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CARBONYL REGENERATION FROM p-TOLUENSULFONHYLHYDRAZONES BY TRIMETHYLCHLOROSILANE-DIMETHYLSULFOXIDE

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Abstract. Treatment of p-tosylhydrazones of saturated and α,β-unsaturated ketones and aldehydes with trimethylchlorosilane-dimethyl sulphoxide in dry acetonitrile affords the corresponding carbonyl compounds in excellent yields under mild conditions.

Tosylhydrazones have been widely used in organic synthesis for the deoxygenations[1] as well as conversions[2] to olefins, methyl ethers and heterocyclic compounds.

These highly crystalline derivatives, are very useful for the characterization and purification of carbonyl compounds. Their applications as protecting carbonyl groups have been limited however due to their resistance to hydrolytic cleavage.

Previously regeneration methods[3] have used either strongly oxidative or reducing conditions, rather basic or acidic media, or involving tedious work-ups or expensive reagents. Although mild procedures have been developed[4], in our expe-

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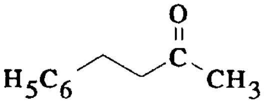
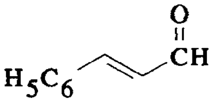
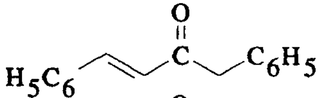
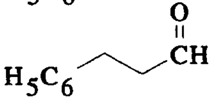
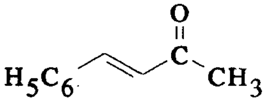
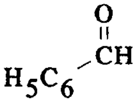
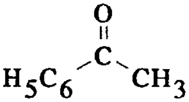
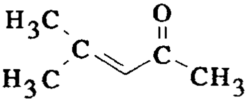
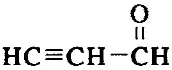
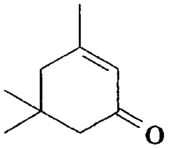
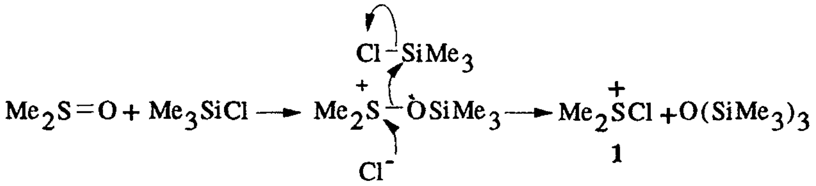
Table

Tosylhydrazone of	Reaction time (h)	Yield(%) of isolated aldehyde or ketone
	2.0	98
	3.0	87
	2.5	94
	3.0	88
	2.0	96
 H_5C_6CHO	2.5	90
 $H_5C_6COCH_3$	2.0	97
	2.0	93
 $HC{\equiv}CH{-}\overset{O}{\overset{\parallel}{C}}H$	2.0	87
	2.0	93



$$Me_2S{=}O + Me_3SiCl \longrightarrow Me_2\overset{+}{S}{-}OSiMe_3\ Cl^- \longrightarrow \underset{\mathbf{1}}{Me_2\overset{+}{S}Cl} + O(SiMe_3)_3$$

Scheme 1

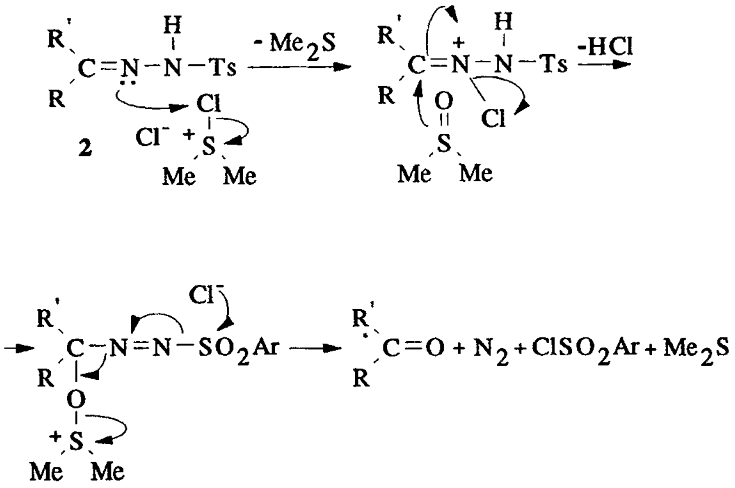
rience, these rarely yield purified aldehydes and unsaturated carbonyl compounds greater than 70%.

Here we report a new and efficient method for regenerating carbonyl compounds from their corresponding p-tosylhydrazones, under quite mild conditions, using trimethylchlorosilane-dimethylsulfoxide (TMCS-DMSO) in dry acetonitrile.

As indicated in theTable, very good yields were obtained, p-toluensulphonyl chloride ($ArSO_2Cl$) being formed as side product. Aldehydic, olefinic and one acetylenic substrates give very satisfactory regenerations to the corresponding carbonyl parents.

