

Selective Transdithioacetalization of Acetals, Ketals, Oxathioacetals and Oxathioketals Catalyzed by Envirocat EPZ10^R†

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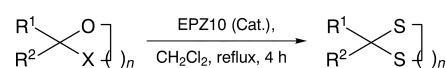
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Envirocat EPZ10^R has been found to be a remarkable reusable heterogeneous catalyst for selective transdithioacetalization of acetals, ketals, oxathioacetals and oxathioketals with HSCH₂CH₂SH and HSCH₂CH₂CH₂SH.

The protection of carbonyl group as a thioacetal is quite often a necessary requirement in the synthesis of complex multifunctional organic molecules¹ since these sulfur functionalities are quite stable towards a wide variety of reagents.² Dithioacetals are also useful in organic synthesis as acyl carbanion equivalents in C—C bond-forming reactions² and as intermediates for the conversion of the carbonyl function to the parent hydrocarbon.³ Numerous methods have been reported for this conversion.

However, some of these methods suffer from harsh conditions, expensive and hazardous reagents, sometimes cumbersome extraction procedures and are ineffective in the case of hindered ketones. Although, there are chemoselective methods for thioacetalization of aldehydes in the presence of ketones, very little is known about transdithioacetalization of acetals and ketals which is gaining prominence as a newer method of choice.⁶ In this context, a solid supported reusable catalyst would be more advantageous over classical acids.

In recent years, there has been a considerable growth in interest in the catalysis of organic reactions by inorganic



Scheme 1 R¹, R² = alkyl, aryl, H, cyclic; X = O, S; n = 1, 2

reagents supported on high surface area inorganic materials.⁷ Envirocat^R, a new family of supported reagents, is a breakthrough in environmentally friendly chemistry.⁸ Envirocat EPZ10^R (clayzic) is such a supported catalyst which exhibits both Brønsted and Lewis acid characteristics.⁸

Here we report the application of Envirocat EPZ10^R as an efficient catalyst for selective transdithioacetalization of acetals, ketals, oxathioacetals and oxathioketals with ethane-1,2-dithiol and propane-1,3-dithiol (Scheme 1).

Envirocat EPZ10^R catalyzes transdithioacetalization of a variety of acetals and ketals (aliphatic, aromatic, α,β -unsaturated) with ethane-1,2-dithiol (Table 1, entries 1–7, 9–13 and 15–20) in good yields. This method is not only useful for transdithioacetalization of acetals and ketals but also for oxathioacetal (entry 13) and oxathioketals (entries

Table 1 Transdithioacetalization of acetals, ketals and oxathioacetals with ethane-1,2-dithiol or propane-1,3-dithiol catalyzed by Envirocat EPZ10^R

Entry	Substrate	Product	Yield ^a (%)	MS (70 eV, 130 °C): M ⁺ = m/z (% rel. intensity)
1			85	61 (40), 69 (42), 79 (53), 105 (100), 148 (48)
2			72	59 (28), 71 (100), 103 (100), 132 (75)
3			90	58 (32), 105 (100), 147 (37), 162 (100)
4			91	74 (42), 106 (38), 119 (44), 134 (54)
5			95	58 (30), 71 (41), 81 (87), 131 (100), 146 (52), 173 (39)
6			65	77 (50), 93 (100), 126 (65), 158 (79), 186 (48)
7			68	59 (44), 105 (51), 117 (76), 161 (100), 176 (51), 199 (65), 268 (43)

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11 and 20). The transdithioacetalization of acetal (entry 14) and ketal (entry 8) was also achieved with propane-1,3-dithiol in good yields. A special feature of this catalytic process is that α,β -unsaturated acetals (entries 2 and 18) and

Table 1 Continued

Entry	Substrate	Product	Yield ^a (%)	MS (70 eV, 130 °C): M ⁺ = m/z (% rel. intensity)
8			83	81 (69), 95 (56), 137 (75), 159 (84), 244 (100)
9			78	55 (52), 131 (100), 197 (61), 230 (23)
10			84	60 (40), 71 (43), 83 (48), 98 (55), 115 (70), 131 (100), 197 (52), 258 (30)
11			73	77 (50), 92 (34), 135 (100), 212 (4)
12			75	100 (16), 121 (22), 151 (90), 226 (100)
13			89	58 (50), 120 (50), 166 (100), 196 (59), 227 (32)
14			91	75 (64), 112 (82), 155 (100), 216 (34)
15			95	103 (48), 115 (100), 147 (85), 179 (32), 208 (84)
16			92	60 (89), 77 (83), 105 (100), 121 (69), 165 (23), 196 (18)
17			91	60 (89), 77 (83), 105 (100), 121 (69), 165 (23), 196 (18)

^aIsolated yield, characterized by IR, ¹H NMR and MS.

ketals (entries 6 and 7) underwent transdithioacetalization without a double bond shift or 1,4-addition. It is also noteworthy that keto acetals undergo chemoselective transdithioacetalization in preference to ketone protection in excellent yield (entry 3). Even sterically hindered ketals (entries 8 and 19) and oxathioketal (entry 20) have been successfully transformed into dithioacetals in high yields. The Envirocat EPZ10^R catalyst was recovered and reused at least four times without any loss of activity.

Experimental

Envirocat EPZ10^R was procured from Contract Chemicals, Merseyside, England, and activated 1 h prior to use by using a Dean-Stark apparatus.

Typical Reaction Procedure.—A mixture of cinnamyl acetal (5 mmol), ethane-1,2-dithiol (5 mmol) and Envirocat EPZ10^R (100 mg) in CH₂Cl₂ (15 ml) was refluxed for 4 h. After the reaction was complete (TLC), the Envirocat EPZ10^R catalyst was filtered off and washed with CH₂Cl₂ (3 × 5 ml). The filtrate was washed with 5% NaOH and water. The organic layer was dried over anhydrous sodium sulfate, concentrated and purified by flash chromatography to give the 1,3-dithioacetal derivative (entry 18) in excellent yield (95%).⁹

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- 9 Mp 59 °C; IR 2900–2800, 1440, 1370, 970 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 3.22–3.42 (m, 4 H), 5.22 (d, *J* = 1, Hz, 1 H), 6.15–6.22 (dd, *J* = 1, 2 Hz, 1 H), 6.52 (d, *J* = 2 Hz, 1 H), 7.2–7.4 (m, 5 H); MS (70 eV, 130 °C); *m/z* (% rel. intensity): 208 (84), 179 (32), 147 (85), 115 (100), 103 (48).