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# Bismuth Compounds in Organic Synthesis. Synthesis of Resorcinarenes using Bismuth Triflate

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## Bismuth compounds in organic synthesis. Synthesis of resorcinarenes using bismuth triflate.

Katherine E. Peterson, Russell C. Smith and Ram S. Mohan

**Abstract**—Bismuth triflate (5 mol%) smoothly catalyzes the condensation of aromatic and aliphatic aldehydes with resorcinol to give tetrameric cyclic products, resorcinarenes. With benzaldehyde, the product is obtained as a mixture of two diastereomers and the ratio of the diastereomers depends on reaction time. On the other hand, a single diastereomer is obtained with aliphatic aldehydes. The low toxicity and ease of handling of bismuth compounds coupled with fast reaction times make this method an attractive alternative to the existing methods for resorcinarene formation.

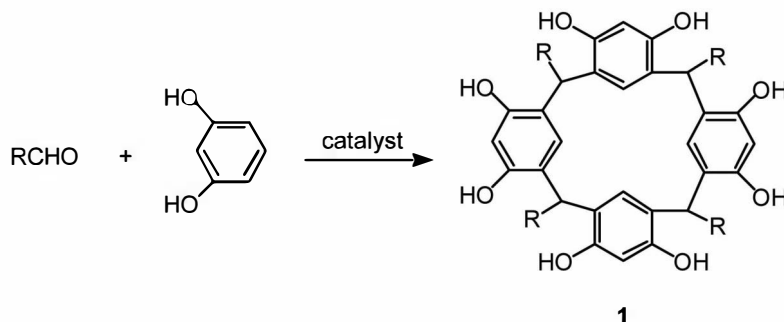
**Keywords:** bismuth and compounds; resorcinarenes; Lewis acids; environment- friendly catalysts.

As early as 1872, von Baeyer discovered that the condensation of benzaldehyde and resorcinol in the presence of concentrated sulfuric acid gave a red-colored product (Scheme 1).<sup>1</sup> It was not until 1968 that Erdtman established the structure of such condensation products by X-ray analysis.<sup>2</sup>

Recently, the name resorcinarenes has been suggested for such compounds.<sup>3</sup> Resorcinarenes are of considerable interest because (1) they serve as starting materials for a variety of cavitands or compounds that contain a cavity that can accommodate other ions or molecules<sup>4</sup> and (2) with appropriate choice of the R groups on the resorcinarene, they exhibit liquid crystalline behavior.<sup>5</sup> They

have also found application as HPLC stationary phases.<sup>6</sup> They can be prepared by acid-catalyzed condensation of an aldehyde with resorcinol.<sup>7</sup> More recently, a Lewis acid, Yb(OTf)<sub>3</sub>, catalyzed condensation reaction between aldehydes and resorcinol has been reported.<sup>8</sup> A solvent-free synthesis of resorcinarenes using *p*-TsOH as the catalyst has also been reported.<sup>9</sup> A drawback of these procedures is that they suffer from either the use of large quantities of concentrated HCl, use toxic catalysts such as *p*-TsOH or require long reaction times, such as with Yb(OTf)<sub>3</sub> (48 h).

Our continued interest in bismuth compounds prompted us to investigate the utility of bismuth triflate



Scheme 1.

as a catalyst for the formation of resorcinarenes. Bismuth compounds have recently attracted attention due to their low cost, ease of handling and remarkably low toxicity.<sup>10,11</sup> We now report that bismuth triflate,  $\text{Bi}(\text{CF}_3\text{SO}_3)_3 \cdot 4\text{H}_2\text{O}$  (5.0 mol%) is an efficient catalyst for the synthesis of resorcinarenes. Bismuth triflate has previously been used as a catalyst for Friedel–Crafts acylations,<sup>12</sup> sulfonylation of arenes,<sup>13</sup> Diels–Alder reactions,<sup>14</sup> aza–Diels–Alder reactions,<sup>15</sup> rearrangement of epoxides,<sup>16</sup> formation of acylals,<sup>17</sup> deprotection and formation of acetals.<sup>18,19</sup> Bismuth triflate is not commercially available but can be easily synthesized in the lab.<sup>20</sup>

