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A NOVEL SYNTHESIS OF AROMATIC NITRILE BY THE REACTION OF AROMATIC ALDEHYDE WITH TRIMETHYLSILYL AZIDE

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In the presence of zinc chloride, the reaction of aromatic aldehydes with trimethylsilyl azide (TMSA) gave readily the corresponding nitriles in good yields under mild conditions.

It is well-known that aldoximes, prepared by condensation of aldehydes with hydroxylamine, give the nitriles.$^{1)}$ Other nitrile syntheses are also established, *e.g.* aromatic amines yield the compounds *via* arene diazonium salts and amides afford those by removal of water.$^{1)}$ On the other hand, we are recently interested in the synthetic utilities of azides containing silicon atom.$^{2)}$ Among our investigations of TMSA, it has become clear that TMSA was reactive to carbonyl group$^{2c)}$ in contrast to the reported studies.$^{3)}$ Birkofer, *et al.*,$^{4)}$ reported that the reaction of TMSA with aliphatic aldehydes gave 1:1-adducts, trimethylsiloxy azides, which were thermally decomposed to afford *N*-trimethylsily amides. We considered that such an adduct of aldehydes and TMSA would be regarded as a precursor of the nitriles by nitrogen evolution and formal elimination of silanol. In this communication, we would like to report a novel synthesis of aromatic nitriles by the reaction of aromatic aldehydes with TMSA under non-aqueous, mild, and neutral conditions.

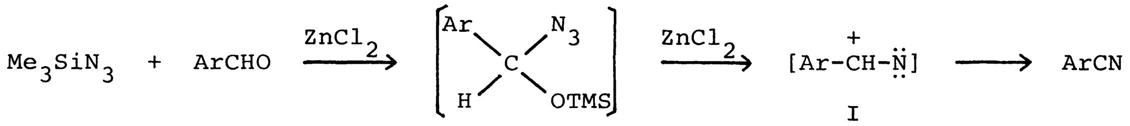
To a mixture of benzaldehyde and an equimolar of zinc chloride in dichloromethane was added dropwise with stirring a solution of TMSA (1.3 equiv.) in dichloromethane at room temperature. Then the mixture was kept at the temperature for 4 h, and work-up of the reaction mixture gave 62% of benzonitrile as a sole product by column chromatography on alumina. Other aromatic aldehydes were treated in a similar manner and the results are shown in Table 1. With aldehydes having electron-donating group, the nitriles were obtained in a range of 60-97% yields. When the reaction was carried out at 80 °C for 1.5 h using 0.06 equiv. of the catalyst, the yield of the nitriles was almost same as above. Similarly, cinnamaldehyde, TMSA (1.3 equiv.), and $ZnCl_2$ (1 equiv.) gave 75% of cinnamonitrile at 0 °C for 3 h. Though nitro-substituted aldehydes did not give the nitriles by either methods, these aldehydes gave the corresponding nitriles in fairly good yields using an equimolar of $ZnCl_2$ at elevated temperature. These show that there are two different procedures of the nitrile syntheses from aldehyde and TMSA; (i) an equimolar amount of $ZnCl_2$ at room temperature or (ii) catalytic amount (*ca.* 0.06 equiv.) of $ZnCl_2$ at higher temperature. However, conversion of aldehyde having electron-withdrawing group to nitrile can be achieved both an equimolar amount of

Table 1. Synthesis of Aromatic Nitriles from Aldehydes and TMSA[a)]

Aldehyde	Solvent	Temp	Isolated yield[b)]/%		
C_6H_5CHO	CH_2Cl_2	r.t.[c)]	C_6H_5CN	62	(59)[d)]
p-MeC_6H_4CHO	CH_2Cl_2	r.t.	p-MeC_6H_4CN	92	(93)
p-$MeOC_6H_4CHO$	CH_2Cl_2	r.t.	p-$MeOC_6H_4CN$	97	(95)
p-ClC_6H_4CHO	CH_2Cl_2	r.t.	p-ClC_6H_4CN	75	(61)
p-$O_2NC_6H_4CHO$	$CHCl_3$	reflux	p-$O_2NC_6H_4CN$	74	(0)
m-$O_2NC_6H_4CHO$	C_6H_6	reflux	m-$O_2NC_6H_4CN$	68	(0)

a) Detailed procedure is described in text and molar ratio of reagents is aldehyde/TMSA/$ZnCl_2$=1/1.3/1. b) Yield not optimized. The nitriles were identified by comparison with the authentic materials. c) room temperature d) Yield under condition (ii), see text.

$ZnCl_2$ and higher temperature. Zinc chloride would act as the catalyst of both the addition process of TMSA to carbonyl group and the decomposition process of azido group. We postulate that the reaction takes place as in equation (1) on the basis of the previous study[2c)] and these findings.



(1)

Since aromatic aldehydes and cinnamaldehyde gave the corresponding nitriles, it is likely that the anticipated course of the reaction depends upon the stability of a benzyl-like cation intermediate I. It is supported by the fact that electron-withdrawing group decreases the yield of nitriles and the reaction requires relatively drastic conditions. Aliphatic and α,β-unsaturated aldehydes did not give the corresponding nitriles under the employed conditions because these groups would be impossible to stabilize effectively the intermediate I.

The reaction of aldehyde with TMSA, which was carried out at room temperature in the presence of $SnCl_2$ (0.06 equiv.), gave diazide $[RCH(N_3)_2]$.[2c,5)] Decomposition of the diazide by $ZnCl_2$ provided not only the nitrile (45-60%) but 1-aryltetrazole (10-50%). It shows that an intermediate of the reaction described above is not the diazide but the 1:1-adduct.

Aromatic nitriles could easily be synthesized from the aldehydes with TMSA as one-pot reaction products. Simplicity and ease of the synthetic method described in this communication are comparable with the reported ones.

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