# SULFONATED CHARCOAL, A MILD AND EFFICIENT REAGENT FOR THE PREPARATION OF CYCLIC ACETALS, DITHIOACETALS AND BENZODIOXEPINES

#### Harish K. Patney

Department of Chemistry, School of Physical Sciences University of Technology, Sydney, P. O. Box 123, Broadway, SYDNEY, NSW 2007, AUSTRALIA

**Summary:** 1,3-Dioxolanes, 1,3-Ditholanes and 1,5-dihydro-<u>3H</u>-2,4-benzodioxepines were prepared by the direct condensation of carbonyl compounds with 1,2-ethanediol, 1,2-ethanedithiol or 1,2-benzenedimethanol under the heterogeneous conditions of sulfonated charcoal catalyst.

The protection of carbonyl compounds as acetals or dithioacetals constitutes an important technique for many organic synthetic transformations <sup>1,2</sup>. Numerous methods that are reported in the literature for acetalisation include the use of protic acids<sup>3</sup>, Lewis acids<sup>4</sup>, ion-exchange resins<sup>5</sup>, rhodium compexes<sup>6</sup> and transition metals such as rhodium, iridium, palladium, platinum supported on carbon<sup>7</sup>. Similarly, dithioacetalisation of carbonyl compounds has been reported by the use of protic acids<sup>8</sup>, Lewis acids<sup>8,9</sup>, and more recently Nafion-H catalyst<sup>10</sup>, silica gel treated with thionyl chloride<sup>11</sup> and anhydrous lanthanum trichloride<sup>12</sup>. 1,5-Dihydro-3<u>H</u>-2,4-benzodioxepines have recently<sup>13</sup> been reported as a novel means of protecting carbonyl compounds that can easily be cleaved under nonacidic conditions by catalytic hydrogenolysis. These authors reported that these 2,4-benzodioxepines could be obtained in only a very low yield (15-20%) by direct condensation of 1,2-benzenedimenthanol (1) with carbonyl compounds (2) in the presence of a catalytic amount of **p**-toluenesulfonic acid (Eqn 1). The yield of these 2,4-benzodioxepines (3) was improved by these workers by first converting (1) into an orthoformate (4) and then treating the latter with aldehydes/ketones (2) under the conditions shown in Eqn. 2.



We report herein that cyclic acetals, dithioacetals and benzodioxepines can all be prepared in excellent yields (88-98%, see Tables 1 & 2) by the direct condensation of 1,2-ethanediol, 1,2-ethanedithiol or 1,2-benzenedimethanol with aldehydes/ketones (2) under heterogeneous conditions by employing sulfonated charcoal catalyst<sup>14,15</sup>. Both reaction conditions and work-up procedures are very simple and convenient. Carbonyl compounds (2), 1,2-ethanediol, 1,2-ethanedithiol or 1,2-benzenedimethanol, benzene and sulfonated charcoal catalyst are heated and stirred under reflux, with water removed azeotropically. For the preparation of benzodioxepines (3), the molar ratio of carbonyl compound (2) to (1) was varied from 1 - 2 depending upon volatility of (2) (see Table 2). Any excess (2) can easily be removed during the work-up procedure.

The synthetic applications of acidic sulfonated activated charcoal are very rare. It has been used recently for the preparation of carboxylic esters<sup>14</sup> and to the author's knowledge the only other report that has been cited is in a patent for the preparation of enolacetates<sup>15</sup>. The sulfonated charcoal used in this work was prepared by treating active charcoal with fuming sulfuric acid at 120° for 16 h (ref 15), filtering, washing with water until washings gave a negative barium chloride test. The acidity of the dried product was found to be due to both sulfonic acid and carboxylic acid groups (0.28 milliequivalent and 0.44 milliequivalent respectively per gram of the catalyst) as reported previously<sup>15</sup>. The effectiveness of the present catalyst may well be due to both its acidic nature

(sulfonic acid and carboxylic acid groups) and to the adsorption of reactant molecules on its surface.

