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# THIOCARBONYLS INTO CARBONYLS :
# EFFICIENT CONVERSION BY CLAY-SUPPORTED FERRIC NITRATE

Stéphane CHALAIS, André CORNELIS, Pierre LASZLO* and Arthur MATHY

Institut de Chimie Organique
Université de Liège au Sart-Tilman
4000 Liège, Belgium

Abstract

A simple and inexpensive procedure is proposed for achieving the title transformation. The method works best with thiobenzophenones (60-100 % yields).

THERE are many ways to turn thiocarbonyl into carbonyl compounds[1-12]. Two attractive and efficient recent methods use the nitrosonium $NO^+$ ion [13-14]. We show here how recourse to a salt such as $NO^+ BF_4^-$ [14] can be avoided : the much less expensive "clayfen", i.e. clay-supported ferric nitrate [15], gives equally good results. With aromatic substituents ($Ar^1$, $Ar^2$), in most cases nearly quantitative conversions are achieved (Table).

| $Ar^1$ | $Ar^2$ | reaction time | isolated yield (%) |
|---|---|---|---|
| $C_6H_5$ | $C_6H_5$ | 1h | 90 |
| $C_6H_5$ | p-$NO_2C_6H_4$ | 1h | 94 |
| $C_6H_5$ | p-$H_3CC_6H_4$ | 0.5h | 93 |
| $C_6H_5$ | m-$H_3CC_6H_4$ | 1.5h | 90 |
| $C_6H_5$ | o-$H_3CC_6H_4$ | 15h[a] | 77 |
| $C_6H_5$ | p-$BrC_6H_4$ | 1h | 95 |
| $C_6H_5$ | o-$ClC_6H_4$ | 15h[a] | 78 |
| $C_6H_5$ | p-$ClC_6H_4$ | 1h | 95 |
| $C_6H_5$ | p-$H_3COC_6H_4$ | 0.5h | 85 |
| p-$H_3COC_6H_4$ | p-$H_3COC_6H_4$ | 0.5h | 100 |
| $C_6H_5$ | 3-pyridyl | 6h | 60 |

[a] reaction time can be reduced to 8h by the use of 2g of clayfen for 1mM of thioketone.

While this method using "clayfen" works best with ketones having aromatic substituents, it can be applied also to other thioketones such as fenchone (17%), dicyclopropyl ketone (39%), camphor (30%), or 2-adamantanone (68%) with "claycop"[15a] i.e. clay-supported cupric nitrate. A typical procedure is :

*To a solution of 10 mM of thioketone in 100 ml of dichloromethane under nitrogen,* at room temperature, 10 g of "clayfen" is added in one portion, with efficient stirring. After a few minutes, red-brown vapors are evolved. The mixture is stirred for the time stated in the table. The reaction mixture is filtered, washed with water and dried. After solvent evaporation, the residual material may be recrystallized or chromatographed.

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