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Oxidation of Aldehydes to Acyl Azides Using Triazidochlorosilane (TACS)-Active Manganese Dioxide Reagent.

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Abstract: *Triazidochlorosilane (TACS) - active manganese dioxide is a new and versatile system for the efficient oxidation of aldehydes to the corresponding acyl azides at 0°C, in dichloromethane.*

Triazidochlorosilane (TACS) is a readily hydrolysable solid, which may be generated in situ by interaction of cheap, readily available tetrachlorosilane with three equivalents of sodium azide[1].

Oxidation with manganese dioxide reagents in anhydrous conditions[2,3] and the applications of the reagent combinations of chromic anhydride-chlorotrimethylsilane[4-6] and chromic anhydride-azidotrichlorosilane[7] have found much use in organic chemistry. But the use of manganese dioxxide as oxidant with azidosilanes in anhydrous conditions has not yet been explored.

In our laboratory we have developed many reagents from tetrachlorosilane[8]. So the combination of active manganese dioxide and triazidochlorosilane ($SiCl_4/NaN_3$ in situ), was a focus of our attention. We found that active manganese dioxide mixed with triazidochlorosilane is superior to any other oxidizing reagent for the direct oxidation of aldehydes to the corresponding acyl azides in dichloromethane at 0°C in very good yield. Moreover, aromatic acyl azides can be isolated without Curtius rearrangement to alkyl isocyanates because the reaction conditions are so mild.

The aromatic aldehydes may contain either an electron donating group (exp. no. 5, 6, 7) or an electron withdrawing group (exp. 4). Indeed, the reaction tolerates a wide range of functional groups (Cl, Me_2N, NO_2, Me, MeO, olefinic bond) and hence should be widely applicable.

The procedure is simple and straightforward. After cooling the mixture of tetrachlorosilane (10 mmol), sodium azide (30 mmol) and active manganese dioxide (20 mmol) (according to Fatiadi's[2] procedure, active MnO_2 was prepared from manganese dichloride tetrahydrate and potassium permanganate to yield activity gradient A) in dichloromethane (25 ml) the aldehyde (10 mmol) was added. The reaction mixture was stirred at 0°C, then hydrolyzed with sodium carbonate solution and the product was extracted with $CHCl_3$. The filtrate was concentrated and the residue chromatographed to obtain the acyl azide.

The reaction pathway which might involve manganoyl azide $[(N_3)_2MnO]$ as may be the reactive species, so can be added to the carbonyl group of the aldehyde $[ArCH(N_3)\text{-}O\text{-}Mn(N_3)O]$

in a fashion reminiscent of the well documented Lee reaction[6]. At some stage an oxidation reaction for the intermediate with active manganese dioxide takes place, to give acyl azide

Table 1. Oxidation of Aldehydes with TACS-MnO_2 in Dichloromethane.

Exp. No.	Substrate	Time (hr)	Product	(%) Yield
1	benzaldehyde	1	benzoyl azide	89
2	4-chlorobenzaldehyde	1	4-chlorobenzoyl azide	95
3	3-chlorobenzaldehyde	2	3-chlorobenzoyl azide	84
4	4-nitrobenzaldehyde	1	4-nitreobenzoyl azide	86
5	4-(dimethylamino)-benzaldehyde	2	4-(dimethylamino)-benzoyl azide	78
6	4-methylbenzaldehyde	2	4-methylbenzoyl azide	76
7	4-methoxybenzaldehyde	2	4-methoxybenzoyl azide	77
8	cinnamaldehyde	3	cinnamoyl azide	68

a)All yields are for isolated, crystallized products. All products were fully characterized by nmr, mass spectra and elemental analysis .

It is clear from the results presented in the table 1 that, the reagent also works well with α,β-unsaturated aldehyde (exp. 8) and it appears that its use is not restricted in cases where functional groups like olefins are present Further investigations of the scope and pathway of reaction of aliphatic aldehydes with the reagent will be reported separately. Much work remains to be done to fully understand the nature of this oxidizing system, but whatever the detailed pathway , the process is an effective conversion of aldehydes to acyl azides.

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