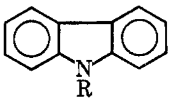
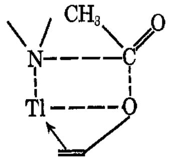
It is proposed that the thallium(I)-induced reaction of carbazole and vinyl acetate occurs *via* a four-center transition state (**2**) in which an important factor is coordination between the vinyl group and thallium,[7] since this reaction fails when the substrate is a simple ester, *e.g.*, ethyl acetate, or a sterically hindered ester, *e.g.*, vinyl pivalate or vinyl benzoate.



1a, R = CHMeOCOMe
b, R = CHMeOMe
c, R = COMe



2

$CH_2{=}CHOTl$
3

$CH_2{=}CHOCO_2Tl$
4

The potassium-induced reaction is envisaged as occurring *via* addition of potassium carbazole to the carbonyl group of vinyl acetate, and subsequent attack by a carbazolyl anion at the activated α-carbon atom (*cf.*[8] reactivity of vinyl ethers toward nucleophiles); likewise this reaction fails with sterically hindered esters (vinyl pivalate).

The differing mechanisms which operate for the thallium(I)- and potassium-induced reactions are seen to reflect the bonding in the respective metal–nitrogen bonds. Gray[9] has interpreted the somewhat short Tl–N distance (2.98 Å) in thallium(I) azide (*cf.* K–N 2.96 Å in potassium azide; ionic radii Tl^+ 1.49, K^+ 1.33) as indicating that the thallium–nitrogen bond is partially covalent. Further evidence in support of the proposed four-center reaction mechanism is available from Pearson's hard–soft acid–base principle.[10] Thallium(I) is a soft Lewis acid, whereas potassium (K^+) is a hard Lewis acid, and the former would be expected to exhibit a much greater tendency to coordinate to the vinyl group.

It is interesting to note that reaction of carbazole with vinyl acetate catalyzed by mercury(II) compounds yields exclusively *N*-vinylcarbazole.[11]

Experimental Section

Ir spectra were recorded for Nujol mulls. Mass spectra were measured by the Physico-Chemical Measurements Unit, Harwell. ^1H nmr spectra were recorded at 60 MHz with tetramethylsilane as internal standard.

N-Acetylcarbazole, mp 68–69° (lit.[12] mp 68–69°), was prepared from carbazole and acetic anhydride, as described.[11] *N*-(α-Methoxyethyl)carbazole, mp 88–90° (lit.[4] mp 89–90), was prepared from *N*-vinylcarbazole and methanol.

***N*-(α-Acetoxyethyl)carbazole.**—Vinyl acetate (10 g) was added dropwise to a stirred mixture of carbazole (10 g) and powdered potassium hydroxide (0.5 g) in acetone (25 ml) cooled in a carbon tetrachloride–Dry Ice bath (*ca.* −35°). The reaction mixture was stirred for 2 hr and then allowed to warm up to room temperature and filtered. The filtrate was evaporated and the resulting oil was recrystallized from petrol (bp 40–60°) to afford *N*-(α-acetoxyethyl)carbazole[13] (8.5 g, 57%): mp 87–88° (lit.[3] mp 85–87°); ν_{max} 1745, 1730 (C=O), 1598, 1490, 1335, 1238, 1210, 1155, 1085, 1058, 1010, 985, 920, 750, and 720 cm^{-1}; nmr τ [$(CD_3)_2CO$] 1.9–3.0 (9 H, m, ArH and NCHO–), 8.05 (3 H, s, $COCH_3$), and 8.16 (3 H, d, J = 7 Hz, CH_3); mass spectrum m/e (rel intensity) 253 (M^+, 12), 194 ($M - MeCO_2$, 20), 193 ($M - C_2H_4O_2$, 42), 192 (10), 168 (12), 167 ($M - C_4H_6O_2$, 100), 166 (14), 140 (20), and 139 (10).

N-(α-Acetoxyethyl)carbazole was refluxed in methanol for 0.5 hr to afford *N*-(α-methoxyethyl)carbazole, mp and mmp 86–88° (lit.[4] mp 89–90°), from methanol: nmr [$(CD_3)_2CO$] 1.9–3.1 (8 H, m, ArH), 4.55 (1 H, q, J = 7 Hz, NCHO), 6.91 (3 H, s, $COCH_3$), and 8.32 (3 H, d, CH_3).

Reaction of Vinyl Acetate with Carbazole and Thallium(I) Ethoxide.—Thallium(I) ethoxide (3.0 g) was added to a solution of carbazole (1.7 g) in DMF–ether (25 ml, 1:1 v/v), and the mixture was stirred at room temperature for 0.5 hr. Vinyl acetate (4.0 g) was then added and the mixture was stirred at room temperature for a further 2 hr, during which time a white precipitate was deposited. The reaction mixture was filtered free of solid material and poured into water, and the aqueous mixture was extracted with ether and dried ($MgSO_4$). Evaporation afforded an oil which was recrystallized from aqueous methanol to give *N*-acetylcarbazole (1.2 g, 57%), mp and mmp 68–70° (lit.[12] mp 68–69°).

