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The Iodotrichlorosilane Induced Reactions of Aromatic Aldehydes with Acrylonitrile : A Unique Route to Unsaturated Iminoaldehydes

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Abstract. We describe a unique interaction of aromatic aldehydes with acrylonitrile, induced by iodotrichlorosilane (ITCS), which directly yields arylidene-3-aminoprop-2-enals.

We recently disclosed[1] a unique and general redox reaction of aliphatic or aromatic aldehydes with simple aliphatic or aromatic nitriles, which leads directly to amides (equation 1). The use of iodotrichlorosilane (ITCS) (generated *in situ*) to effect this reaction is mandatory.

$$R^1CHO + R^2CN + 2ISiCl_3 + 2H_2O \longrightarrow R^1CH_2NHCOR^2 + I_2 + 2Cl_3SiOH \qquad (1)$$

As part of a programme to explore the reaction we have used an αβ-unsaturated nitrile, acrylonitrile to replace the acetonitrile and benzonitrile previously used. We here report that the ITCS induced reaction of acrylonitrile with aromatic aldehydes takes a most unusual route, as outlined in equation (2) to give compounds (**1**). The results of our initial survey of the reaction are given in the Table.

$$ArCHO + CH_2{=}CHCN \xrightarrow[H_2O]{ISiCl_3} \underset{\mathbf{(1)}}{ArCH{=}N{-}CH{=}CH{-}CH{=}O} \qquad (2)$$

TABLE[a]

Experiment	Substrate	Time (h)	% Yields of (1)[b]
1	PhCHO	4	57
2	4-$MeOC_6H_4CHO$	9	51
3	4-$Me_2NC_6H_4CHO$	8	91
4	α-Naphthaldehyde	12	84
5	3-Formylchromone	6	45
6	PhCH=CHCHO	6	49[c]

[a)] All reactions carried out at 25°C in 1,2-dichloroethane. [b)] All yields are of isolated, fully characterised products. [c)] 3-Iodo-3-phenylpropanal (26%) also isolated.

The reaction works satisfactorily for simple aldehydes (Table, exp. 1-4). No other products were observed and the modest yields in experiments 1 and 2 reflect the experimental difficulty of handling and purifying the labile iminoaldehydes (**1**). The heterocyclic aldehyde, 3-formylchromone (Table, exp. 5), also gave (**1**) (Ar=3-chromonyl) despite the well documented ability of ITCS to cleave ethers.[2,3] In the case of the reaction of an $\alpha\beta$-unsaturated aldehyde (Table, exp. 6) there is competition from 1,4-addition of ITCS, but nevertheless the highly unsaturated product (**1**) (Ar = PhCH=CH) was isolated pure in 49% yield. The reaction is therefore reasonably general.

To our knowledge, there is no analogy in the literature for this reaction which, unlike that in equation (1), does not formally involve ITCS as a redox reagent. However, ITCS cannot be replaced by tetrachlorosilane. The pathway taken, although obviously favoured, is not at all obvious, and though it is possible to delineate a route proceeding *via* cycloaddition of $CH_2=CH\text{-}C(I)=NSiCl_3$ to ArCHO, speculation is best restrained until more evidence is to hand. The reaction, however, is a viable direct route to the unsaturated aldehydes (**1**) and further illustrates the interesting properties of ITCS.

3-[(*p*-(N,N-Dimethylamino)phenylmethylene)amino]-prop-2-enal. Tetrachlorosilane (2.4 ml, 20 mmol) in 1,2-dichloroethane (10 ml) was added dropwise to p-(N,N-dimethylamino)benzaldehyde (1.4 g, 10 mmol) and sodium iodide (3.0 g, 20 mmol) in acrylonitrile (0.65 ml, 10 mmol). The reaction mixture was stirred for 8h at *ca.* 25°C with exclusion of moisture, and then poured into water. The organic layer was rapidly separated, the aqueous layer extracted with $CHCl_3$ (2 x 25 ml) and the combined organic extracts dried ($MgSO_4$), filtered and concentrated. Purification on silica gel ($CHCl_3 : C_6H_{14} = 1 : 1$) gave the ***product*** (1.86 g) as a solid, m.p. 127°C; Found C,71.35; H,6.81; N,13.91%. $C_{12}H_{14}N_2O$ requires C, 71.29; H,6.93; N,13.86%. ^1H nmr δ 9.7 (d,1H,CHO); 7.7 - 6.5 (m,7H), 1.3(s,6H). υ_{max} 1730 (CHO), 1660 (C=N), 1600 cm^{-1} (C=C).

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