Tetrahedron Letters,Vol.27,No.14,pp 1625-1626,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain

ENAMINOTHIONES OF IMIDAZOLIDINE NITROXIDES, A NEW ROUTE TO ACETYLENIC COMPOUNDS OF 3-IMIDAZOLINE

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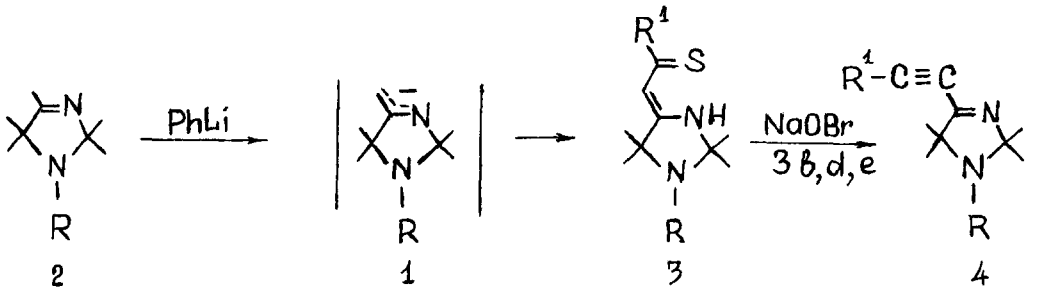
Summary: The title compounds were prepared and their reaction with NaOBr was investigated. Transformation of the enaminothiones and enaminodithiocarboxylates to acetylenic compounds was observed.

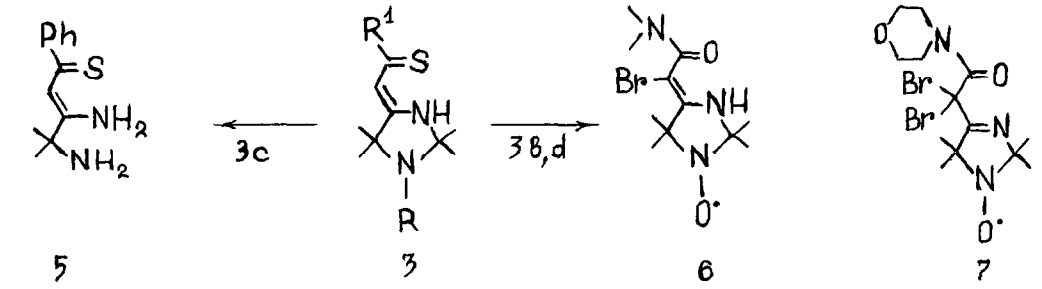
Earlier we have shown that the anion 1a (R = O^-), generated by treatment of 1-hydroxy imidazoline 2a with phenyllithium, reacts with various esters to give, after oxidation, enaminones of the imidazolidine nitroxides[1]. Under these conditions reaction of 1a with dithiocarbonate esters gives enaminothiones 3 (R^1 = C_6H_5, 50%, m. p. 162-163°; R^1 = CH_3, 40%, m. p. 120-121°)[2]. The reaction of 1a with methyl N,N-dimethyldithiocarbamate leads to the enaminothioamide 3f (40%, m. p. 144-145°). Treatment of 1a with carbon disulphide followed by dimethylsulphate alkylation and oxidation gives the enaminodithiocarboxylate 3d (45%, m. p. 170-172°).

We find that reaction of the enaminothione 3b with NaOBr in water-THF solution at 0° gives the acetylene derivative 4a [80%, m. p. 95-96° (hexane), IR: 2270 cm^{-1}; UV: 274 nm ($lg\varepsilon$ = 4.33)] . Similarly, the enaminodithiocarboxylate 3d reacted with NaOBr to give 4b [70%, m. p. 68-69° (hexane), IR: 2160 cm^{-1}; UV: 223 nm ($lg\,\varepsilon$ = 4.15), 263 nm ($lg\,\varepsilon$ = 4.15)], and the methoxy derivative 3e similarly yielded 4c [70%, oil, IR: 2160 cm^{-1}, UV: 220 nm ($lg\,\varepsilon$ = 3.96), 267 nm ($lg\,\varepsilon$ =4.0)] . In contrast the reaction of 3c proceeded with cleavage of the imidazolidine ring to give the aminoenaminothione 5 in 15% yield.



3	a	b	c	d	e	f	g
R	O•	O•	H	O•	OCH_3	O•	O•
R^1	CH_3	C_6H_5	C_6H_5	SCH_3	SCH_3	$N(CH_3)_2$	N⟨O⟩

4	a	b	c
R	O•	O•	OCH_3
R^1	C_6H_5	SCH_3	SCH_3



Enaminothiones with a nitrogen substituent at the thicarbonyl group reacted in the same conditions in another way. Thus, the reaction of the enaminothioamide 3f proceeded with replacement of the sulphur atom by oxygen, followed by bromination to give the bromo derivative 6, and reaction of 3g, prepared from the enaminodithiocarboxylate 3d with morpholine, leads to the dibromo derivative 7.

The above described results show the enaminothiocarbonyl compounds with C- or S-substituents at the thiocarbonyl group to be convenient precussors to acetylenic derivatives of 3-imidazoline, including imidazoline nitroxides. The scope and applications of the reaction are currently being investigated.

REFERENCES AND NOTES

1. Reznikov V.A., Reznikova T.I., Volodarsky L.B., Zh. Org. Khim., 1982, 18, 2135.
2. All new products were completely characterised and give the expected analytical and spectral data.

(Received in UK 28 November 1985)