Sulfonated charcoal used in the present work acted as a heterogeneous catalyst<sup>16,17</sup> and could be reused (washing with acetone, drying at ca. 100°C overnight) without affecting the yields. After the completion of the reaction (followed by IR and NMR spectroscopy), the catalyst was simply filtered off. The method described here does not require any basic aqueous work-up and the product isolation is simply achieved by filtration and evaporation followed by recrystallisation or distillation.

#### General Procedure for the Preparation of Cyclic Acetals/Dithioacetals/Benzodioxepines:

To a stirred solution of carbonyl compound (20mmol) and 1,2-ethanediol/1,2-ethanedithiol (24mmol) or 1,2-benzenedimethanol (10-20 mmol, see Table 2) in benzene (25ml) was added sulfonated charcoal catalyst (500mg). The mixture was stirred and heated under reflux using a Dean-Stark apparatus for water separation. The progress of the reaction was followed by IR and NMR spectroscopy. Upon completion of the reaction (8-16h), the mixture was filtered hot and the residue washed with hot benzene (2 x 10ml). Normal work-up, followed by distillation or recrystallisation was used to isolate the pure product.

In conclusion, cyclic acetals/dithioacetals and 2,4-benzodioxepines can be best prepared by the use of a heterogeneous catalyst described here and in view of the mild conditions employed and the simple work-up procedure, this method should find applications both on industrial and laboratory scales.

Entry	Substrate	Yield <sup>a</sup> (%) Ketal <sup>b,c</sup>	Yield <sup>a</sup> (%) Thioketal <sup>b,c</sup>		
1	Cyclopentanone	98	98		
2	Cyclohexanone	98	96		
3	2-Octanone	83	96		
4	2-Methylcyclohexanone	96	91		
5	4-Methylcyclohexanone	98	93		
6	Acetophenone	98 <sup>d</sup>	97 <sup>d</sup>		
7	Benzaldehyde	98 <sup>d</sup>	93 <sup>d</sup>		
8	p-Nitrobenzaldehyde	96 <sup>d</sup>	97 <sup>d</sup>		

### Table 1. Sulfonated Charcoal Catalysed Preparation of Cyclic Acetals/Dithioacetals

a) Yield of isolated products; b) Products characterised by physical and spectral data; c) The purity of the product ( $\geq 99\%$ ) was confirmed by G.L.C. analysis using a fused silica - BP<sub>1</sub> type column (12m x 0.32mm) on Shimadzu GC-RIA chromatograph; d) Reaction required ca 40 h of reflux.

Entry	Substrate	Substr <sup>a</sup> ratio	Yield <sup>b</sup> (%) Benzodioxepine <sup>C</sup>	m.p.[°C] <sup>d</sup> found	reported
	Cualonantanana	1.5	02	70.71	
2	Cyclohexanone	1.3	93 98	84-85	72-73 86-87
3	Butanal	2.0	98 <sup>°</sup>	31-33	33-34
4	2-Pentanone	2.0	88 <sup>e</sup>	Oil <sup>f</sup>	-
5	3-Pentanone	2.0	91	77-78	79-80
6	2-Butanone	2.0	92	35-37	37-38
7	2-Octanone	1.0	88	$\mathbf{Oil}^{\mathbf{f}}$	-
8	2-Methylcyclohexanone	1.2	95	88-90	90-91
9	4-Methylcyclohexanone	1.2	98	94-96	96-98
10	Benzaldehyde	1.0	94	80-82	-
11	4-Nitrobenzaldehyde	1.0	83	188-190	-

Table	2.	Sulfonated	Charcoal	Cataly	sed Pres	paration o	of 2.	4-Benz	odioxe	oines	(3)

a) (Carbonyl compound)/(1); b) Yield of isolated product characterized by physical and spectral data; c) See Table 1; d) Uncorrected; e) The reported  $^{13}$  yields for entry 3 and 4 were 20% and 15% respectively when p-toluenesulfonic acid was employed as the catalyst; f) Solidified at O<sup>o</sup>C.

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- 16. After 2 h reaction time in one experiment, the catlyst was filtered off and reflux continued under the azeotropic conditions for 20 h. No more product formation took place during this time but the reaction proceeded to completion after adding fresh catalyst.
- 17. Use of untreated charcoal under similar conditions showed no product formation.

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