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NOTE

N-Chlorosulfonamide, a Useful Reagent for Chlorination of Various Carbanionic Substrates

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N,N-Dichloro-4-methylbenzenesulfonamide prepared in high yield by treatment of corresponding sulfonamide with saturated solution of calcium hypochlorite, acts as site-selective electrophilic chlorinating agent towards carbanionic substrates. β-Ketoesters and β-diketones were chlorinated by this reagent without using any bases. The reagent can be recovered, rechlorinated and reused several times.

While the introduction of chlorine into organic molecules is of broad interest, being used extensively in physical, theoretical and mechanistic studies, methodology for the chlorination of carbanions remains limited.

Various reagents have been applied to chlorinate organic compounds. These contain *N*-chlorosuccinimide for chlorination of nitro compounds[1] and phenylacetylene[2], dichlorosulphoxide in CH_2Cl_2 for the chlorination of β-ketoesters[3,4], triphenylphosphine in CCl_4 and phosphorus trichloride for cholorinatin of β-diketones[5–7], phosgene[8], acetyl chloride[9], thionyl chloride[10], phosphoryl chloride[11] and oxalyl dichloride[12] were also applied for chlorination of organic compounds.

Polyhaloalkanes such as tetrachloromethane in the presence of phase transfer catalyst "tetrabutylammonium fluoride" are introduced to chlorinate acidic organic compounds[13].

All these reagents have some disadvantages such as low yield, toxic reagents, nonselective and tedious work-up.

Very recently, it was shown that N-chlorosulfonamides can chlorinate aromatic compounds[14] and also can oxidize primary and secondary alcohols to their corresponding carbonyl compounds[15]. We wish to report that N,N-dichlorosulfonamides are effective reagents for the selective chlorination of a broad variety of carbanions under mild conditions. The N,N-dichloro-4-methylbenzenesulfonamide is in general a stable crystalline compound, easily prepared[16] by treatment of 4-methyl benzenesulfonamide with calcium hypochlorite. Treatment of carbanions with N,N-dichloro-4-methylbenzenesulfonamide results in transfer of chlorine from nitrogen to carbon.

$$RSO_2NCl_2 + R' \rightarrow R'Cl + RSO_2NCl^- \quad R = p\text{-tolyl}$$

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A broad variety of anions, including malonates, nitroalkanes, alkynes, β-ketoesters and β-diketones can be chlorinated in high yield (Table-1).

In the case of β-dicarbonyl compounds (*e.g.*, 2,4-pentanedione) dichlorinated products were obtained in excellent yields.

It should also be mentioned that β-diketones and β-ketoesters are chlorinated at 50°C, without using any base. The sulfonamide formed in this reaction is easily recovered, rechlorinated and reused several times.

TABLE-1
CHLORINATION OF ANIONS

Entry	Substrate	Product	Base	Temp. (°C)	Time (min)	Yield (%)
1	$CH_3CHNO_2CH_3$	$CH_3CClNO_2CH_3$	NaH	0	40	87
2.	$PhC{\equiv}CCl$	$PhC{\equiv}CCl$	NaH	0	50	86
3.	$C_4H_9C{\equiv}CH$	$C_4H_9C{\equiv}CCl$	NaH	0	50	81
4.	$CH_3COCH_2COCH_3$	$CH_3COCCl_2COCH_3$	—	40	250	92
5.	$PhCOCH_2COPh$	$PhCOCCl_2COPh$	—	40	210	71[a]
6.	$CH_3COCH_2COOC_2H_5$	$CH_3COCCl_2COOC_2H_5$	—	50	270	83
7.	$CH_2(COOC_2H_5)_2$	$CCl_2(COOC_2H_5)_2$	NaH	0	60	88
8.	$CH_3CH(COOC_2H_5)_2$	$CH_3CCl(COOC_2H_5)_2$	NaH	0	50	95
9.	$CNCH_2COOC_2H_5$	$CNCCl_2COOC_2H_5$	NaH	0	50	88
10.	$PhCOCH_3$	$PhCOCH_2Cl$	NaH	RT	90	20
11.	$PhCOCH_2CH_3$	$PhCOCHClCH_3$	NaH	RT	90	15

[a]Purified by column chromatography on silica gel; RT = room temperature.

General procedure

(a) *Chlorination of acidic organic compound in the presence of base*: A solution of carbanion in anhydrous tetrahydrofuran [prepared in conventional fashion by adding an 80% dispersion of NaH (12 mmol) in oil to acidic organic compound (10 mmol) in THF (10 mL)] was added under dry nitrogen to a stirred slurry of reagent (10 mmol) in CH_2Cl_2 (15 mL) at 0°C. The reaction mixture was allowed to warm to room temperature and then diluted with diethyl ether (50 mL). The mixture was then washed with 0.5 M oxalic acid (30 mL), 10% aqueous potssium hydrogen carbonate (30 mL), and saturated brine (30 mL), dried ($MgSO_4$), and evaporated under reduced pressure. The residue was worked up by washing with normal hexane and filtered.

The filtrates were evaporated to give pure products in 15–95% yields (Table-1). The solid phase was removed by filtration and recrystallized with ethanol and water; the yields of the recovery sulfonamide were 70–80%.

(b) *Chlorination of β-ketoesters and β-diketones without base*: A mixture of β-diketone of β-ketoesters (10 mmol) and reagent (10 mmol) in THF was heated (Table-1). After the completion of the reaction the mixture was evaporated under reduced pressure. The residue was worked up by washing with normal hexane and filtered.

All products were characterized by physical and spectral methods (m.p., IR, NMR, C, H, N-analyses).

2-Chloro-2-nitropropane 1: ^{1}H NMR (CCl_4) δ: 2.1 (s, 6H, $2CH_3$).

1-Chloro-2-phenylacetylene 2: ^{1}H NMR (CCl_4) δ: 6.8 (s, 5H, aromatic H).

1-Chloro-1-hexyne 3: ^{1}H NMR (CCl_4) δ: 1.1 (m, 9H, $3CH_2$, CH_3).

3,3-Dichloro-1,3-diphenyl-1,3-propanedione 5: ^{1}H NMR (CCl_4) δ: 7 (d, 10H, aromatic H).

Dichloroethyl acetoacetate 6: ^{1}H NMR (CCl_4) δ: 4.1 (q, 2H, CH_2), 2.4 (s, 3H, CH_3), 1.2 (t, 3H, CH_3),

Diethyl-2,2-dichloro malonate 7: ^{1}H NMR (CCl_4) δ: 4 (q, 4H, $2CH_2$), 2.2 (t, 6H, $2CH_3$).

Diethyl-2-chloro-2-methylmalonate 8: ^{1}H NMR (CCl_4) δ: 4.3 (q, 4H, $2CH_2$), 1.9 (s, 3H, CH_3), 1.3 (t, 6H, $2CH_3$).

Dichloroethyl cyanoacetate 9: ^{1}H NMR (CCl_4) δ: 4 (q, 2H, CH_2) 1.2 (t, 3H, CH_3).

Phenacyl chloride 10: ^{1}H NMR (CCl_4) δ: 7.2 (m, 5H, aromatic H), 4.1 (s, 2H, CH), 4.1 (s, 2H, CH_2, CH_2Cl).

α-Chloro propiophenone 11: ^{1}H NMR (CCl_4) δ: 7.1 (m, 5H, aromatic H) 3.9 (q, 1H, CHCl), 1.1 (d, 3H, CH_3).

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