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NOVEL CYCLIZATION OF 2-(HYDROXYIMINO)-2-PHENYLETHYL DITHIOCARBOXYLATES

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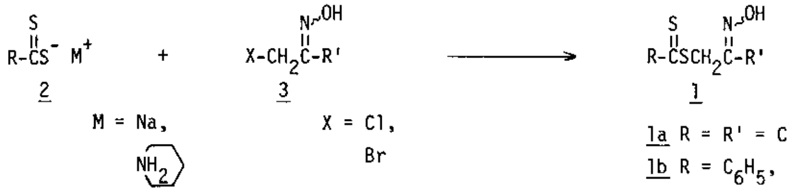
In the course of our research to develop new synthetic applications of dithiocarboxylic acid derivatives,[1] we have been interested in the nucleophilicity of sulfur atom of the thiocarbonyl moiety.[2] We report here the syntheses and some reactions of the new dithiocarboxylic acid oxime derivatives (1).

The oximes (1) were prepared from piperidinium or sodium dithiocarboxylates (2) and halo oxime (3) in moderate yields (Eq. 1).



$$R\text{-}\overset{S}{\overset{\|}{C}}S^-\ M^+ \quad + \quad X\text{-}CH_2\overset{N\sim OH}{\overset{\|}{C}}\text{-}R' \longrightarrow R\text{-}\overset{S}{\overset{\|}{C}}SCH_2\overset{N\sim OH}{\overset{\|}{C}}\text{-}R' \qquad (1)$$

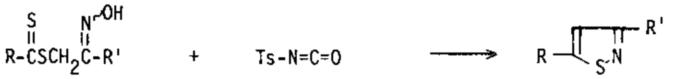
2: M = Na,

3: X = Cl, Br

1

1a R = R' = C_6H_5: 86%
1b R = C_6H_5, R'= CH_3: 53%
1c R = 4-$CH_3C_6H_4$, R'= H: 71%
1d R = i-C_3H_7, R'= 4-BrC_6H_4: 63%

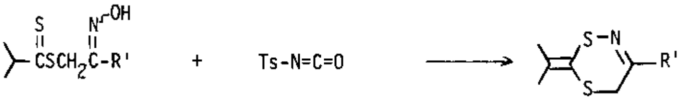
The oximes (1a-c) (R = Ar) were easily cyclized to the corresponding isothiazoles (4) by the treatment with tosyl isocyanate (Eq. 2). On the other hand, similar treatment of the oxime (1d) (R = i-C_3H_7) led to 84% of the novel heterocyclic compound, 6H-2-isopropylidene-1,3,4-dithiazine (5)(Eq. 3). In these reactions, no Beckmann rearrangement products were detected.



(2)

1a-c 4

4a: 65%
4b: 49%
4c: 32%



(3)

1d (R'= 4-BrC_6H_4)

5; 84%

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[1] S. Kato et al., Z. Naturforsch., 36b, 739 (1981).

[2] M. Ishida, S. Kato, and M. Mizuta, Z. Naturforsch., 36b, 1047 (1981).