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YNAMINETHIOETHERS FROM THE ISOMERIC DICHLOROETHYLENE THIOETHERS AND LITHIUM DIALKYLAMIDES;

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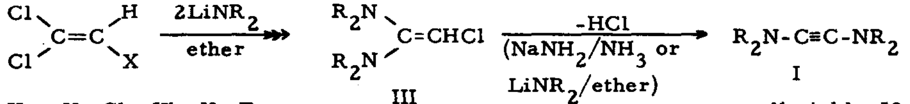
Ynamines R-C≡C-NR'R" are useful reagents(1). Of the heterosubstituted ynamines the ynediamines I have attracted our particular interest. They have become accessible recently by a general and new synthesis via α-elimination and "onium rearrangement"(2). They arise from trihaloethylenes (IIa and IIb) and lithium-N,N-disubstituted amides LiNRR' via β-chloroketene N,N-acetals III :



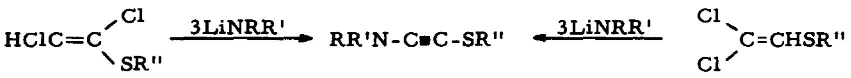
III

I

IIa : X= Cl ; IIb: X= F

overall yield : 50 to 60%

Similarly to amino groups, thioether groups undergo "onium rearrangement"(2). Consequently ynamine thioethers IV have now been synthesized from the three isomeric dichloroethylenethioethers V-VII by reaction with LiNRR' as shown in table 1. Obviously, several reaction mechanisms such as sequences of substitution and elimination or vice versa with or without "onium rearrangement" may lead to IV :



IV

VII

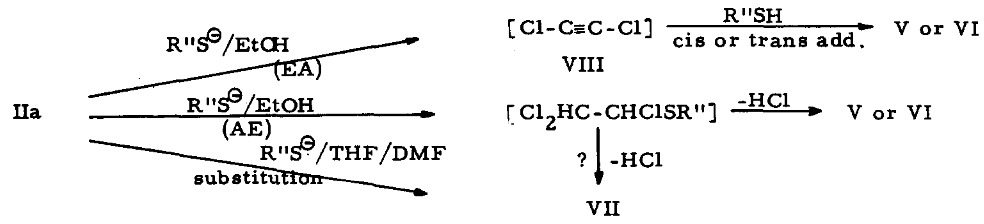
V (Cl, Cl trans) ; VI (Cl, Cl cis)

V-VII and their sulphones are known compounds(3-11). Spectroscopic control(12) has shown us that often mixtures of isomers are obtained whose composition depends mainly on the applied solvent. Thus addition of IIa to an alcoholic solution of thiolate(8) leads to at least 95% V besides traces of VI whereas addition of an alcoholic thiolate solution to boiling IIa(4) produces about 90% V and 10% VII. Surprisingly(11), VII is the major component if IIa is reacted with thiolates in DMF-THF solution :

$$\text{V } (\sim 90\%) + \text{VII } (\sim 10\%) \xleftarrow{\text{EtOH}} \text{IIa} + \text{R''SNa} \xrightarrow{\text{DMF/THF}} \text{V } (\sim 20\%) + \text{VII } (\sim 80\%)$$

Since V-VII do not undergo secondary isomerization under these reaction conditions, they must be formed by different reaction mechanisms.

Whereas V was shown(7,8) to derive from IIa by an elimination-addition sequence (EA) via dichloroacetylene VIII and subsequent thiolate trans addition, VI may be formed either by cis addition in the last step or from IIa by an addition-elimination sequence (AE), by analogy with earlier results reported on thiolate addition to IIb(2). The formation of VII from IIa excludes an EA mechanism. It remains open whether in DMF/THF an AE mechanism or direct chlorine substitution leads to VII :



These multiple mechanisms in thiolate reactions with IIa promise mechanistic diversity for reactions of V, VI and VII with LiNRR' to give IV. In practice, however, high yields of IV were obtained on treatment of an ethereal solution of V, VI or VII at -78° with a trimolar ratio of lithium amides followed by decomposition after 60 minutes with dilute HCl and distillation of the organic layer. Satisfactory elemental analyses were obtained for all compounds reported. The strong C≡C stretching frequency in the 4.7μ region is characteristic of IV.

Ynamine thioethers remain unchanged for several weeks at room temperature under nitrogen. In view of their ynamine structure, they can be expected to be useful and versatile reagents.

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Table 1.

$R''S-C\equiv C-NRR'$	Yield %[(a)]	B.p. °C/mm[(b)]
$R''=CH_3$, $R=R'=C_2H_5$	60 (V)	78-80/10
$R''=CH_3$, $R=R'=C_2H_5$	40 (VII)	(c)
$R''=C_2H_5$, $R=R'=CH_3$	58 (VII)	50-55/1
$R''=C_2H_5$, $R=R'=C_2H_5$	50 (VII)	65-70/0.1
$R''=C_2H_5$, $R=CH_3$, $R'=p.CH_3C_6H_4$	50 (VII)	80-85/0.1
$R''=C_2H_5$, NRR'=piperidine	60 (VII)	90-95/0.1
$R''=n\ C_4H_9$, $R=R'=C_2H_5$	35 (V)	105-110/0.5
$R''=n\ C_4H_9$, $R=R'=C_2H_5$	42 (VII)	105-110/0.5
$R''=iso.C_3H_7$, $R=R'=C_2H_5$	52 (VII)	70-75/0.01
$R''=C_6H_5$, $R=R'=C_2H_5$	68 (V+VI)	100-115/0.01
$R''=p.CH_3C_6H_4$, $R=R'=C_2H_5$	70 (V+VI)	80-83/0.01
$R''=p.CH_3C_6H_4$, $R=CH_3$, $R'=C_6H_5$	55 (V+VI)	(d)

(a) the starting olefin is indicated in brackets.

(b) using a "Kugelrohr" distillation apparatus.

(c) isolated by preparative vapour-phase chromatography.

(d) M.p. : 98-99°.

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(12) The following chemical shifts have been found for the vinyl hydrogen in C_6D_6 (concentration : 30% ; ref. TMS) V : 3.94 ; VI : 3.58 ; VII : 3.77 ; V (sulfone) : 2.43 ; VI (sulfone) : 4.00 ; VII (sulfone) : 3.50. The following values have been reported for VII : 3.50(9) and 3.62(10). Both determinations were made in CCl_4 solution (ref.TMS) ; the concentration was 15% in the former case, it was not specified for the latter. We have observed that identification of V-VII by N.M.R. is uncertain in CCl_4 solution since the chemical shifts are very similar. The following τ_H have been reported for the vinyl hydrogen in the sulphone corresponding to VII : 3.04 ($CDCl_3$, 15%)(9) ; 3.11 (CCl_4)(10).

Several different values are found in the literature for the m.p. of the sulphones (4, 6, 11). These discrepancies may be due to different ratios of the possible isomers. We have observed the following m.p. for the sulphones : V : 49-50° ; VI : 68° ; VII : 55°.