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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

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Chromium Trioxide in Dimethyl
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To cite this article: Wen-Xing Lou & Ji-Dong Lou (1992) A New and Convenient Method for the Preparation of Aldehydes by Oxidation of Primary Alcohols with Chromium Trioxide in Dimethyl Sulfoxide, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 22:5, 767-772, DOI: 10.1080/00397919208019278

To link to this article: http://dx.doi.org/10.1080/00397919208019278

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A NEW AND CONVENIENT METHOD FOR THE PREPARATION OF ALDEHYDES BY OXIDATION OF PRIMARY ALCOHOLS WITH CHROMIUM TRIOXIDE IN DIMETHYL SULFOXIDE

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ABSTRACT: A new and convenient method is described to oxidize primary alcohols into the corresponding aldehydes utilizing chromium trioxide-dimethyl sulfoxide system.

The oxidation of primary alcohols to the corresponding aldehydes is an important reaction in synthetic organic chemistry. For this transformation,

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768 LOU AND LOU

a number of procedures with chromium trioxide (CrO₃)¹ as oxidant have been reviewed²⁻⁵ in the past. Over the past ten years, considerable research has been reported on methods of oxidation utilizing chromium trioxide, such as chromium trioxide on anion exchange resin,⁶ chromium trioxide on divinylbenzene-styrene-vinylpyridine,⁷ chromium trioxide-halosilanes,^{8,9} chromium trioxide-crown ether,¹⁰ chromium trioxide-quaternary ammonium species,¹¹ chromium trioxide-quaternary ammonium species on pyridinium or on quaternary ammonium resin,¹¹ chromium trioxide on silica gel,¹² chromium trioxide on aluminium silicate,¹³ aqueous chromium trioxide-diethyl ether,¹⁴ chromium trioxide on kieselguhr¹⁵ and chromium trioxide-halosilanes on alumina¹⁶ etc.

Apart from these, two polar aprotic solvents, N,N-dimethyl formamide (DMF)¹⁷ and hexamethylphosphorous triamide (HMPT), have respectively been used to replace the traditional acidic media in the oxidation of alcohols into aldehydes by chromium trioxide with the advantages of mild reaction condition and convenient isolation of the oxidized product.

In connection with work on the oxidation of alcohols by chromium trioxide in polar aprotic media we report here that chromium trioxide-dimethyl sulfoxide (DMSO) is a new system which offers a simple and efficient oxidation method for the preparation of

aldehydes 2 from the corresponding primary alcohols 1.

The present oxidation method has the advantage of

$$\operatorname{CrO}_3$$
, DMSO, R.T.

RCH₂OH

2

shorter reaction time and higher yield than that of chromium trioxide in other polar aprotic media described above. It compares favorably with both chromium trioxide-DMF and chromium trioxide-HMPT systems. In addition, commercial DMSO may be used without further purification.

To determine the role that DMSO plays in the present oxidation method, we observe that oxidation of benzyl alcohol is not caused by DMSO alone at 30°C although it does occur at reflux. 20,21 Furthermore, we find that by addition of a solution of chromium trioxide in DMSO to a solution of benzyl alcohol in DMSO at 30°C oxidation into the corresponding aldehyde takes place. Therefore, we conclude that DMSO acts as an excellent solvent in this method.

The present oxidation method is very simple. The chromium trioxide in DMSO is stirred with primary alcohols in DMSO at room temperature and the corresponding aldehydes are obtained in high yield by extraction. Our results are summarized in the Table.

770 LOU AND LOU

Table. Oxidation of primary alcohols to aldehydes

Alcohol	Aldehyde ^a	Yield ^b (%)
Me(CH ₂) ₄ OH	Me(CH ₂) ₃ CHO	68
CH ₂ =CHCH ₂ OH	CH ₂ =CHCHO	81
MeC(C1)=CHCH2OH	MeC(C1)=CHCHO	79 ^c
PhCH ₂ OH	PhCHO	87
PhCH=CHCH2OH	PhCH=CHCHO	90 ^c
p-MeOC ₆ H ₄ CH ₂ OH	p-MeOC ₆ H ₄ CHO	82°

a. All the aldehydes have been described previously in the literature and were identified by their infrared spectra or the infrared spectra of their 2,4-dinitrophenylhydrazones.

- b. Distilled product.
- c. Isolated as the 2,4-dinitrophenylhydrazone.

EXPERIMENTAL SECTION

Oxidation of benzyl alcohol to benzaldehyde;
Typical procedure: Benzyl alcohol (5.4 g, 0.05 mol)
and DMSO (10 ml) are placed in a flask fitted with a
condenser. The mixture is stirred with a magnetic
stirrer and a solution of chromium trioxide (9.9 g,
0.1 mol) in DMSO (100 ml) is added dropwise over

30 min. Care is taken to maintain temperature of the reaction mixture at 30° C or so. After 4 h at room temperature, cold water (500 ml) is added to the reaction mixture, and the product is extracted with diethyl ether (5 x 20 ml). The combined extracts are washed with saturated sodium bicarbonate (30 ml) then water (3 x 20 ml), and dried over anhydrous magnesium sulfate and then distilled through a short Vigreux column to give benzaldehyde; Yield: 4.6 g (87 %).

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(Received in USA 24 September, 1991)