
3c	52	118–119°	$C_{22}H_{17}NO_2S_2$ (391.5)	6.48 (d, J=16 Hz, 1H); 6.60 (d, J=10 Hz, 1H); 7.22 (s, 5H); 7.30 (s, 5H); 7.4–8.0 (m, 5H)	261 (4.53), 350 (4.73)
3d	88	113–114°	$C_{23}H_{20}S_2$ (360.6)	2.40 (s, 3H); 6.74 (d, J=16 Hz, 1H); 7.1–7.5 (m, 15H); 7.87 (d, J=16 Hz, 1H)	235 (4.57), 312 (4.60), 346 (4.74)
3e	70[b] 80[c]	126–127°	$C_{28}H_{22}S_2$ (422.6)	6.05 (d, J=17 Hz, 1H); 7.1–7.3 (m, 20H); 7.93 (d, J=17 Hz, 1H)	277 (4.32), 287 (4.29), 353 (4.70)
3f	79	oil	$C_{18}H_{18}S_2$ (298.5)	1.73 (d, J=1 Hz, 3H); 1.78 (d, J=1 Hz, 3H); 6.40 (dd, J=11 Hz, J=1 Hz); 6.93 (d, J=11 Hz, 1H); 7.12 (s, 5H); 7.15 (s, 5H)	260 (4.43), 304 (4.39)
3g	87	96–97°	$C_{28}H_{22}S_2$ (422.6)	6.66 (d, J=11 Hz, 1H); 7.9–7.4 (m, 21H)	249 (4.59), 351 (4.77)
3h	55	oil	$C_{18}H_{18}S_2$ (298.5)	0.98 (t, J=7 Hz, 3H); 1.9–2.3 (m, 2H); 5.73 (dt, J=17 Hz, J=7 Hz, 1H); 6.4–6.8 (m, 2H); 7.13 (s, 5H); 7.17 (s, 5H)	255 (4.38)
3i	69	oil	$C_{19}H_{20}S_2$ (312.5)	0.87 (t, J=7 Hz, 3H); 1.2–1.6 (m, 2H); 1.9–2.3 (m, 2H); 5.73 (dt, J=17 Hz, J=10 Hz, 1H); 6.4–6.8 (m, 2H); 7.13 (s, 5H); 7.20 (s, 5H)	257 (4.38)[d]
3j	55	oil	$C_{20}H_{22}S_2$ (326.5)	0.90 (t, J=7 Hz, 3H); 1.1–1.6 (m, 4H); 1.9–2.4 (m, 2H); 5.75 (dt, J=17 Hz, J=10 Hz, 1H); 6.3–6.7 (m, 2H); 7.1–7.4 (m, 10H)	254 (4.44)

[a] All compounds gave satisfactory microanalyses: C ±0.35; H ±0.3; S ±0.5.

[b] Product was obtained from (R^*,S^*)-**2e**.

[c] Product was obtained from (R^*,R^*)-**2e**.

[d] The sample was dissolved in dioxan.

of the coupling constants of the vicinal olefinic protons in the ^{1}H-N.M.R. spectra of the compounds **3a–e, h–j** are indicative of the *trans*-configuration for the disubstituted double bond (Table 2).

The configuration of the starting *gem*-diphenylthiocyclopropylcarbinols **2** does not seem to have any considerable importance in their use in the synthesis of α,β-unsaturated ketene diphenylthioacetals, because one and the same diene **3e** was formed as a result of dehydration of individual (R^*,R^*)-**2e** and (R^*,S^*)-**2e** alcohols (see Table 1).

gem-Diphenylthiocyclopropylcarbinols (2a–e, h–j); General Procedure: To a solution of *gem*-diphenylthiocyclopropyl ketone **1** (10 mmol) in tetrahydrofuran (50 ml) is added sodium borohydride (0.48 g, 10 mmol) dissolved in methanol (10 ml) at room temperature with stirring. The reaction mixture is stirred for 1 h, and treated with water (50 ml). The organic solvent is evaporated in vacuo. The residue is extracted with ether (3 × 30 ml). The extract is washed with brine (3 × 30 ml) and dried with anhydrous sodium sulphate. The solvent is evaporated in vacuo and the solid obtained is recrystallized from 2-propanol or from a mixture of 2-propanol and hexane (Table 1). The oily products are used without further purification.

gem-Diphenylthiocyclopropylcarbinols (2f, g); General Procedure: To a solution of methylmagnesium iodide or phenylmagnesium bromide (12 mmol) in ether (15 ml) the appropriate *gem*-diphenylthiocyclopropyl ketone **1** (10 mmol) in dry ether (100 ml) is added with stirring at such rate that the ether refluxes moderately. The reaction mixture is stirred for 0.5 h and then decomposed by addition of 5% hydrochloric acid (10 ml). The organic layer is separated and the aqueous layer is extracted with ether (3 × 30 ml). The combined organic layer is washed with brine (50 ml) and dried with anhydrous sodium sulphate. The ether is evaporated in vacuo and the residue is crystallized from 2-propanol (Table 1).

α,β-Unsaturated Ketene Diphenylthioacetals 3a–g; General Procedure: To a solution of **2a–g** (5 mmol) in dichloromethane (10 ml) *p*-toluenesulphonic acid (20 mg) is added and the mixture is refluxed for 5–9 h in the case of compounds **2a, b, d–g** and 50 h for **2c**. It is then cooled to room temperature and washed with saturated sodium carbonate solution (10 ml). The aqueous layer is extracted with ether (2 × 5 ml), the extracts are combined with the organic phase, and dried with anhydrous sodium sulphate. The solvent is evaporated in vacuo and the product is recrystallized from 2-propanol or subjected to column chromatography on alumina using hexane as eluent (Table 2).

α,β-Unsaturated Ketene Diphenylthioacetals 3h–j; General Procedure: A solution of **2h–j** (5 mmol), methanesulphonyl chloride (0.7 g, 6 mmol) and pyridine (0.5 ml) in dry benzene (10 ml) is refluxed for 5–7 h, and then cooled to room temperature. The crystals formed are filtered and washed with ether. The filtrate is washed with saturated sodium carbonate (2 × 5 ml) and the aqueous layer is extracted with ether (2 × 5 ml). The ether extracts are combined and dried with anhydrous sodium sulphate. The solvent is evaporated in vacuo and the residue is subjected to column chromatography on alumina using hexane as eluent (Table 2).

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[1] B.-T. Gröbel, D. Seebach, *Synthesis* **1977**, 357.

[2] B. Cazes, S. Julia, *Tetrahedron Lett.* **1978**, 4065.

[3] P. Gosselin, S. Masson, A. Thuiller, *C. R. Acad. Sci. Paris, Ser. C* **291**, 183 (1980).

[4] F. A. Carey, A. S. Court, *J. Org. Chem.* **37**, 4474 (1972).

[5] M. Petrzilka, J. I. Grayson, *Synthesis* **1981**, 753.

[6] S. Masson, A. Thuiller, *Tetrahedron Lett.* **21**, 4085 (1980); and references cited therein.

[7] I. G. Tishchenko, O. G. Kulinkovich, Y. V. Glazkov, *Zh. Org. Khim.* **11**, 581 (1975); *C. A.* **83**, 28027 (1975).

[8] O. G. Kulinkovich, I. G. Tishchenko, I. V. Reznikov, N. A. Roslik, *Zh. Org. Khim.* **18**, in press.

[9] I. G. Tishchenko, O. G. Kulinkovich, V. P. Krischkevich, A. I. Vrublevsky, *Zh. Org. Khim.* **15**, 2079 (1979); *C. A.* **92**, 128266 (1980).