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

Envirocat EPZG® as a New Heterogenous Catalyst for the Solvent-Free Tetrahydropyranylation of Alcohols and Phenols

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To cite this article: B. P. Bandgar, S. R. Jagtap, B. B. Aghade & P. P. Wadgaonkar (1995) Envirocat EPZG® as a New Heterogenous Catalyst for the Solvent-Free Tetrahydropyranylation of Alcohols and Phenols, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 25:15, 2211-2215, DOI: 10.1080/00397919508011775

To link to this article: http://dx.doi.org/10.1080/00397919508011775

SYNTHETIC COMMUNICATIONS, 25(15), 2211-2215 (1995)

ENVIROCAT EPZG^R AS A NEW HETEROGENOUS CATALYST FOR THE SOLVENT-FREE TETRAHYDROPYRANYLATION OF ALCOHOLS AND PHENOLS[1]

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Abstract : Envirocat EPZG^R was used as a solid supported acid catalyst for tetrahydropyranylation of alcohols and phenols in the absence of a solvent. This new method is rapid, efficient and convenient giving the corresponding products in high yields and purity.

Tetrahydropyranylation is one of the most frequently used methods to protect alcohols and phenols, in view of the outstanding stability of the resulting ethers to strongly basic media, reduction with hydrides, to oxidation and Grignard reagents.[2] A variety of reagents that are reported for this conversion include the use of protic acids,[3] Lewis acids,[4] pyridinium p-toluenesulfonate,[5], ion-exchange resins,[6] poly (4-vinylpyridine) as the p-toluenesulfonate[7] and hydrochloride,[8] 2,3-dichloro-5,6-dicyano-p-benzoquinone,[9] aluminium phosphate,[10] aluminium phosphate-aluminium trioxide,[10] sulfuric acid adsorbed on silica gel, [11] lanthanum trichloride,[12] sulfonated charcoal,[13] molybdenyl (VI)

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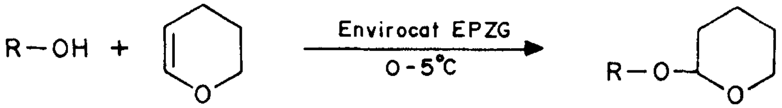
acetylacetone,[14] ceric ammonium nitrate,[15] montmorillonite clay K-10,[16] zeolite[17] and spanish sepiolite clay[18].

There has been a considerable growth in interest in recent years in the catalysis of organic reactions by inorganic reagents supported on high surface area inorganic materials.[19] Envirocats,^{R} a new family of supported reagents,[20] are a significant breakthrough in environmentally friendly chemistry. These reagents are capable of catalysing Friedel-Craft's alkylation and acylation, sulfonylation, oxidation and other related processes.[20] We have previously reported their use as heterogenous catalyst for acid catalysed reactions.[21-22]

We now wish to report a simple, convenient and mild approach to the tetrahydropyranylation of alcohols and phenols with 3,4-dihydro-2H-pyran under heterogenous liquid-solid catalysis on Envirocat EPZG^R catalyst and in the absence of a solvent. The reactions proceeded smoothly giving the corresponding products in high yields and purity. The results are summarized in the table.



Scheme

In summary, Envirocat EPZG^R has been found to be a useful and very effective catalyst for tetrahydropyranylation of alcohols and phenols under mild conditions. The obvious advantages of Envirocat in terms of easy separation, high yields and recyclability are noteworthy. Currently work is in progress to study the reactions catalyzed by Envirocats.

Experimental

All Chemicals were commercial and analytical grade purchased from Aldrich and purified prior to use. 3,4 - Dihydro - 2H- pyran was double

Table. Envirocat EPZG^R Catalyzed Tetrahydropyranylation of Alcohols and Phenols.

Entry	Substrate	Reaction Time (min.)	Yield (%)
1	n - Butanol	10	88
2	2 - Methylbutanol	20	87
3	Isopropanol	10	94
4	Isobutanol	20	93
5	Cyclohexanol	30	98
6	Benzyl alcohol	100	99
7	Chloroethanol	15	97
8	Tetrahydro furfuryl alcohol	60	98
9	Allyl alcohol	50	82
10	tert-Butanol	40	76
11	Cholesterol	15	99
12	Phenol	10	96
13	α-Naphthol	30	95

distilled. Envirocat EPZG^R was obtained from Contract Chemicals, England and activated 1 h prior to use by azeotropic drying or heating at 300-350°C and cooling in a flow of nitrogen. The products were characterized by their physical properties and spectral characteristics (^{1}H NMR, IR etc.). PMR spectra were recorded in $CDCl_3$ on 60 MHz or FT 90 MHz instrument using TMS as internal reference. IR spectra were recorded in nujol on Perkin Elmer IR spectrometer : model PE - 883.

General procedure

The alcohol or phenol (10 mmol), 3,4-dihydro - 2H-pyran (40 mmol) and Envirocat EPZG^R (200 mg) were stirred at 0-5° for the specified period of time (Table). The reaction was monitored by TLC. After completion of the reaction, the reaction mixture was treated with dichloromethane (10 mL). The catalyst was removed by filtration and washed with dichloromethane (2 x 10 mL). Removal of the solvent under reduced pressure afforded products in high yields and almost pure form.

Acknowledgement. We thank contract chemicals, England for the generous gift of Envirocat EPZG^R and Prof. S.F. Patil (Univ.of Poona, Pune) and Principal Vijay Kasbekar for their encouragement.

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(Received in the UK 19 December 1994)