The precipitate (1.0 g), mp 80–85° dec, which discolored upon standing in daylight, was tentatively identified as vinyloxythallium(I). *Anal.* Calcd for C_2H_3TlO: C, 9.7; H, 1.2. Found: C, 9.7, H, 1.2. Upon standing this material reacted with carbon dioxide (air) to form vinylcarbonatothallium: ν_{max} 1620–1500 (br, carbonate), 1285, 1210, 1015, 950, and 920 cm^{-1} (vinyl); mass spectrum m/e (rel intensity) 249/247 ($M - C_2H_3O$, 23/5), 221/219 ($M - C_3H_3O_2$, 2/1), 205/203 (100/47, $^{205}Tl^+/^{203}Tl^+$), 60 (60), 45 (72), and 43 (81); measured mass 246.9621 (calcd for $CO_2{}^{203}Tl$, 246.9631).

Registry No.—**3**, 39542-29-5; **4**, 39542-30-8; vinyl acetate, 108-05-4; carbazole, 86-74-8; thallium(I) ethoxide, 20398-06-5.

Acknowledgments.—We thank the SRC for a Research Assistantship (to L. J. K.).

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[7] F. A. Cotton and L. T. Reynolds, *J. Amer. Chem. Soc.*, **80**, 269 (1958).

[8] Houben-Weyl, "Methoden der Organishen Chemie," Georg Thieme Verlag, Stuttgart, 1965, p 90, 185.

[9] P. Gray, *Quart. Rev., Chem. Soc.*, **17**, 441 (1963); A. G. Lee, "The Chemistry of Thallium," Elsevier, Amsterdam, 1971.

[10] R. G. Pearson, *J. Amer. Chem. Soc.*, **85**, 3533 (1963).

[11] H. Kaye, *Polym. Lett.*, **7**, 1 (1969).

[12] A. A. Berlin, *J. Gen. Chem. USSR*, **14**, 438 (1944); *cf. Chem. Abstr.*, **39**, 4606 (1945).

[13] This material was stored below 5°.

A Novel Aryl Cyanide Synthesis Using Trichloroacetonitrile

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Received February 23, 1973

Although there exist a great number of ways to effect dehydration of aldoximes, interest in this area remains unabated.[1] Since most methods either utilize acidic reagents or are attended by the generation of acidic side products which might be detrimental to sensitive molecules, the development of procedures involving strictly neutral conditions is highly desirable. We wish to report a novel method for converting aryl aldoximes to the corresponding cyanides which fulfills this criterion; furthermore, the present procedure is simple, efficient, and economical.

Trichloroacetonitrile exhibits a remarkable capability of mediating the replacement of a hydroxy group by chlorine[2] under very mild conditions; it is also useful

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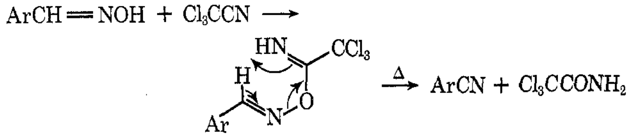
[1] J. K. Chakrabarti and T. M. Hotten, *J. Chem. Soc., Chem. Commun.*, 1226 (1972), and references cited therein.

[2] F. Cramer and H.-J. Baldauf, *Chem. Ber.*, **92**, 370 (1959).

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.

Acknowledgment.—We thank the National Research Council of Canada for partial financial support.

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[3] F. Cramer, W. Rittersdorf, and W. Böhm, *Justis Liebigs Ann. Chem.*, **654**, 180 (1962).

[4] F. Cramer, K.-H. Scheit, and H.-J. Baldauf, *Chem. Ber.*, **95**, 1657 (1962).

A New Synthesis of Thioimino Esters

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Received January 25, 1973

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]

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

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.

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

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.

Table I

Reactant $RCSNH_2$	Registry no.	Yield of product,[a] % $R(C{=}NH_2)SC_2H_5{}^+Cl^-$	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.

Acknowledgment.—We gratefully acknowledge the Robert A. Welch Foundation (Grant No. T-124) and the Office of Organized Research of East Texas State University for supporting this research.

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[2] F. H. Suydam, W. E. Greth, and N. R. Langerman, *J. Org. Chem.*, **34**, 292 (1969).

[3] E. Emmett Reid, "Organic Chemistry of Bivalent Sulfur," Vol. IV, Chemical Publishing Co., New York, N. Y., 1962, pp 45–52.

[4] A. Hantzsch, *Ber.*, **64**, 665 (1931).