

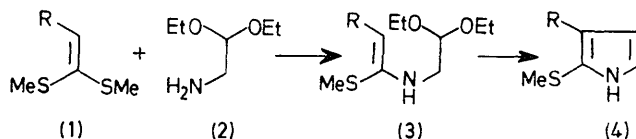
General Method for the Synthesis of 2-Methylthio-3-substituted Pyrroles using Keten Dithioacetals

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Summary The 2,3-substituted pyrroles (**4**) have been prepared by a general method by cyclization in cold ethereal HCl of the methylthio-amino-vinyl compounds (**3**), which were obtained by condensation of the keten dithioacetals (**1**) with 2,2-diethoxyethylamine (**2**).

ALTHOUGH there are several synthetic routes to pyrrole and its derivatives,¹ no method is available for the synthesis

of the hitherto unknown class of pyrroles (**4**) functionalised in the 2- and 3-positions. We report here a useful synthetic route to these derivatives (**4**) from (**3**).



a; R = PhCO
b; R = *p*-MeC₆H₄CO
c; R = *p*-MeOC₆H₄CO
d; R = *p*-EtOC₆H₄CO
e; R = *p*-ClC₆H₄CO
f; R = *p*-BrC₆H₄CO
g; R = MeCO
h; R = NO₂

In a general procedure, a solution of compound (**3a**)^{‡§} [prepared by the reaction of equimolar amounts of (**1a**)² and (**2**) in refluxing EtOH for 25–40 h] in dry ethereal HCl at 10 °C was stirred at room temperature for 1–2.5 h, to give the pyrrole (**4a**) in 62% yield. The pyrroles (**4b–h**)[‡] were prepared similarly (Table).

Compound	Yield/%	Compound	M.p./°C	Yield ^a /%
(3a)	55	(4a)	129–130	62
(3b)	59	(4b)	152–153	56
(3c)	61	(4c)	156–157	54
(3d)	57	(4d)	105–106	50
(3e)	59	(4e)	153–154	52 ^b
(3f)	58	(4f)	160–161	50 ^b
(3g)	61	(4g)	158	58
(3h)	62	(4h)	193–194	55

^a Reaction time 1 h unless otherwise noted. ^b Reaction time 2.5 h.

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‡ All compounds were characterised by i.r., n.m.r., and mass spectral data and elemental analysis.

§ Compounds (**3a–h**) were oils or low melting solids, purified by passing through a silica gel column.

The method is particularly useful for the synthesis of 3-acyl or -aroyl pyrroles, since none of the known reactions of pyrroles leads to preferential substitution in the 3-position.³ The method can also be extended to *N*-substituted

pyrroles by using the appropriate compound (2).

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² S. M. S. Chauhan and H. Junjappa, *Tetrahedron*, in the press.

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