Reaction of Keten Dithio-acetals with Aziridine. Iodide Ion-catalysed Rearrangement of Thio-aziridino-methylene Compounds to Novel Δ^1-2-Methylthio-3,3-disubstituted Pyrrolines

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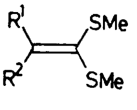
Summary The keten dithioacetals (**1**) and (**5**) react readily with aziridine (**2**) to give the corresponding thio-aziridinemethylene compounds (**3**) and (**6**) respectively, which on iodide ion-catalysed rearrangement, undergo ring expansion to give the pyrrolines (**4**) and (**7**) respectively.

The isomerisation of aziridine derivatives has provided useful synthetic routes to a variety of heterocyclic ring sytems.[1] However, *N*-vinylaziridines have not been studied extensively,[2] apparently because of their labile nature and the difficulty in their preparation. Although the polarised keten dithioacetals (**1**) are known to undergo ready displacement reactions with amines to give the corresponding thio-amino-methylene compounds,[3] a similar reaction of these intermediates with (**2**) has not been reported. In continuation of our interest[4] in the synthetic utility of keten dithioacetals, we report our preliminary results on the reaction of (**1**), (**5**), and (**9**) with (**2**) and further isomerisation of the intermediates (**3**) and (**6**) in the presence of iodide ion.

In a general procedure for the preparation of (**3**) and (**6**), a mixture of (**1**) or (**5**) (10 mmol) and (**2**) (50 mmol) in ether (150 ml) was stirred at 5—20 °C for 2—3 h. Removal of the solvent under reduced pressure yielded (**3**) and (**6**), respectively (Table). The n.m.r. spectra ($CDCl_3$) of (**3a**—**d**) and (**6a**—**f**) exhibited signals in the range δ 2·48—2·71



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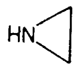

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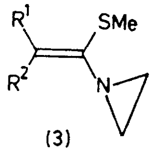

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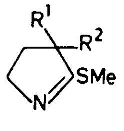

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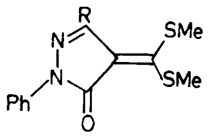

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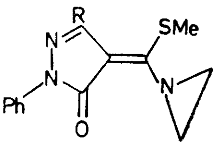

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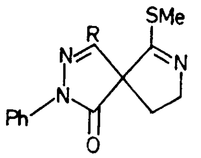

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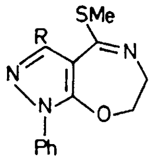

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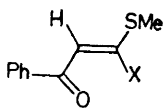

(9) X = SMe
(10) X = –N 
(11) X = $NH_2[CH_2]_2SMe$

Table

	Compound (3)[a] R1	R2	M.p./°C	Yield/%	Compound (4)[b] M.p. (b.p. at 1 mmHg)/°C	Yield[c]/%
a	CN	CO_2Et	96	87	(155)	85
b	CN	$CONH_2$	105—106	89	125—126	80
c	MeCO	CO_2Et	Oil	70[d]	e	e
d	CN	CN	109	85	f	f

	Compound (6)[a] R	M.p./°C	Yield/%	Compound (7)[b] M.p./°C	Yield[c]/%
a	Ph	111—113	96	144	80
b	*p*-MeC_6H_4	115	97	145—146	80
c	*p*-$MeOC_6H_4$	122—123	81	130—131	74
d	*p*-ClC_6H_4	134	94	139—140	75
e	*p*-BrC_6H_4	145—146	96	159—160	78
f	Me	119—120	54	80—82	78

[a] Compounds (**3**) and (**6**) were characterized by i.r., n.m.r., and mass spectral data, and were analysed only for nitrogen, since they partially decomposed during purification. [b] Compounds (**4**) and (**7**) gave satisfactory elemental analyses. [c] Yields are for the I^- ion-catalysed reaction; thermal isomerization gave poor yields of products containing impurities. Compounds (**7a**—**f**) were isolated directly by diluting the reaction mixture with H_2O. [d] Isolated after stirring for 12 h. [e] Compound (**4**; R^1 = H, R^2 = CO_2Et), b.p. 105—108 °C at 1 mmHg, and not (**4c**), was isolated in 45% yield. [f] Polymeric products were obtained from the attempted isomerization of (**3**[d]).

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s, 3H, SMe) and δ 2·16—2·75br (s, 4H, aziridine). In a similar reaction of (**9**) and (**2**), unchanged (**9**) was obtained. However, when (**2**) and (**9**) were heated (165 °C; 24 h) in a sealed tube in benzene, (**11**)‡ was formed exclusively (60%) instead of (**10**).

The I^- catalysed rearrangements of (**3**) and (**6**) were next examined. In a typical experiment, a mixture of (**3a**) (10 mmol) and KI (20 mmol) in dry acetone (150 ml) was stirred (20 °C; 2 h) and the reaction was monitored by t.l.c. The excess of solvent was removed, and the residue was diluted (H_2O) and extracted with CH_2Cl_2 to give (**4a**). Similarly (**3b**) yielded (**4b**), whereas (**3c**) underwent simultaneous deacetylation to give (**4c**) (Table). However, the attempted isomerisation of (**3d**) to (**4d**), both under thermal (refluxing C_6H_6, toluene, or xylene) as well as I^- catalysed conditions led only to polymeric products. Compounds (**6a**—**f**), under both I^- catalysed and thermal conditions yielded the spiro-compounds (**7**) and no traces of (**8**) were detected (t.l.c., single spot).§¶

The formation of both (**4**) and (**7**) has not been observed in any of the rearrangements studied previously, involving aziridine ring expansion. The scope of this method is apparently governed by the ease with which (**2**) can react with keten dithioacetals to give the required *N*-vinylaziridines without the strained three-membered ring being destroyed.

The keten dithioacetals (**1a**—**d**)[3] and (**5a**—**f**)[5] were prepared by reported procedures.

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‡ Oil, separated by column chromatography; satisfactory elemental analysis; n.m.r. ($CDCl_3$): δ 2·15 (s, 3H, SMe), 2·45 (s, 3H, SMe), 2·73 (t, 2H, CH_2SMe), 3·61 (m, 2H, NHCH_2), 5·70 (s, 1H, vinylic), 7·43 (m, 5H, ArH), and 12·06br (s, 1H, N*H*).

§ Compounds (**7a**—**f**) showed strong absorption in the range ν_{max} (KBr) 1690—1700 cm^{-1} (C=O), which precludes the formation of (**8**).

¶ The n.m.r. spectra (Varian A60, $CDCl_3$), of (**4a**—**c**) and (**7a**—**f**) were fully in accord with their structures; *e.g.* (**4a**) showed signals at δ 1·35 (t, 3H, OCH_2Me), 2·50 (s, 3H, SMe), 2·80 (m, 2H, CH_2), and 4·28 (m, 4H, overlapping =NCH_2 and OCH_2Me), and (**7a**) at δ 2·52 (s, 3H, SMe), 2·74 (m, 2H, CH_2), 4·45 (m, 2H, =NCH_2), and 7·52—8·12 (m, 10H, ArH). Compounds (**4b,c**) and (**7b**—**f**) gave analogous data.

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