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EFFICIENT CONVERSION OF HYDRAZINES TO AZIDES WITH CLAY-SUPPORTED FERRIC NITRATE

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Abstract : Azides are prepared in good yield in dichloromethane under mild conditions using the extremely inexpensive clay-supported ferric nitrate.

PROLIFIC in their multiple uses for preparing amines[1], azomethines[1,2], nitriles[1], diazo[3] and azo[1] compounds, iminophosphoranes[4] and iminosulphuranes[5], isocyanates through the Curtius rearrangement[1,6], aziridines[7] and diaziridines[1], peptides[8] and truly proligerous in their numerous heterocyclic offspring[1,9], often through nitrene intermediates[10], azides are essential to organic synthesis despite their instability and toxicity.

The azides are formed, usually, by substitution on carbon of a preformed azide moiety, by its addition to various multiple bonds, or by processes in which the azide groups are introduced in a stepwise manner from diazotation and by related reactions under a variety of different, more or less drastic, conditions suffering furthermore from the use of expensive reagents[11]. The synthesis of azides by nitrosation of hydrazine derivatives[11] has been employed often. Based upon the analogy of the transformation of hydrazines into azides using nitrous acid[12,17b,d], nitrosyl chloride[13] and organic nitrites[14] we were led to try our "clayfen"[15] reagent which appears to function as a source[16] of nitrosonium NO^+ ions.

Indeed, treatment of different types of hydrazines by "clayfen" in methylene chloride under very mild conditions gives good yields of the corresponding azido derivatives[17] (Table).

$$\underset{1}{R - NH - NH_2} \xrightarrow[CH_2Cl_2,\ time\ (t)]{\text{"clayfen"}} \underset{2}{R - N_3}$$

Product[18]	Time (t/hour)	Isolated yield of azide 2 (%)
p-CH_3-C_6H_4-SO_2 (2a)	1.5	83
C_6H_5 (2b)	2	63
C_6H_5CO (2c)	0.3	58
t-BuOCO (2d)	2.5	55-71
2,4-$(NO_2)C_6H_3$ (2e)[19a]	5-7	-[19b]
C_6H_5NHCO (2f)[19a]	15-24	-[19b]

Table : Transformation of Hydrazines into Azides through the Agency of K-10 Supported Ferric Nitrate.

A typical procedure for these conversions is as follows. To an efficiently stirred solution of hydrazine (10 mmol) in dichloromethane is added 8 g (8,8 mmol $Fe(NO_3)_3$) of freshly prepared "clayfen"[16a] reagent. Stirring is maintained at gently reflux until the reaction is complete (Table). The reaction is monitored by TLC (Al_2O_3, CH_2Cl_2 or hexane/ ethyl acetate 8:2 or 6:4). After full disappearance of the starting material, the mixture is filtered to remove the clay and the residue is washed with enough solvent (4x25ml). The organic phase is washed with water and dried with $MgSO_4$. Evaporation of the solvent gives the essentially pure azide[20]. Further purification is done by column chromatography (Al_2O_3, CH_2Cl_2) wherever necessary or by recrystallization (2 c; acetone-petroleum ether 30-60°C).

A likely mechanistic sequence for the conversion of hydrazine to azide is as follows :

$$2\ NO_2 \rightleftarrows N_2O_4 \quad (\rightleftarrows NO^+ + NO_3^-)$$

$$Fe(NO_3)_3 + N_2O_4 \rightleftarrows [Fe(NO_3)_4]^- \ NO^+$$

$$RNH - NH_2 + NO^+ \rightleftarrows RNH - NH - NO + H^+$$

$$R - NH - NH - NO \rightleftarrows R - N{=}\overset{+}{N}H - \overset{-}{N}OH \rightarrow R - N{=}\overset{\oplus}{N}{=}\overset{-}{N} + H_2O$$

Nitrogen oxide[21] is probably in equilibrium with the N_2O_4 dimer which is known to form an adduct[22] with ferric nitrate which in turn serves as a nitrosonium ion source. The nitrosation of hydrazine derivatives shown in the scheme leads to the azide, via formation of the β-nitroso hydrazine[23] and its dehydration.

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    e. Alkyl azides are not obtained by nitrosation of alkyl hydrazines.
18. (**2**a) ^{1}H nmr ($CDCl_3$/TMS) : δ = 7.80 (d, 2H, J = 8 Hz); 7.33 (d, 2H, J = 8 Hz); 2.45 (s, 3H). ir (neat, cm^{-1}) : ν_{N3} = 2340 (w), 2130 (s); ν_{SO2} = 1170 (s).
    (**2**b) ^{1}H nmr ($CDCl_3$/TMS) : δ = 7.60 - 6.91 (m, 5H). ir (neat, cm^{-1}) : ν_{N3} = 2410 (w), 2110(s), 2090 (s).
    (**2**c) ^{1}H nmr ($CDCl_3$/TMS) : δ = 8.00 (d, 2H, J = 8 Hz); 7.77-7.23 (m, 3H). ir (neat, cm^{-1}) : ν_{N3} = 2340 (w), 2160 (sh), 2130 (s), 1230 (s), 1175 (s); $\nu_{C=O}$ = 1690 (s).
    (**2**d) ^{1}H nmr ($CDCl_3$/TMS) : δ = 1.50 (s, 9H). ir (neat, cm^{-1}) : ν_{N3} = 2420 (w), 2180 (s), 2120 (s), 1240 (s), 1140 (s); $\nu_{C=O}$ = 1750 (sh), 1725 (s).
19. a. The conversion is carried out in THF.
    b. Under the reaction condition, the azide could not be isolated and rearranges to the heterocycle. Further work along these lines is in progress and will be published elsewhere.
20. The purity of the isolated compounds is checked by ir, ^{1}H nmr and tlc analysis.
21. "Clayfen" is easily observed to decompose spontaneously with evolution of red vapours (NO_2) rather than producing colorless vapours (NO) subsequently oxidized into NO_2.
22. The ferric nitrate N_2O_4 adduct ($Fe(NO_3)_3$-N_2O_4) is in fact the ionic compound $[Fe(NO_3)_4]^-$ NO^+; see L.J. Blackwell, E.K. Nunn, S.C. Wallwork, *J. Chem. Soc. Dalton Trans.*, 2068 (1975) and C.C. Addison, *Chem. Rev.*, *80*, 21 (1980).
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