Herein we report that the bismuth triflate (5 mol%) catalyzed condensation of aldehydes and resorcinol proceeds smoothly in ethanol to give the corresponding resorcinarenes in good yields (Scheme 2). The condensation of benzaldehyde with resorcinol required only 75 min for completion (as judged by disappearance of starting materials by TLC) while aliphatic aldehydes reacted in few hours to a day. With benzaldehyde, the product was obtained as a mixture of diastereomers **2a** (all-*cis*) and **2b** (*cis*–*trans*–*trans*) (**2a**:**2b** = 0.78:1.0) while aliphatic aldehydes gave only the thermodynamically favored all-*cis* diastereomer **2a**. The tetrameric nature of the products was confirmed by FAB mass spectrometry analysis and the ratio of the diastereomers was determined by  $^1\text{H}$  NMR analysis of the products in  $d^6$ -DMSO.<sup>21</sup> The absolute configuration of the two isomers has been previously determined by X-ray analysis of the corresponding octabutyrate and the NMR spectra observed by us is consistent with that reported in the literature.<sup>22</sup>

Previous studies have shown that the ratio of the diastereomers depends on reaction time suggesting that isomerization via ring opening of the tetrameric product occurs.<sup>8</sup> In light of this observation, the reac-

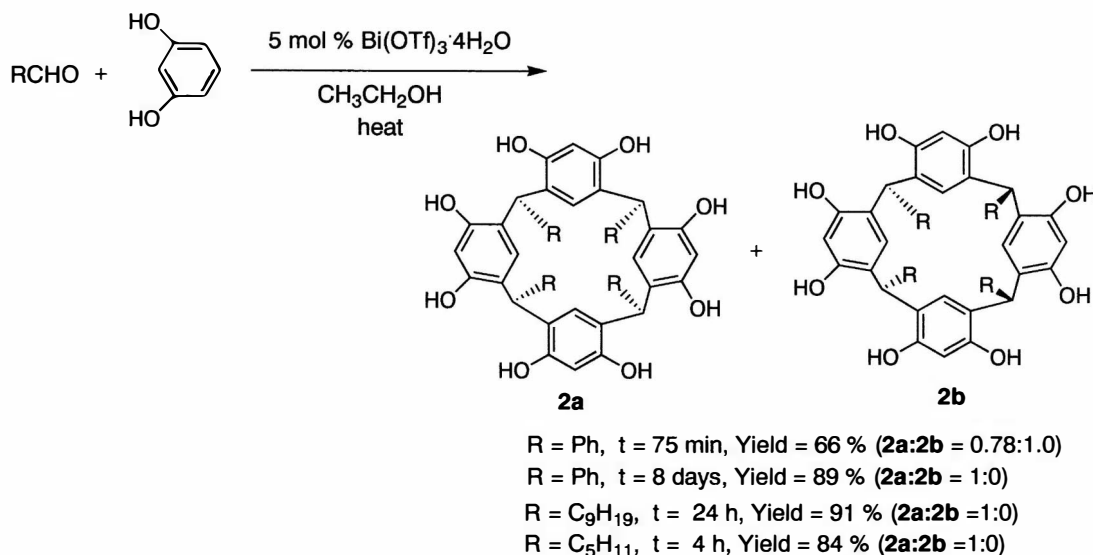
tion between benzaldehyde and resorcinol catalyzed by bismuth triflate was allowed to proceed for 8 days. The product of this reaction was the all *cis* diastereomer **2a**. None of the other isomer **2b** could be detected by NMR spectroscopy. The diastereomeric mixture of **2a**/**2b**, isolated from the 75 min reaction was also subjected to the reaction conditions (5 mol% bismuth triflate, ethanol, 80°C) for 10 days. The resulting product mixture consisted primarily of the *cis*-isomer **2a** (**2a**:**2b** = 1.0:0.11). A systematic study of the bismuth triflate catalyzed reaction of a variety of aldehydes with various substituted resorcinols is now underway.

*A representative procedure is given here:* A solution of resorcinol (2.095 g, 19.03 mmol) and benzaldehyde (2.019 g, 19.03 mmol) in 35 mL of absolute ethanol was stirred as bismuth triflate (0.624 g, 5 mol%) was added. The reaction was then heated in an oil bath at 80°C for 75 min under  $\text{N}_2$ , cooled and poured onto 80 mL of ice-cold water. The resulting precipitate was collected by suction filtration, washed with water and dried at 90°C under vacuum to yield 2.50 g (66%) of a tan colored solid that was characterized by NMR spectroscopy and FAB-MS analysis.

In conclusion, bismuth triflate smoothly catalyzes the condensation of aldehydes with resorcinol. The advantages of this method include fast reaction times and the use of a relatively non-toxic and easy to handle catalyst.

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Scheme 2.

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