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Environmentally Friendly Arylmethylation of Aromatics with Benzyl Halides Using Envirocat EPZ10® as the Catalyst

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Summary. The *Friedel-Crafts* arylmethylation of aromatics with benzyl halides or *bis*-(bromomethyl)-benzene in the presence of Envirocat EPZ10® affords selectively *para*-arylmethylated products in good yields. Isolation of pure products involving an eco-friendly procedure and recyclability of the catalyst are important features of this method.

Keywords. Envirocat EPZ10®; Arylmethylation; Eco-friendly; Catalyst; *Friedel-Crafts* reaction.

Introduction

The benzylation of aromatic rings under *Friedel-Crafts* conditions is of substantial synthetic, industrial, and pharmacological significance [1–4]. Using homogenous catalysis employing *Lewis* acids like $AlCl_3$ and $FeCl_3$, significant volumes of solvent are required and unwanted by-products are formed. Moreover, catalysts cannot be reused, and transalkylation, dealkylation, rearrangements, and polyalkylations are difficult to avoid [4]. Therefore, alternative synthetic ways are of considerable interest [5].

In recent years there has been a considerable growth of interest in the catalysis of organic reactions by inorganic reagents supported on high surface area inorganic materials [6]. These reactions often proceed with greater selectivity than analogous homogenous reactions. Envirocats, a new family of solid-supported reagents, have constituted a significant breakthrough in environmentally friendly chemistry [6]. These supported reagents are non-toxic and reusable powers of both *Brønsted* and *Lewis* acid characteristics [6]. We report herein the *Friedel-Crafts* arylmethylation of phenol and anisole with various benzyl halides using Envirocat EPZ10® as a novel catalyst.

Results and Discussion

The results of arylmethylation are summarized in Table 1. The treatment of activated aromatic compounds like phenol and anisole with benzyl halides or *bis*-

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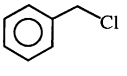
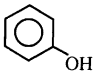
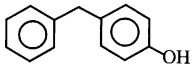
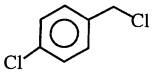
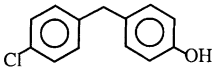
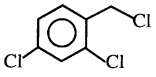
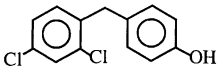
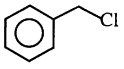
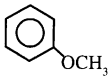
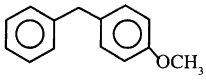
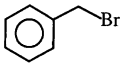
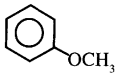
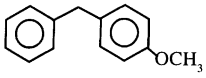
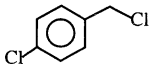
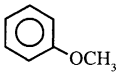
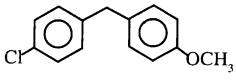
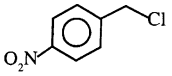
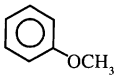
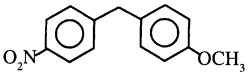
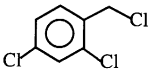
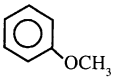
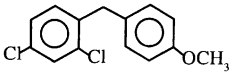
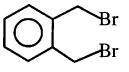
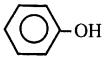
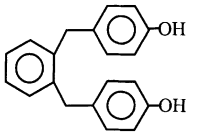
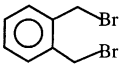
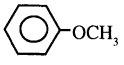
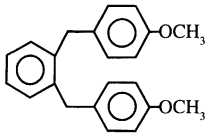
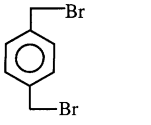
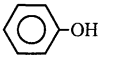
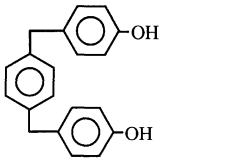
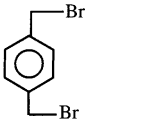
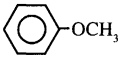
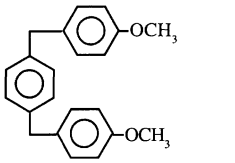
Table 1. Arylmethylation of aromatic substrates catalyzed by Envirocat EPZ10®

	Benzyl halide	Substrate	Product[a]	*t*/min	Yield/%[b] (*o*:*p*)
1				60	88 (1:4)
2				45	77 (1:4)
3				35	87 (1:4)
4				35	78 (1:3)
5				10	84 (1:4)
6				25	88 (1:4)
7				25	85 (1:5)
8				45	75 (1:4)
9				40	82 (1:4)
10				30	78 (1:4)
11				20	85 (1:4)
12				20	80 (1:4)

[a] Products were characterized by their physical constants [7], their IR and ^{1}H NMR spectra, and by comparison with authentic samples; [b]isolated products

(bromomethyl)-benzene in the presence of catalytic amounts of Envirocat EPZ10® afforded mainly the corresponding *para*-arylmethylated products (*o*: *p* = 1:4). The *para*-selectivity is impressive compared with that achieved employing aluminum chloride [1–3]. In the synthesis of the pharmaceutical intermediate 4-chloro-4′-hydroxydiphenylmethane (entry 2), the use of Envirocat EPZ10® offers a commercially feasible route; the catalyst can be reused for several cycles without loss of activity.

Experimental

Envirocat EPZ10® was obtained from Contract Chemicals, England, and used without activation. IR spectra were recorded on a Bomen MB 104 FT-IR spectrometer, ^{1}H NMR spectra on a Perkin-Elmer 90 MHz instrument using *TMS* as an internal standard.

A mixture of 5 mmol benzyl halide, 100 mmol phenol or anisole, and 100 mg Envirocat EPZ10® was refluxed for the time specified in Table 1. After completion of the reaction (TLC), the catalyst was filtered off and washed with ether ($2 \times 10\,cm^3$). The solvent was removed under reduced pressure, and the products were purified by column chromatography (silica gel G, ethyl acetate:petroleum ether = 1:19).

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