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Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/lsyc20

A Mild and Efficient Method for the Protection of Carbonyl Compounds as 1,5-Dihydro-2,4benzodithiepines Using Anhydrous Iron(III) Chloride Dispersed on Silica Gel

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To cite this article: Harish K. Patney (1993) A Mild and Efficient Method for the Protection of Carbonyl Compounds as 1,5-Dihydro-2,4-benzodithiepines Using Anhydrous Iron(III) Chloride Dispersed on Silica Gel, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 23:13, 1829-1833, DOI: <u>10.1080/00397919308011283</u>

To link to this article: http://dx.doi.org/10.1080/00397919308011283

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A MILD AND EFFICIENT METHOD FOR THE PROTECTION OF CARBONYL COMPOUNDS AS 1,5-DIHYDRO-2,4-BENZODITHIEPINES USING ANHYDROUS IRON (III) CHLORIDE DISPERSED ON SILICA GEL

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Abstract: A mild and efficient procedure for the protection of carbonyl compounds as 1,5-dihydro-2,4-benzodithiepines rapidly and in high yields is described by using 1,2-benzenedimethanethiol and anhydrous iron (III) chloride dispersed on silica gel as a catalyst.

1,3- Dithiolanes have long been used as protective groups for carbonyl compounds^{1,2} and as synthons in a variety of synthetic operations³. The preparation of these dithiolanes employs thiol or dithiol reagents which generally have unpleasant odours, as do the products. To overcome this problem 1,2-benzenedimethanethiol $(\underline{1a})^{4,5}$ offers a useful alternative reagent for condensation with carbonyl compounds. The products (<u>3a</u>) formed are crystalline solids with mild odour and easily purifiable. Although a dimethyl derivative of 1,2-benzenedimethanethiol $(\underline{1b})^6$ has been utilised, the catalysts employed for this transformation were strong protic acids such as concd HCl(aq) for aldehydes, ZnCl₂-HCl(g) or concd H₂SO₄ for ketones.

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It appears that the synthetic usefulness of this reaction has not been fully exploited, especially when the 2,4-benzodithiepine derivatives (3) can easily be cleaved back to carbonyl compounds and can also act as masked methylene functions⁶. Recently we reported the use of anhydrous iron (III) chloride dispersed on silica gel⁷ as a rapid, high yielding and mild reagent for thioacetalization of aldehydes and ketones. We now extend the scope of this remarkable reagent by reporting that 2,4-benzodithiepines (3a) can be prepared rapidly by direct condensation of carbonyl compounds with 1,2benzenedimethanethiol $(\underline{1a})^5$ under mild conditions and in high yields. The reaction proceeds very cleanly and the work-up procedure is simple. When a mixture of carbonyl compound (2) and (1a) in dichloromethane is treated with anhyd. iron (III) chloride - silica reagent at room temperature, excellent yields of (3a) are obtained. The method described here is not only mild but also very rapid. Aliphatic, aromatic and conjugated aldehydes reacted within 1 minute and aliphatic, cyclic ketones reacted in 5-10 minutes. The high reactivity of this reagent is clearly manifested in that the less reactive aromatic ketones reacted quickly at room temperatures (Table, Entries 13-15) and gave excellent yields of benzodithiepines (3a). The efficiency of the anhyd. iron (III) chloride-silica reagent is probably due to its strong affinity for oxygenated organic compounds and its remarkable ability to act as a water scavenger.

Table:Preparation of 2,4-Benzodithiepines (3a)Using Anhyd.FeCl3-SiO2Reagent9

Entry	Substrate	Substr. ^a	Reaction	Yield ^b	m.p.
		ratio	time, min	(%) (<u>3a</u>)	[0C]c
1	2-Adamantanone	1.0	5	95	147-148
2	Cyclohexanone	1.2	5	95d	96-98f
3	2-Methylcyclohexanone	1.2	5	91	78-79
4	Cyclopentanone	1.2	10	99	121-123
5	3-Pentanone	1.2	10	95	72-73
6	Acetone	1.2	7	93d	130-131 ^f
7	Phenylacetaldehyde	1.5	1	90	76-78
8	Benzaldehyde	1.2	1	99	174-176 ^f
9	p-Chlorobenzaldehyde	1.0	1	98	211-213
10	Cyclohexanecarboxaldehyde	1.5	1	99	111-113
11	Anisaldehyde	1.2	1	95	189-191
12	Cinnamaldehyde	1.2	1.	91	167-168
13	Acetophenone	1.2	10	98e	131-133
14	9-Fluorenone	1.0	15	96e	245-246 (dec)
15	Benzophenone	1.0	20	89e	189-191
16	Trioxane	1.1	3	84d,g	156-158

a) (Carbonyl compound)/(<u>1a</u>), any excess of (<u>2</u>) easily removed during the workup procedure; b) Yield of isolated product characterized by physical and spectral data; c) Uncorrected; d) The reported⁸ yields for entry 2, 6 and 16 were 43% (ptoluenesulfonic acid, reflux conditions), 72% (HCl gas, r.t.) and 62% (conc. HCl, r.t.) respectively; e) 4.0g of anhyd. FeCl₃-SiO₂ reagent used; f) Reported values for entries (2), (6), (8) and (16) were 96-98° (ref 8), 136-137° (ref 8), 170° (ref 4) and 155-156° (ref 8) respectively; g) 6.0 g of FeCl₃-SiO₂ used. In conclusion, anhydrous iron (III) chloride - silica reagent is a very effective and convenient reagent for the protection of carbonyl compounds as 2,4-benzodithiepines under mild reaction conditions. This method should provide a useful alternative to the currently used thioacetalization as the products formed are crystalline solids, have mild odour and the blocking group is easily removable.

Acknowledgement: The author wishes to thank Dr. J Kalman for helpful discussions, Mr J Keegan for running the mass spectra and Mrs L Ambrose for the technical assistance.

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- This compound is commercially available, however, it could be conveniently prepared in 90% yield from α,α'-dibromo-o-xylene (Aldrich Chemical Co.) as described in ref. 6 for the preparation of (<u>1b</u>).
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PROTECTION OF CARBONYL COMPOUNDS

9. Typical Procedure: To a magnetically stirred solution of (<u>1a</u>) (10mmol), carbonyl compound (10-15 mmol, see Table), dicholoromethane (20 ml) at r.t. was added anhyd. FeCl₃-SiO₂ reagent⁷ (2.0g, equivalent to 2mmol of FeCl₃) (unless stated otherwise) in one portion. After stirring the reaction mixture for the specified time (Table), during which time it turned orange - red, was quenched with 1M NaOH and the product isolated by decantation from the solids, evaporation and recrystallization from hot ethanol or acetone-ethanol.

(Received in UK 8 February 1993)