COMMUNICATIONS

- New or improved synthetic methods
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A Modified Synthesis of Alkylidene-1,3-dithianes

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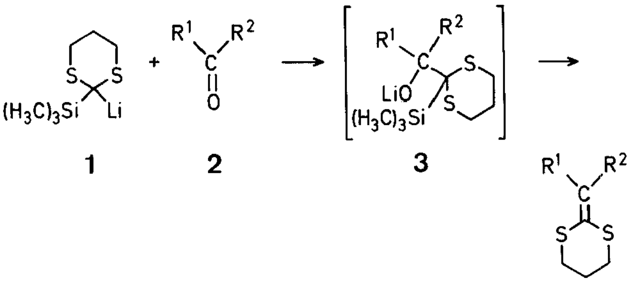
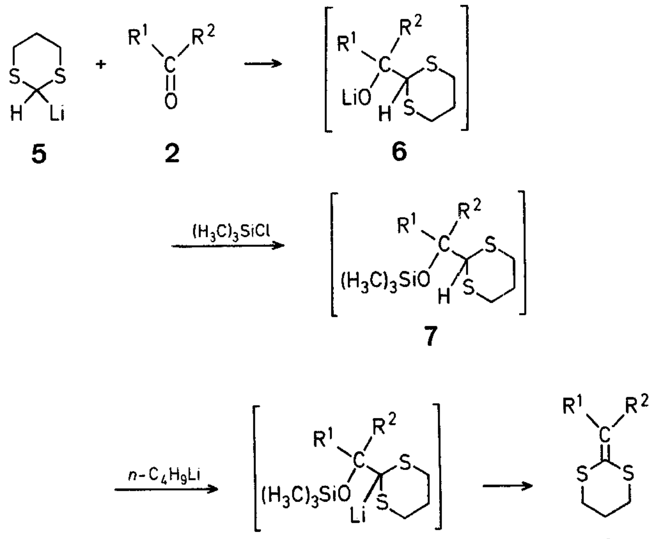
The Peterson olefination reaction between 2-lithio-2-trimethylsilyl-1,3-dithiane (**1**) and carbonyl compounds **2** to produce alkylidene-1,3-dithianes (ketene dithioacetals) **4** as represented in Scheme **A** has received considerable attention due to its practical simplicity, high yield, and the products' potential as synthetic intermediates[1-7].

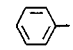
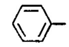
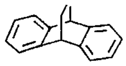
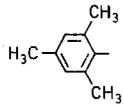
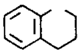
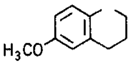
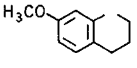


Scheme **A**



Scheme **B**

Table. Alkylidene-1,3-dithianes **4a-i** prepared

Product[a] No.	R[1]	R[2]	Yield [%]	b.p. [°C]/torr[b] or m.p. [°C][c]	Molecular formula[d] or Lit. b.p. or m.p.	M.S.[e] m/e (M^+, 100%)	^{1}H-N.M.R. (CCl_4 or $CDCl_3$/TMS)[f] δ [ppm]
4a	H		85	100°/0.05	148°/0.2[3]	208	1.9-2.3 (m, 2H); 2.8-3.0 (m, 4H); 6.68 (s, 1H); 7.0-7.5 (m, 5H)
4b[4]	H_3C		96	100°/0.05	$C_{12}H_{14}S_2$ (222.4)	222	1.8-2.3 (m, 2H); 2.16 (s, 3H); 2.6-3.05 (m, 4H); 7.16 (br s, 5H)
4c			97	138-139°	132.8-133.6°[3]	284	2.11 (quin, 2H, $J=7$ Hz); 2.98 (t, 4H, $J=7$ Hz); 7.29 (s, 10H)
4d			see procedure				
4e	H		80	100°/0.05	$C_{14}H_{18}S_2$ (250.4)	250	1.9-2.3 (m, 2H); 2.2 (m, 6H); 2.22 (s, 3H); 2.7-3.0 (m, 4H); 6.61 (s, 1H); 6.72 (s, 2H)
4f	H_3C	$t-C_4H_9$	57	100°/0.05	$C_{10}H_{18}S_2$ (202.4)	202	1.24 (s, 9H); 1.89 (s, 3H); 1.8-2.2 (m, 2H); 2.75-3.0 (m, 4H)
4g			70	60-61°	$C_{14}H_{16}S_2$ (248.4)	248	1.65-2.3 (m, 4H); 2.6-3.15 (m, 8H); 7.1-7.6 (m, 4H)
4h			78	121-122.5°	$C_{15}H_{18}OS_2$ (278.4)	278	1.6-2.3 (m, 4H); 2.5-3.1 (m, 8H); 3.79 (s, 3H); 6.65 (d, 1H, $J=2.5$ Hz); 6.73 (dd, 1H, $J=7$ Hz, 2.5 Hz); 7.46 (d, 1H, $J=7$ Hz)
4i			75	96-97°	$C_{15}H_{18}OS_2$ (278.4)	278	1.6-2.3 (m, 4H); 2.5-3.1 (m, 8H); 3.81 (s, 3H); 6.69 (dd, 1H, $J=8$ Hz, 2.5 Hz); 6.96 (d, 1H, $J=8$ Hz); 7.10 (d, 1H, $J=2.5$ Hz)