With respect to the source of the carbonyl oxygen, we have previously reported[5] that TMCS-DMSO gives rise to a chlorodimethylsulphonium species as intermediate **1** (Scheme 1), which, under mild conditions, is able to halogenate ketones [5] in the α-position or to add methanesulfenyl chloride to olefins[6].

We are proposing that since species **1** is produced as an intermediate, the carbonyl regeneration occurs according to the following scheme; the process starts with a chlorine electrophilic attack to the tosyl-bearing nitrogen in **2** (Scheme 2), which increases the reactivity of the imino carbon towards nucleophilic addition by the dimethylsulfoxide oxygen atom.



Scheme 2

The overall process may thus be analogous to those suggested for carbonyl regeneration from p-tosylhydrazones with N-bromosuccinimide in methanol[7] or with alkali hypochlorite[8]. In both cases, however, the conversion of any olefinic or acetylenic substrates has not been reported. This is probably due to the possible oxidation by the reagent. In addition the hypochlorite procedure has been quoted as not suitable for the cleavage of aldehydic derivatives[8].

The regenerated compounds were identified by comparison with parent carbonyls and characterized by MS and NMR spectra.

Experimental

General reaction procedure. DMSO(30 mmol) and TMCS(30 mmol) were sequentially added to a stirred solution of substrates (1-10)[9] (10 mmol), in acetonitrile (10 ml) in a two-necked round bottomed flask equipped with a reflux condenser and a two dropping funnels. The reaction mixture was then refluxed, while being monitored by GCL. After the time reported in Table 1, the mixture was then poured into water (60 ml) and extracted with diethyl ether (3 x 30 ml). The collected organic phases was dried (Na_2SO_4) and then evaporated at 20-40 mmHg. The residue was purified by chromatography on silica gel with n.hexane-diethyl ether gradient. The products were further purified by distillation or by crystallization.

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Notes and References

(1) L.Caglioti and P.Grasselli, Chem. Ind. (London), 1964, 153; L.Caglioti, Tetrahedron, 1966, 22, 487; M.Fischer, Z. Pelah, H.Williams, and C.Djerassi, Chem. Ber., 1965, 98, 3236; R.O.Hutchins, M. Kacher, and L.Rua, J.Org.Chem., 1975, 40, 923.

(2) R.H.Shaphiro, and M.J.Heath, J.A.C.S., 1967, 89, 5734; I.Elphinoff-Felkin, and M.Verrier, Tetrahedron Lett., 1968, 12, 1515; E.J.Taylor, and C.Djerassi, J.A.C.S., 1976, 98, 2275; R.H.Shapiro, " Organic Reactions," 1976, pp. 405-507; G.W.Kabalka, R.Hutchins, N.R.Natale, D.T.C.Yang, and V.Broach, "Organic Reactions," 1979; pp. 42-48; L.A.Paquette. W.E.Fristad, D.S.Dime,and T.R.Bailey, J.Org.Chem., 1980, 45, 3017; R.Grandi, A.Marchesini,U.M.Pagnoni, and R.Trave, J.Org.Chem., 1976, 41, 1755; R.Grandi, W.Messerotti, U.M. Pagnoni, and R.Trave, J.Chem.Res.(S), 1979, 247; R.Grandi, U.M.Pagnoni, and R.Trave, J.Chem.Res.(S),1979, 327; F.Bellesia, R.Grandi, U.M.Pagnoni, and R.Trave, Gazz.Chim.It., 1981, 111, 289; R.Grandi, P. Vivarelli, J.Chem.Res.(S), 1989, 186.

(3) L.Caglioti, F.Gasparini, Synthesis, 1079, 207; R.N.Butler, G.J. Morris, and A.M.O'Donohue, J.Chem.Res.(S), 1981, 61; O.Attanasi, M.Grossi, and F.Serra-

Zanetti, J.Chem.Res., 1983, 322; Y.H.Kim, H.K.Lee, and H.S.Chang, Tetrahedron Lett., 1987, 28, 4285; G.A.Olah, Y.D.Vankar, G.K.S.Prakash, Synthesis, 1979, 113; P.Laszlo, and E.Polla, Synthesis, 1985, 439.

(4) C.E.Sacks, P.L.Fuchs, Synthesis, 1976, 456; L. Pelawin, and G. Erker, J.Org.Chem., 1975, 22, 3302.

(5) F.Bellesia, F.Ghelfi, R.Grandi, and U.M.Pagnoni, J.Chem.Res.(S), 1986, 426.

(6) F.Bellesia, F.Ghelfi, U.M.Pagnoni, and A.Pinetti, J.Chem.Res.(S), 1987, 238.

(7) G.Rosini, J.Org.Chem., 1974, 39, 3504.

(8) Tse-Lok Ho and C.M Wong, J. Org. Chem., 1974, 23, 3453.

(9) R.Grandi, A.Marchesini, U.M.Pagnoni, and R.Trave, J.Org.Chem., 1976, 41, 1755; R.Grandi, W.Messerotti, U.M.Pagnoni, and R.Trave, J.Org.Chem., 1977, 42, 1352; R.Grandi, U.M. Pagnoni, and R.Trave, J.Chem.Res.(S), 1979, 327.

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