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Solid Supported Reactions and Reagents XIV [1]: Envirocat EPZG® as a Novel Catalyst for Selective Acetalization of Aldehydes and Ketones

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Summary. Envirocat EPZG® is an efficient reusable catalyst for acetalization of aldehydes and ketones. The isolation of pure products in high yields by simple filtration and evaporation of the solvent is an important feature of this method.

Key words. Aldehydes and ketones; Envirocat EPZG®; Protection of carbonyl groups; Selective acetalization.

Festkörperunterstützte Reaktionen und Reagentien, 14. Mitt. [1]: **Envirocat EPZG® als neuer Katalysator für die selektive Acetalisierung von Aldehyden und Ketonen**

Zusammenfassung. Envirocat EPZG® ist ein effizienter, wiederverwendbarer Katalysator für die Acetalisierung von Aldehyden und Ketonen. Die Isolierung reiner Produkte durch einfache Filtration und Verdampfen des Lösungsmittels ist ein wesentliches Kennzeichen dieser Methode.

Introduction

The carbonyl group is one of the most versatile functional groups in organic chemistry, and a great deal of synthetic work has been dedicated to the protection of carbonyl compounds as acetals and thioacetals [2]. The most convenient and practical methods for the syntheses of acetals from aldehydes and ketones are to react carbonyl compounds with alcohols or diols in the presence of an appropriate acid catalyst with azeotropic removal of water [3]. A variety of methods have been reported for the acetalization of carbonyl compounds employing different reagents [4–10].

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 [11]. Envirocat®, a new family of supported reagents, provides a significant break-through in an environmentally friendly chemistry. The members of this

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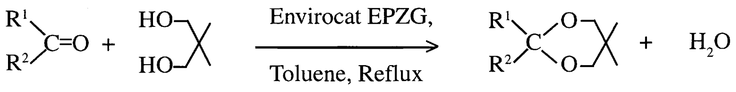
group are capable of catalyzing *Friedel-Crafts* alkylations and acylations, sulfonylations, oxidations, and other related processes [12]. Envirocat® are non-toxic powders composed of iron trichloride (19.6%) supported on inert material (80.4%) which can be filtered off easily and may be reused several times before they are exhausted [12].

Envirocat EPZG® is one of the solid supported acid catalysts which exhibits both *Bronsted* and *Lewis* acid characteristics [12]. We have reported the use of Envirocat EPZG® as an efficient heterogenous catalyst for the synthesis of conjugated nitroolefins [13], chemoselective silylation of alcohols [14], methoxymethylation of alcohols [15], and conversion of aldoximes into nitriles [16]. Recently, Envirocat EPZG® has been used for the generation of ketones from their tosylhydrazones [17]. We now report a simple and efficient high yield method for the acetalization of aldehydes and ketones catalyzed by Envirocat EPZG®.

Results and Discussion

The results of acetalization (Scheme 1) are presented in Table 1. The work-up procedure is exceedingly simple and involves merely filtration. Envirocat EPZG® is recovered and reactivated for reuse by azeotropic distillation. This procedure of acetalization appears to be quite general and selective. Both aldehydes and ketones were smoothly converted into acetals in excellent yields. It was observed that Envirocat EPZG® catalyzes acetalization of some more reactive carbonyl compounds in the presence of less reactive or sterically hindered carbonyl compounds. For example, when a mixture of *o*-nitrobenzaldehyde (**1g**) and 3-methoxy-4-hydroxy-benzaldehyde (**1f**) was allowed to react with one equivalent of **2** and a catalytic amount of Envirocat EPZG® in toluene at reflux temperature for 3 h, a high yield (93%) of **3g** was obtained, whereas **1f** was recovered unchanged. Under similar experimental conditions, mixtures of **1c** and **1k**, **1m** and **1k**, or **1l** and **1o** were allowed to react with one equivalent of 2,2-dimethyl-1,3-propanediol and a catalytic amount of EPZG® in toluene under reflux for 3.5 h, 1.5 h, and 7 h,



1 **2** **3**

	*R*¹	*R*²		*R*¹	*R*²
a	H	2-Furfuryl	i	H	4-NO_2-C_6H_4
b	H	C_6H_5	j	H	$C_6H_5CH{=}CH$
c	H	4-Cl-C_6H_4	k	CH_3	C_6H_5
d	H	2,4-Cl_2-C_6H_3	l	CH_3	4-Cl-C_6H_4
e	H	4-MeO-C_6H_4	m	tetramethylene	
f	H	3-MeO,4-OH-C_6H_3	n	pentamethylene	
g	H	2-NO_2-C_6H_4	o	C_6H_5	C_6H_5
h	H	3-NO_2-C_6H_4			

