A Facile Synthesis of 2-Phenylthio-2-ethylenic Carbonyl Compounds

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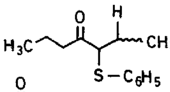
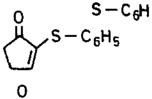
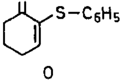
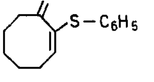
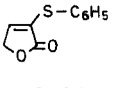
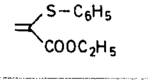
2-Arylthio- or 2-alkylthio-2-ethylenic ketones[1-6], esters[7], and lactones[8] are very useful synthetic intermediates. For instance, they have been used in the preparation of 2,3-dihydrofurans[3] and several 1,4- and 1,5-dicarbonyl compounds[9]. More recently, they have also been used in the regioselective alkylation of cyclohexanones[4], in the formation of angular carbon-carbon bonds[10], and in the synthesis of alkyl-Δ^1-butenolides[8]. However, the preparation of such intermediates usually requires many steps and starting materials which are not readily available.

In a previous publication[11] we reported the preparation of 2-phenylsulfinyl ketones by the direct phenylsulfinylation of ketones. We have now developed a very mild method of conversion of these and other phenylsulfinyl carbonyl compounds into the corresponding 2-phenylthio-2-ethylenic derivatives. The method, which involves a Pummerer rearrangement[12], consists in the treatment of phenylsulfinyl compounds of the type **1** with acetic anhydride and a catalytic amount of methanesulfonic acid in dichloromethane at room temperature. Under these conditions the reaction is complete in a few hours, and no appreciable loss of phenylsulfenic acid is observed[8,13]. In many cases 65–97% yields of practically pure rearranged products (**2a–f**) can be secured simply by removal of the solvent and resulting acetic acid under vacuum, followed by chromatography of the crude product on a florisil column.

The procedure, coupled with the previously described[11] preparation of 2-phenylsulfinyl ketones, is presently the shortest and most convenient route to some of these important intermediates (Table 1).

Table 1. Preparation of 2-Phenylthio-2-ethylenic Carbonyl Compounds (**2**)

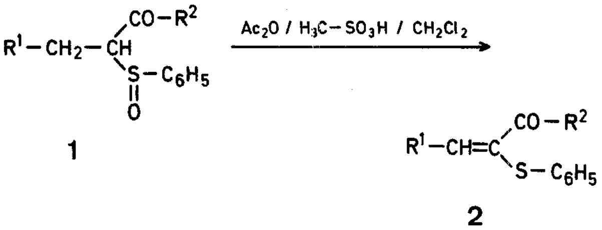
Product		Yield (%)[a]	M.p. (solvent) or b.p.[b]	Elemental Analysis			
2a		65[c]	b.p. 100°/0.3 torr	$C_{13}H_{16}OS$	calc.	C 70.86	H 7.32
				(220.33)	found	70.97	7.40
2b		73[c]	m.p. 64–65° (*n*-hexane)	$C_{11}H_{10}OS$	calc.	C 69.44	H 5.30
			Lit.[3]: 66–67°	(190.26)	found	69.56	5.12
2c		86	m.p. 50–51° (*i*-propyl alcohol)	$C_{12}H_{12}OS$	calc.	C 70.55	H 5.92
			Lit.[3]: 57–58°	(204.29)	found	70.70	6.05
2d		75	b.p. 110°/0.3 torr	$C_{14}H_{16}OS$	calc.	C 72.37	H 6.94
				(232.35)	found	72.51	7.03
2e		97[c]	m.p. 58–60° (*n*-hexane)	$C_{10}H_8O_2S$	calc.	C 62.48	H 4.19
			Lit.[8]: 57.5–59°	(192.23)	found	62.44	4.03
2f		92[d]	b.p. 85°/0.6 torr	$C_{11}H_{12}O_2S$	calc.	C 63.43	H 5.81
				(208.28)	found	63.65	5.96

[a] Yield of isolated product.

[b] Bath temperature, short path still.

[c] Parent phenylsulfinyl compound prepared according to Ref.[11].

[d] Parent ethyl 2-phenylsulfinylpropanoate prepared by sodium periodate oxidation[14] of ethyl 2-phenylthiopropanoate in dilute acetonitrile.



1 **2**

Table 2. Spectral Characteristics of 2-Phenylthio-2-ethylenic Carbonyl Compounds (**2a-f**)

Product	I.R.[a] $\nu_{C=O}$ cm^{-1}	^{1}H-N.M.R.[b] δ (ppm)	U.V.[c] λ_{max} nm ($\varepsilon \times 10^3$)
2a	1685	7.18 (q, 1 H, J=7 Hz), 2.0 (d, 3 H, J=7 Hz)	250(13.6), 270(3.3)
2b	1690	6.92 (t[d], 1 H, J=2 Hz)	232(6.8), 260(6.3), 281(5.4)
2c	1673	6.32 (t, 1 H, J=6 Hz)	235(6.5), 256(4.1), 272(4.1)
2d	1685	6.22 (t, 1 H, J=6 Hz)	239(6.5), 259(6.6)
2e	1745	6.60 (t, 1 H, J=2 Hz), 4.67 (d, 2 H, J=2 Hz)	227(6.7), 252(7.9), 268(6.1)
2f	1718	6.10 (s, 1 H), 5.13 (s, 1 H)	230(3.7), 255(4.5), 282(2.9)

[a] Recorded on a Perkin-Elmer IR-467 spectrophotometer as neat liquid or KBr pellet.

[b] Recorded on a Varian A-60D spectrometer as CCl_4 solution.

[c] Recorded on a Carl Zeiss Specord UV-VIS spectrophotometer as *n*-hexane solution.

[d] Slightly split triplet.

Typical Procedure; Synthesis of 2-Phenylthio-2-cyclohexenone (2c): Acetic anhydride (0.5 ml, 0.0053 mol) and methanesulfonic acid (0.04 ml, 0.0006 mol) were added to a solution of 2-phenylsulfinylcyclohexanone[11] (1.0 g, 0.0045 mol) in dichloromethane (25 ml) under nitrogen at room temperature. The solution was left standing for 16 h, the solvent and resulting acetic acid removed under vacuum, and the crude product chromatographed on a dry florisil column (petroleum ether 35–60°). After discarding the fore fractions, which contained small amounts of diphenyl disulfide, 2-phenylthio-2-cyclohexenone (**2c**) was recovered by evaporation of the solvent and crystallization from isopropyl alcohol; yield: 0.79 g (86%).

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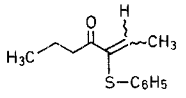
Errata:

S. H. Ruetman, *Synthesis* **1975**, 382:
The title should be:
Synthesis of Perchlorinated Indene and 5*H*-1-Pyrindine

H. J. Monteiro, A. L. Gemal, *Synthesis* **1975**, 437:
Compound **2a** in Table 1, page 437, should be:



G. E. Veenstra, B. Zwanenburg, *Synthesis* **1975**, 519:
The authors names should be:
Gauka E. Veenstra, Binne Zwanenburg

P. Savignac, J. Petrova, M. Dreux, P. Coutrot, *Synthes*
1975, 535:
The title should be:
α-Chlorination and Carbonyl Olefination; Preparation of 1,1-D chloroalkenes from Carbonyl Compounds.