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Clay supported Ammonium Nitrate "Clayan" : A Mild and Eco-friendly Reagent for Dethioacetalization.

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Abstract: A variety of thioacetals and dithianes are deprotected into their carbonyl compounds in mild conditions using clay supported ammonium nitrate. The fertilizing nature of ammonium nitrate makes the procedure environmentally safe. © 1997 Elsevier Science Ltd.

Carbonyl compounds are routinely protected as thio acetals and ketals in organic synthesis[1] and particularly in multistep natural product synthesis,[2] due to their stability both in acidic and basic conditions. Their deprotection into parent carbonyl compounds is not straight forward. Therefore, various dethioacetalization methods[3] have been devised earlier using heavy metal salts, such as mercury (II) chloride[4], mercury (II) oxide-boron trifluoride etherate[5], ceric ammonium nitrate[6] and selenium dioxide[7] which are very toxic to the environment. The non metallic reagents like trimethyloxonium tetrafluoroborate[8], methyl fluorosulfonate[9a] and more recently oxides of nitrogen[9b] are also used for deprotection. But these are very expensive and their preparation is very difficult. Bismuth (III) nitrate[10] and clay supported ferric nitrate has been used both in solvent[11] and solvent free[12] conditions for successful dethioacetalization, however the presence of metal ion in catalyst may still cause damage to the environment. The methods using photolytic[13] and eletrochemical[14] technique, on the other hand are safe to the environment but require expensive equipment. In view of the present literature methods, it is desirable to develop a metal ion free, environmentally safe and convenient method with easily accessible and cheaper reagents.

Recently, the supported reagents [15,16] for organic transformation is an area of growing interest. In particular, clay supported reagents[17] have gained wide applications because of their simple work up and inexpense. In continuation of our work[18] on a clay supported non metallic catalyst,[19] we wish to report herein a environmentally safe, inexpensive and mild procedure for dethioacetalization using clay supported ammonium nitrate.

R_1 = H, Alkyl; R_2 = H, Alkyl, Aryl; R_3 = $-(CH_2)_3-$, Et Et, Clayan = Clay supported NH_4NO_3

The general procedure for the deprotection is as follows: To a solution of thiol derivatives of carbonyl compounds (1 mmol) in dry dichloromethane (50 ml) was added powdered clay supported

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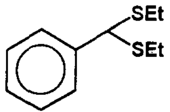
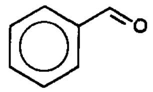
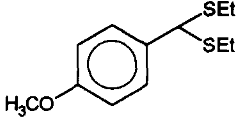
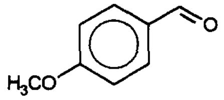
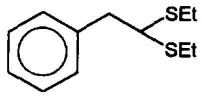
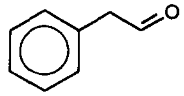
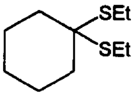
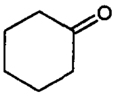
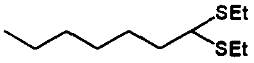
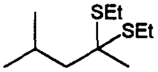
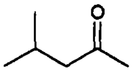
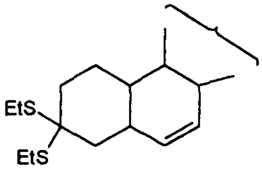
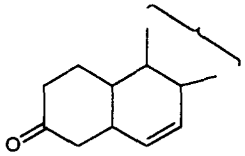
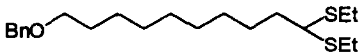
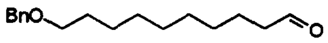
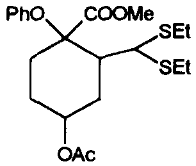
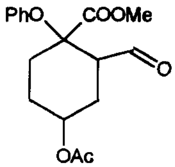
ammonium nitrate "clayan"[20] (1:7 ratio of NH_4NO_3 in reagent). The mixture is stirred at r.t. in nitrogen atm. for the stipulated period (see table) and the progress of the reaction is monitored by tlc. At the end of the reaction, the used reagent is removed by filtration and the filtered solid is washed with more dichloromethane (3 x 25 ml). After reducing the volume of solvent, it is passed through the neutral alumina bed which gives pure carbonyl compounds. The removed disulfur moiety polymerizes[21] and is adsorbed on the spent support whereas in the case of the monosulfur derivative, the thiol impurities are removed by washing with hexane to give pure carbonyl compounds.

