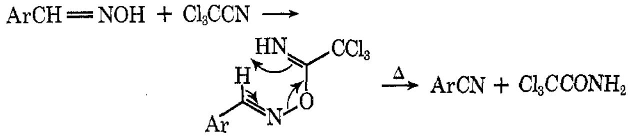
in phosphorylation of alcohols,[3] and conversion of symmetrical pyrophosphates into phosphate diesters.[4] We have now observed that aryl aldoximes are readily dehydrated upon refluxing with trichloroacetonitrile. The by-product, trichloroacetamide, is generally obtained in quantitative yield and can be easily removed. The reaction can be depicted as follows.



The initial configuration of the aldoxime does not seem to affect the results. Dehydration of aliphatic aldoximes under similar conditions is not so efficient.

Table I

Cl_3CCN Dehydration of ArCH=NOH

Oxime of	Registry no.	Nitrile yield, %	Registry no.
C_6H_5CHO	932-90-1	81	100-47-0
$4\text{-}CH_3C_6H_4CHO$	3235-02-7	94	104-85-8
$3,4\text{-}(CH_3O)_2C_6H_3CHO$	2169-98-4	75	2024-83-1
$1\text{-}C_{10}H_7CHO$	13504-46-6	95	86-53-3
$C_6H_5CH{=}CHCHO$	13372-81-1	92	4360-47-8

Experimental Section

Dehydration of Aryl Aldoximes. General Procedure.—A mixture of the aldoxime (3 mmol) and trichloroacetonitrile (1 ml) was refluxed for 0.5 hr with the exclusion of atmospheric moisture. The excess reagent was removed *in vacuo,* and the residue was digested thrice with warm hexane. The combined hexane solution was washed with water, dried over $MgSO_4$, and evaporated to afford the nitrile, which was distilled or recrystallized and identified by comparison with authentic sample (ir, nmr, tlc). Yields are given in Table I.

Registry No.—Trichloroacetonitrile, 545-06-2.

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A New Synthesis of Thioimino Esters

S. L. Razniak,* E. M. Flagg, and F. Siebenthall

Department of Chemistry, East Texas State University, Commerce, Texas 75428

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As part of our studies on the synthesis of substituted dithio acids and their derivatives we have had occasion to prepare thioimino esters. The methods most commonly employed for the preparation of these compounds are variants of the original procedure reported by Autenreith and Bruning.[1] The recent report by Suydam, Greth, and Langerman[2] for the preparation of imino esters from amides and ethyl chloroformate suggested to us the possibility of a parallel synthesis of thioimino esters. We have investigated the reaction of ethyl thiochloroformate with several amides and thio amides. The reaction of amides with ethyl thiochloroformate did not produce the corresponding ethyl thioimino esters. No reaction was observed until the equimolar reaction mixture was heated to reflux temperature, when sudden gas evolution occurred and a white solid was formed which was a mixture of unreacted amide and the amide hemihydrochloride. Suydam[2] reported the formation of acetamide hemihydrochloride in the reaction of acetamide with ethyl chloroformate. The reaction of thio amides with ethyl thiochloroformate, however, produces the corresponding ethyl thioimino esters. When an equimolar amount of ethyl thiochloroformate is added slowly to a thio amide, with exclusion of moisture, a spontaneous exothermic reaction begins immediately. The product formed has been shown, by nmr and comparison to authentic samples prepared by the classical method,[1] to be the thiomino ester hydrochloride corresponding to the starting thio amide. The results of duplicate runs are shown in Table I.

$$RSH + R'CN \xrightarrow{HCl(g)} R'(C{=}NH_2)SR^+Cl^-$$

$$RCSNH_2 + C_2H_5SCOCl \longrightarrow R(C{=}NH_2)SC_2H_5{}^+Cl^-$$

Table I

Reactant $RCSNH_2$	Registry no.	Yield of product,[a] % $R(C{=}NH_2)\text{-}SC_2H_5{}^+Cl^-$	Registry no.
$R = CH_3$	62-55-5	79	5426-05-1
$R = C_2H_5$	631-58-3	59	39549-80-9
$R = C_6H_5$	2227-79-4	48	5442-13-7

[a] Based on crude product.

Since thio amides are readily available from nitriles by several methods,[3] the preparation of thioimino esters by this method offers an alternate synthetic route to the classical reaction.

Experimental Section

The following experimental procedure is representative of the method used for the preparation of ethyl thioimino esters.

The addition of 12.4 g (0.1 mol) of ethyl thiochloroformate to 7.5 g (0.1 mol) of thioacetamide results in an immediate exothermic reaction accompanied by gas evolution. After 6 min the reaction is complete and the reaction mixture solidifies to a white semisolid. The crude product is transferred to a fritted glass filter and washed several times with cold anhydrous ether. After removal of the ether by vacuum filtration the white crystalline product is immediately stored in a vacuum desiccator over P_2O_5. The yield of crude product is 11.1 g (79.2%). One recrystallization from chloroform gives a product melting at 139–141° (lit. mp 143°).[4] The physical properties and nmr spectrum of the product are identical with those of an authentic sample of ethyl thioiminoacetate prepared by the classical method.[1]

Registry No.—Ethyl thiochloroformate, 2941-64-2.

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