Scheme 1

Table 1. Envirocat EPZG® catalyzed acetalizations of carbonyl compounds

	Reaction times (h)	Yield (%)	m.p./b.p. (°C)	^{1}H NMR δ (ppm)
3a	2.5	90	235[a]	0.75 (s, 3H, CH_3), 1.25 (s, 3H, CH_3), 3.65 (s, 4H, $2\times OCH_2$)
3b	3	94	240[a]	0.80 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 3.68 (s, 4H, $2\times OCH_2$), 5.60 (s, 1H, ArCH), 7.10 (m, 5H, Ar- H)
3c	3	98	237[a]	0.80 (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 3.70 (s, 4H, $2\times OCH_2$), 5.37 (s, 1H, ArCH), 7.23 (d, 2H, $J = 4.5$ Hz, Ar-H), 7.70 (d, 2H, $J = 4.5$ Hz, Ar-H)
3d	5	90	>250[a]	0.70 (s, 3H, CH_3), 1.33 (s, 3H, CH_3), 3.66 (s, 4H, $2\times OCH_2$), 5.53 (s, 1H, ArCH), 7.43 (m, 3H, Ar-H)
3e	10	95	60[b]	0.77 (s, 3H, CH_3), 1.23 (s, 3H, CH_3), 3.60 (s, 4H, $2\times OCH_2$), 3.70 (s, 3H, OCH_3), 5.23 (s, 1H, ArCH), 6.67 (d, 2H, $J = 4$ Hz, Ar-H, 7.33 (d, 2H, $J = 4$ Hz, Ar-H)
3f	29	94	80[b]	0.77 (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 3.67 (s, 4H, $2\times OCH_2$), 3.90 (s, 1H, OCH_3), 5.30 (s, 1H, ArCH), 7.00 (m, 3H, Ar-H)
3g	2	93	163[a]	0.80 (s, 3H, CH_3), 1.23 (s, 3H, CH_3), 3.70 (s, 4H, $2\times CH_2$), 6.00 (s, 1H, ArCH), 7.63 (m, 4H, Ar-H)
3h	2.5	80	120[a]	0.79 (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 3.70 (s, 4H, $2\times OCH_2$), 5.37 (s, 1H, ArCH), 7.55 (m, 4H, Ar-H)
3i	2	85	48[b]	0.80 (s, 3H, CH_3), 1.27 (s, 3H, CH_3), 3.71 (s, 4H, $2\times OCH_2$), 5.39 (s, 1H, ArCH), 7.50 (m, 4H, Ar-H)
3j	3	97	45[b]	0.70 (s, 3H, CH_3), 1.22 (s, 3H, CH_3), 3.69 (s, 4H, $2\times OCH_2$), 4.90 s, 1H, $J = 8$ Hz, ArCH), 7.05 (dd, 1H, $J = 16$ Hz, $J = 8$ Hz, $=C\mathit{H}CHO$), 7.40 (d, 1H, $J = 16$ Hz, ArCH$=$), 7.5 (m, 5H, Ar-H)
3k	8	95	148[a]	0.78 (s, 3H, CH_3), 1.25 (s, 3H, CH_3), 2.05 (s, 4H, Ar.CH_3)

[a] b.p.; [b] m.p.

respectively, high yields of the cyclic acetals **3c**, **3m**, and **3l** were obtained (95, 80, 98%); **1k** and **1o** were recovered unchanged.

In conclusion, Envirocat EPZG® has been found to be a useful, effective, and selective heterogenous catalyst for the acetalization of aldehydes and ketones. This method is an alternative to the existing procedures of acetalization. Furthermore, it is advantageous because of ease of separation, high yields, and recyclabilty of the catalyst.

Experimental

Envirocat EPZG® was obtained from Contract Chemicals, England, and activated 1 h prior to use by azeotropic distillation using a *Dean-Stark* apparatus.

General procedure

A mixture of the carbonyl compound (10 mmol), 2,2-dimethyl-1,3-propanediol (**2**, 10 mmol), and Envirocat EPZG® (100 mg) in anhydrous toluene was stirred under reflux for the specified time (Table 1). The water formed was removed azeotropically using a *Dean-Stark* apparatus. The reaction was monitored by TLC. After completion of the reaction, the mixture was filtered, and the catalyst was washed with dichloromethane (3×10 ml). The solvent was removed under reduced pressure to afford the product in almost pure form. All products were identified by their ^1H NMR spectra.

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