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CONVERSION OF N,N-DIMETHYLHYDRAZONES TO CARBONYL COMPOUNDS BY CLAY-SUPPORTED FERRIC NITRATE

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Abstract : Cleavage of N,N-dimethylhydrazones is cleanly effected with good yield in dichloromethane using the extremely inexpensive clay-supported ferric nitrate.

VERSATILITY and usefulness of N,N-dimethylhydrazones as intermediates in organic synthesis have been proven by recent applications to carbon-carbon bond formation[1] and other reactions[2] like epoxidation, hydroboration, oxidation, reduction and hydrolysis. In addition, the past decade has seen considerable interest in recovery of carbonyl compounds from N,N-dimethylhydrazones which has resulted in development of a number of methods including acid hydrolysis[3a], methylation and hydrolysis[2,3a], use of CH_3CO_3H [3b], O_3 [3c], $NaIO_4$ and HIO_4[1d], $Cu(OAc)_2$ [3d], $NOBF_4$ [3e], MoF_6 and $MoOCl_3$ [3f], UF_6 [3c], WF_6 [3h], CoF_3 [3i] and $BF_3.Et_2O$ [3j]. As part of a concerted program[4] to evolve synthetically-useful clay-supported reagents, we came to the idea that "clayfen"[4,5] is a nitrosonium ion source comparable to $NOBF_4$ [3e] and should be capable of effecting cleavage of the above-mentioned protecting group.

We describe herein the procedure we have developed using "clayfen" for efficient regeneration of carbonyl compounds from N,N-dimethylhydrazones under mild conditions. By comparison with the numerous routes available for this purpose[3], our new method offers distinct advantages coming from recourse to a supported reagent[6].

The reaction of N,N-dimethylhydrazones with "clayfen" is fast and exothermic, giving the corresponding carbonyl compounds in very good yield (Table).

Carbonyl compound	Yield (%) [a]	Carbonyl compound	Yield (%) [a]
3-hexanone	78	cycloheptanone	82
4-heptanone	78	2-decalone[b]	79
2-octanone	85	1-indanone	67
cyclopentanone	69	2-norbornanone	79
cyclohexanone	87	acetophenone	91
4-_t_-butylcyclohexanone	85		
3,3,5-trimethylcyclohexanone	80		

[a] yield of isolated product [b] commercial mixture of the two isomers

Table : Cleavage of N,N-Dimethylhydrazones with the "clayfen" Reagent to Give the Corresponding Carbonyl Compounds.

Cleavage of N,N-Dimethylhydrazones by "clayfen" : General Procedure.

To a vigorously stirred solution of the N,N-dimethylhydrazones[7] (10 mmol) in dichloromethane (30 ml) is added 6 g (6.6 mmol $Fe(NO_3)_3$) of freshly prepared[4a] "clayfen" reagent. A slightly exothermic reaction takes place immediately, accompanied by the evolution of white fumes during three to five min. Stirring is continued for 30 min at room temperature, the mixture is then gently refluxed with vigorous stirring for 1-3 h (time determined by GLC monitoring). Upon cooling, the reaction mixture is filtered on sintered glass, and the solid residue is washed with dichloromethane (3 x 25 ml). To the organic phase, water is added (50 ml) and the mixture extracted with chloroform (2 x 25 ml). The extract is dried over magnesium sulfate and evaporated, affording the crude reaction product in good purity. The crude product is dissolved in chloroform or methylene chloride and the solution is filtered through a small column (3 cm x 2 cm) of neutral alumina, giving a colorless filtrate. Evaporation of the solvent gives the pure carbonyl compound. The purity of the isolated compound is checked by comparison of IR and ^{1}H nmr spectra and TLC[8] (conditions : SiO_2, 40:60 ethyl acetate/ hexane) and GLC (OV 1701 capillary column) analysis with those of authentic samples.

Deprotection from N,N-dimethylhydrazones using clay-supported ferric nitrate is thus a rather efficient, mild, easy to run, and very inexpensive method. We are continuing to explore the analogy in modes of reaction of nitrosonium tetrafluoroborate and the considerably less expensive "clayfen".

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5. Ferric nitrate impregnated on K-10 Bentonite clay; "clayfen" for short.

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7. The N,N-dimethylhydrazones are prepared according the described procedure[3g]; see also G.R. Newkome, D.L. Fishel, J. Org. Chem., 31, 677 (1966); P.A.S. Smith, E.E. Most, Jr., J. Org. Chem., 22, 358 (1957).

8. Thin layer chromatography is run on silica gel plates Polygram SilG/UV$_{254}$ (Macherey-Nagel). A mixture of hexane/ethyl acetate (6:4) is used as solvent in all cases. Approximate R_f values for the investigated N,N-dimethylhydrazones are 0.15-0.45. The corresponding oxo compounds showed greater mobility. The developed spots are visualized by phosphomolybdic acid reagent.

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