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[a] The I.R. spectra (Beckman IR 20A spectrophotometer) show C=C absorptions in the region $\nu = 1570-1600$ cm^{-1}, KBr discs for solids or neat liquids.

[b] Bulb-to-bulb distillation, heating bath temperature given.

[c] Recrystallized from ethanol; m.p. not corrected.

[d] Satisfactory microanalyses obtained: C ±0.29, H ±0.25, S ±0.31.

[e] Recorded with a DuPont 21-490B GC-MS instrument.

[f] Recorded with a Varian EM 360L spectrometer, CCl_4 solutions for liquid products, $CDCl_3$ solutions for solid products.

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One drawback of this attractive reaction, however, is the size of the trimethylsilyl group in **1**, which impedes its reaction with hindered ketones. Thus, treatment of **1** with pinacolone **(2f)** or the ketene-anthracene adduct **(2d)**[8] under the established procedure[3,4] did not, at least to our experience, give rise to a detectable amount of the corresponding ketene dithioacetals **4f** or **4d** (a precursor of methylene ketene[9,10]). Instead, the starting ketones **2** were recovered unchanged.

We now demonstrate that this disadvantage can be overcome by a modified, one-pot synthesis as outlined in Scheme **B.**

The reaction of 2-lithio-1,3-dithiane **(5)** with carbonyl compound **2** gave the alkoxide **6** which yielded **7** when chlorotrimethylsilane was added. Addition of *n*-butyllithium to the solution of **7** effected elimination, thus producing the ketene dithioacetal **4**[11]. It is apparent from the Table that the method works well for hindered ketones and promises to be an efficient general method for the synthesis of alkylidene-1,3-dithianes **4.**

Alkylidene-1,3-dithiane 4d; Typical Procedure:

To a 0 °C solution of 2-lithio-1,3-dithiane [**5**; prepared from 1,3-dithiane (480 mg, 4 mmol) in tetrahydrofuran (30 ml) and 1.58 molar *n*-butyllithium in *n*-hexane (2.8 ml, 4.4 mmol)] is slowly added while stirring a solution of the ketone **2d** (880 mg, 4 mmol) in tetrahydrofuran (30 ml) and stirring is continued for 0.5 h at 0 °C. Freshly distilled chlorotrimethylsilane (0.6 ml, 4.7 mmol) is added at −78 °C and the reaction mixture is stirred at 0 °C for 0.5 h. *n*-Butyllithium (4.4 mmol) is introduced to the solution at −78 °C and, again, the mixture is left stirring at 0 °C for 2 h. After work-up by the addition of saturated ammonium chloride solution (20 ml), the product is extracted into ether (400 ml), and evaporation of the extract gives almost pure **4d** which can be crystallized from ethanol to give colourless prisms; yield: 1.13 g (88%); m.p. 193–194 °C.

$C_{20}H_{18}S_2$	calc.	C 74.49	H 5.63	S 19.88
(322.5)	found	74.29	5.88	19.66

M.S.: *m/e* = 322 (M^+, 100%).

^{1}H-N.M.R. ($CDCl_3$/TMS): δ = 1.8–2.2 (m, 2 H); 2.43 (d, 2 H, *J* = 3 Hz); 2.65–2.9 (m, 4 H); 4.43 (t, 1 H, *J* = 3 Hz); 5.61 (m, 4 H); 7.0–7.4 ppm (m, 8 H).

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[11] In the case of **2d**, stepwise manipulation of the reaction led to the isolation and characterization of the sequential intermediates **6d** (as the alcohol) and **7d** in yields of 94% and 89%, respectively.

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