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MICROWAVE THERMOLYSIS VI : A RAPID AND GENERAL METHOD FOR DETHIOACETALIZATION USING "CLAYAN" IN DRY MEDIA

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Abstract : A variety of thioacetals, dithiolanes and dithianes are deprotected into their carbonyl compounds using clay supported ammonium nitrate "Clayan" under microwave irradiation. The present method avoids the use of toxic oxidants and excess of solvent.

Protection of carbonyl compounds as thioacetals and ketals is important in organic synthesis[1] and particularly, in multistep natural product synthesis.[2] This is because of their stability both in acidic and basic conditions. So their deprotection into parent carbonyl compounds is an important task.[3] Dethioacetalization is generally performed using heavy metal salts such as mercury(II) chloride,[4a] mercury(II) oxideboron trifluoride etherate,[4b] ceric ammonium nitrate[4c] and selenium dioxide4[d,c] which are very toxic in view of the conservation of the environment. However, the non-metallic reagents[5] like trimethyloxonium tetrafloroborate, methyl fluorosulfonate and more recently nitrogen tetraoxides have also been used for deprotection. But these methods are less attractive due to the expensiveness and non-availability of reagent. Though the other method

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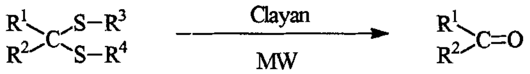
using photolytic[6] and electrochemical[7] technique are safe and preserve the environment, these methods have of less-practical utility. Recently, other methods using metal nitrate[8a-c] and zirconium sulphonyl phosphate[8d] also accomplish the deprotection with different reaction conditions.

In view of the conservation of the green environment, literature[9] demands to develop a metal ion free, environmentally safe and convenient method with easily accessible and cheaper reagent. Since the last decade, supported reagents[10] have attracted attention because of the improved reactivity and ease of manipulation. Particularly, clay-supported reagents in combination with microwave[11] have gained wide popularity because of their simple work-up, reduction in time and dry reaction conditions. During the course of this programme[12] towards the development of environmentally benign methods, we have demonstrated the oxidative capability of "clayan" both in slurry[13] and in dry media under microwave irradiation.[14] In continution of our work, herein we wish to report the dethioacetalization using clay supported ammonium nitrate "clayan" under microwave irradiation (scheme) in solvent free condition.

When a benzaldehyde thioacetal is mixed with clay supported ammonium nitrate "clayan" (1:5 ratio) and subjected to microwave irradiation, the reaction was accomplished in 90 seconds. The present



R = alkyl, aryl; $R^1 = R^2 =$ Et, CH_2-CH_2

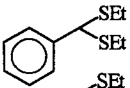
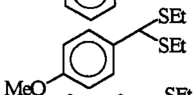
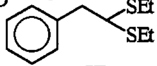
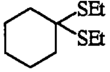
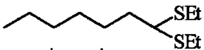
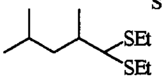
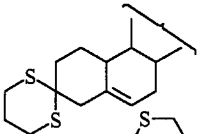
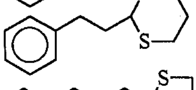
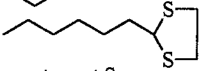
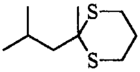
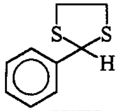
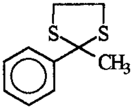
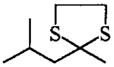
clayan = clay supported ammonium nitrate

R^1, R^2 = alkyl (or) aryl

R^3, R^4 = Et, -CH_2-CH_2-, -$(CH_2)_3$-

Scheme

Table : Cleavage of Thioacetals, Dithianes and Dithiolanes using "Clayan" in dry media.

Entry	Substrates	Time (sec.)	Carbonyl compounds yield (%)	Carbonyl compounds (m.p) or b.p Found	Carbonyl compounds °C/Torr Lit.[b]
1.		110	89	59-62/10	62/10[c]
2.		120	88	131-135/12	134-135/12
3.		115	86	74-78/10	78/10[c]
4.		120	85	75-78/10	78/10
5.		115	83	151-152/76	152.8/760
6.		130	87	115/116/760	116.8/760
7.		160	80	(124-128)	(128-130)
8.		155	85	101-104/13	104-5/13
9.		180	81	150-152/760	152-8/760
10.		160	88	113-116/760	116.8/760
11.		160	84	60-62/10	62/10[c]
12.		165	89	66-67/5	67/5[c]
13.		170	83	113-116/760	116.8/760

a : All the products are characterized by NMR, IR, Mass, m.p. or b.p. and by comparision with a TLC of an authentic sample.
b : From ref. 15
c : From ref. 16

method is very rapid and requires less amount of reagent.[17] This environmentally conscious and manipulatively simple protocol avoids the use of excess of solvents, toxic oxidants and has advantages over the existing methods. It is important to note that the procedure is effective for the deprotection of C-3 dithiane derivative of cholestanone which is usually removed under vigorous conditions.[18] The selectivity of the present method can be demonstrated by the tolerance of common groups like esters and ethers under the same reaction conditions. However, the method failed to deprotect thioketals selectively in the presence of acetonides. It is well documented in literature[18] that the nitrates are the source of NO^+ which is a soft and highly reactive lewis acid species. This has been tested[20] by the convenient reaction test for supported oxidizing reagent[21] which converts thiols into symmetrical disulphides. So we believe that the reaction probably proceeds via the intermediacy of nitrosonium ions.

In conclusion, the present method is rapid, selective and environmentally safe for the deprotection of thioacetals, dithiolanes and dithianes. Easy preparation of reagent and the solvent free conditions make the method more attractive. The fertilizing property of the ammonium nitrate demonstrate the eco-friendly nature of the present procedure.

EXPERIMENTAL

Boiling points and melting points are uncorrected. Melting points were recorded on Buchi R 535 apparatus. Unless mentioned the chemicals were commercially and used without further purification. Montmorillonite K 10 was purchased from Aldrich Chemicals Limited. IR spectra were recorded on IR Nicolet 740 FT IR spectrometer. ^1H NMR spectra were recorded on FT (200 Gemini) spectrometer. Mass spectra were recorded on either Micromass 7070h or Finnigan Mat 1020 B mass spectrometer operating at 70 eV. Thin layer chromatography was done on precoated silica gel 60f 254 (0.5 mm) glass plates. All the carbonyl derivatives were prepared by known literature procedure.[22]

CAUTION : These procedures are worked out safely in our hands but as the nitrates are dangerous compounds, appropriate precaution is recommended for the reaction at elevated temperature. We suggest that the microwave oven be operated carefully and for a shorter time because of possible localised higher temperatures.

General Procedure for the deprotection : The thio acetals, dithiolane or dithiane (2 mmol) was mixed with clay supported ammonium nitrate "Clayan"[12b] (1.6 g, 10 mmol of ammonium nitrate) in a mortar and pastle. The mixture was transferred into a test tube and subjected to microwave irradiation (BPL Make, Hi power) for 2-3 minutes (see table). Reaction was monitored by tlc. After completion of the reaction, it was extracted with dichloromethane (3 X 25 ml). Evaporation of the solvent under reduced pressure gave the product. The product was further purified by passing through a column of neutral alumina using hexane : ethylacetate (9:1) as eluent.

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