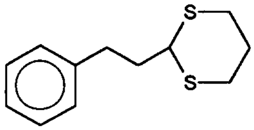
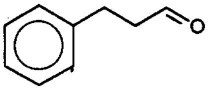
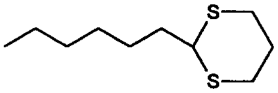
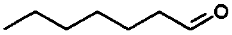
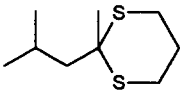
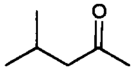
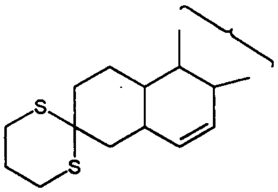
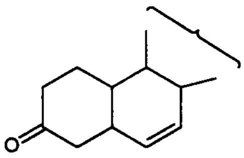
Table-1 : Cleavage of thioacetals by clay supported ammonium nitrate "Clayan"

Entry	Substrates	Products	Time(hrs)	Yields[a]
1.			20	86
2.			18	83
3.			16	80
4.			16	83
5.			16	90
6.			18	84
7.		 Cholestenone	20	78
8.			19	81
9.			20	76

[a] = All the products are identified by comparing IR, Mass, NMR and tlc with that of authentic samples

The thiol derivatives of aldehydes and ketones are readily deprotected into their parent carbonyl compounds in good yields in dichloromethane at room temperature under an inert atmosphere and work up is simply the filtration of used reagent. The deprotection in inert atm demonstrate the oxidative capability of the reagent. It is also important to note that the procedure is effective for the deprotection of C-3 dithiane derivative of cholestenone (Entry-4, Table-2) which is usually removed under vigorous conditions.[22] We have observed the tolerance of common groups like esters (Entry-9, Table-1) and ethers (Entry-2&8, Table-1) in the reaction conditions which shows the mildness and selectivity of the present method. However,the method failed to deprotect thioketals selectively in the presence of acetonides. It has been recently demonstrated that NO^+ -releasing reagents are efficent in transforming S,S-acetals into the corresponding carbonyl compounds.[23] Therefore, we believe that the reaction probably proceeds via the intermediacy of nitrosonium ions.

Table-2 : Cleavage of dithianes by clay supported ammonium nitrate "Clayan"

Entry	Substrates	Products	Time(hrs)	Yields^a
1.			22	82
2.			20	86
3.			22	89
4.		 Cholestenone	27	75

^{a} = All the products are identified by comparing IR, Mass, NMR and tlc with that of authentic samples

In conclusion, the present method is mild, inexpensive and convenient for the deprotection of variety of thioacetals and ketals. The fertilizing property of ammonium nitrate demonstrates the eco-friendly nature of the present procedure.

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19. Meshram, H.M.; Reddy, G.S.; Srinivas, D.; Yadav, J.S. *Tetrahedron Lett.* (communicated).
20. **Preparation of Clay Supported Ammonium Nitrate "Clayan"** : To a solution of ammonium nitrate (5 g) in distilled water (70ml) was added montmorillonite K 10 (Aldrich Chemicals Co.) (5 g) in portions at room temperature and the suspension stirred for 1 h. Water is removed using rotary evaporator at 50-60^{0}C under reduced pressure and the resulting moist solid was dried under vacuum at 40^{0}C for 2 h. and the powdery reagent stored in a stoppered bottle.
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