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OXIDATION OF ALCOHOLS BY SILICA GEL-SUPPORTED BIS (TRIMETHYLSILYL) CHROMATE UNDER MICROWAVE IRRADIATION WITHOUT SOLVENT.

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Abstract: Microwave irradiation of alcohols with silica gel-supported bis (trimethylsilyl) chromate in dry media provides a fast,effecient and simple method for oxidation of alcohols to corresponding carbonyl compounds.

The most important synthetic application of chromium oxidants is the alcohol oxidation to the carbonyls[1]. Pyridinium dichromate[2] and chlorochromate[3] have been often used for this purpose because of mildness and high yields. chromium oxidants absorbed on solid supports such as PCC[4] on alumina, chromic acid on silica[5], chromyl chloride on silica-alumina[6] were reported to give better yields and under milder conditions than the corresponding parent oxidants.

Chromic anhydride mixed with chlorotrimethylsilane has been applied for the oxidation of several functional groups. Bis (triphenylsilyl) chromate[8] and bis (trimethylsilyl) chromate (BTSC)[9] have been known for a long time. Lee *et al* have recently reported the oxidation of alcohols by silica gel supported bis (trimethylsilyl) chromate[10].

In the last 8 years there was a growing interest in microwave activation of organic reactions[11]. The effects usually observed are decreasing reaction times (up to 3 orders of magnitude) and in some cases cleaner reactions with easier work up. Particularly

interesting the coupling with dry media conditions which made possible to work in open vessels thus avoiding the risk of high pressures and carrying out reactions in friendly conditions and on a preparative scale[12].

We report herein our preleminary studies of oxidation of alcohols using silica gel supported bis (trimethylsilyl) chromate under microwave irradiation without solvent.

Heating chromic anhydride with a slight excess of hexamethyldisiloxane in dichloromethane produces a nearly homogeneous solution. BTSC supported on silica gel was conveniently prepared simply by adding silica gel into the vigorously stirred pre-made solution. The dark brown free-flowing solid was obtained on evaporation of volatile materials. The catalyst can be stored in a dark brown bottle without appreciable loss of reactivity for at least 3 months.

The oxidation reactions were carried out simply by mixing 1-1.2 equivalents of BTSC supported silica gel with an alcohol in a beaker and then activated by an exposition to microwave irradiation (480W) during certain times (Table).

1-Octanol for example was oxidized in this way to produce octanal in almost quantitative yields in 5 min. This is in strong contrast with required (60 min) for completion of this oxidation in ordinary condition[10].

Benzyl alcohol and substituted benzyclic alcohols were similarly oxidized usually within 2-5 minutes under microwave irradiation Benzylic alcohol were oxidized to the corresponding aldehyes and an over oxidation of aldehydes to the corresponding derivatives was not observed even after prolonged irradiation with excess supported BTSC.

Aliphatic primary alcohols were oxidized to the corresponding aldehydes and the secondary alcohols to the corresponding ketones. An aryl substituted unsaturated alcohol was successfully oxidized to the corresponding α,β-unsaturated aldehyde. For example cinnamaldehyde was obtained in 94% yield. In this reaction no benzaldehyde was detected. This is in strong contrast to a mer 72% yield in the reaction with BTSC supported in silica gel under ordinary condition along with 26% benzaldehyde .

$$CH_3\ (CH_2)_6\ CH_2OH \xrightarrow[\text{Microwave Irradiation}]{CrO_3\ /\ TMSOTMS} CH_3\ (CH_2)_6\ CHO$$

In conclusion bis (trimethylsilyl)chromate supported on silica gel can be easily serve as an excellent oxidant for the oxidation of various types of alcohols under microwave irradiation without solvent. By comparison with ordinary condition this method decreases the time of reactions dramatically. The products can be isolated by addition of dichoromethane to the crude, and filtration of reaction mixture without aqueous work up. The high reactivity and selectivity of the supported reagent under microwave irradiation

***Table* : Oxidation of Alcohols to Carbonyl Compounds by Bis (trimethylsilyl) chromate Supported on Silca gel Under Microwave Irradiation Without Solvent.**

Alcohol	Reaction Time (Sec)	Product	Yield
Benzyl alcohol	10	Benzaldehyde	98
4-Methyl benzyl alcohol	15	4-Methyl benzaldehyde	99
5-Methyl -2-nitrobenzyl alcohol	60	4-Methyl -2-nitro benzaldehyde	98
Menthol	180	Menthal	84
1-Octanol	300	Octanal	88
2-Ethyl-hexanol	120	2-Ethyl-hexanal	80
2-Octanol	300	2-Octanone	89
Cyclohexanol	120	Cyclohexanone	78
Cinnamyl alcohol	40	Cinnamaldehyde	72.3
Dedecanol	120	Decanone	89

avoid the use of a larger excess of the oxidant which may cause an over-oxidation and other side reactions.

Experimental

All products are known compounds and their physical data were essentially identical with those of authentic samples. Microwave irradiation were carried out in a National oven,Model 5250 at 480 W. For safety reasons all the experiments with microwave ovens should be performed in an efficient hood in order to avoid contact with vapours. If a tall beaker is used and the irradiation sequence is interrupted with a 60 sec cooling there is little vaparization and very high conversion can be observed. Silica gel supported bis (trimethylsilyl) chromate was prepared according to the known precedure[10].

General procedure for oxidation of alcohols using silica gel supported bis (trimethylsilyl) chromate under microwave irradiation without solvent.

A 100ml pyrex beaker was charged with silica gel supported bis (trimethylsilyl) chromate (0.8 g, equivalent to 1.2 mmol of chromium (VI) oxidant) and 1-octanol (136 mg 1.05 m mol). This reaction mixture was mixed thoroughly and kept in the microwave

oven for 5 min. The reaction mixture was poured into dichoromethane (5 mil) and it was gravity filtered and washed with dichloromethane (5 mil). Evaporation of solvent gave 113 mg octanal (88%) of which GC analysis showed negligible ammounts of impurities.

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