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LETTERS

# Rhodium carbenoid mediated cyclisation of $\alpha$ -diazo- $\beta$ -keto- $\delta$ -hydroxy-phenylsulfones

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## Abstract

The title reaction gave rise to 2-phenylsulfonyl-3-oxo-tetrahydrofurans in satisfactory yields providing an entry to some furan derivatives. © 2000 Published by Elsevier Science Ltd.

*Keywords:* carbenoids; diazo compounds; furans; insertion reactions; sulfones.

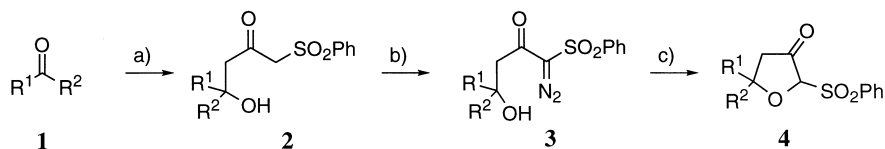
Some years ago, Moody and co-workers prepared a 2-phenylsulfonyloxepan-3-one from the Rh(II)-catalyzed cyclisation of a sulfonyl diazo precursor.<sup>1</sup> To our knowledge this is the only reported example of a carbenoid mediated intramolecular insertion reaction of a hydroxy diazoketosulfone.<sup>2,3</sup> As part of our continuing interest in the chemistry of diazo compounds,<sup>4</sup> and considering the importance of five-membered oxygen heterocycles, we recently decided to examine if the same methodology could be applied to the preparation of furanic derivatives. We report in this note our preliminary results.

The required hydroxy-ketosulfones **2** were prepared by condensation of the dilithium salt of phenylsulfonylacetone and carbonyl compounds **1** (Scheme 1).<sup>5</sup> Compounds **2a–d** were then converted into the corresponding diazo compounds **3** by diazo transfer reaction using tosyl azide.<sup>6</sup>

When a methylene chloride solution of compounds **3** was stirred at room temperature in the presence of a catalytic amount of Rh<sub>2</sub>(OAc)<sub>4</sub> the expected cyclisation reaction occurred to give the tetrahydrofurans **4** in fairly good yields after silica gel chromatography.<sup>7,8</sup> Except for *gem*-dimethyl derivative **4d**, in each case the ketofurans **4** were obtained as a mixture of diastereomers.

To obtain more elaborated compounds we then turned to an alternative route for the preparation of  $\beta$ -keto- $\delta$ -hydroxy-sulfones using the Claisen condensation between the dilithio-anion of methylphenylsulfone and  $\beta$ -hydroxy esters.<sup>9</sup> These conditions were first applied to the optically active ester **5a**, prepared in 43% yield by the baker's yeast asymmetric reduction of

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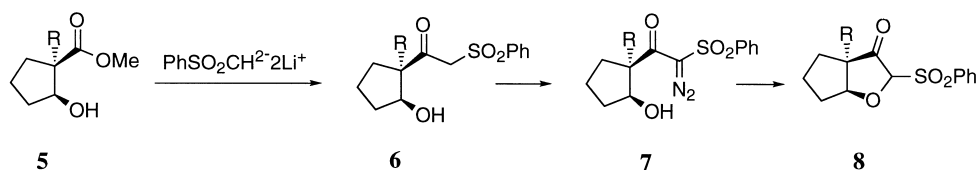


	R <sup>1</sup>	R <sup>2</sup>	2	3	4
<b>a</b>	H	CH <sub>3</sub>	75%	84%	60% (70/30)*
<b>b</b>	H	C <sub>3</sub> H <sub>7</sub>	77%	83%	56% (70/30)
<b>c</b>	H	C <sub>6</sub> H <sub>5</sub>	83%	84%	70% (75/25)
<b>d</b>	H	CH <sub>3</sub>	74%	73%	75%

\* stereomeric ratio (<sup>1</sup>H NMR)

Scheme 1. (a) CH<sub>3</sub>COCH<sub>2</sub>SO<sub>2</sub>Ph, 2 equiv. LDA, THF. (b) TsN<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, MeCN. (c) Rh<sub>2</sub>OAc<sub>4</sub> cat., CH<sub>2</sub>Cl<sub>2</sub>

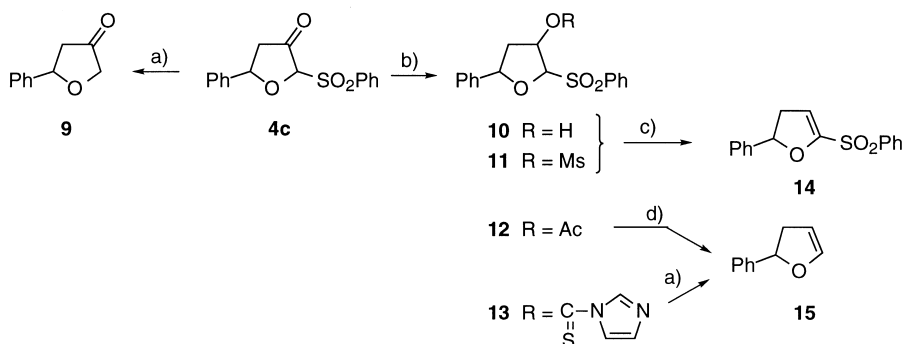
methyl 2-oxocyclopentanecarboxylate according to the Kometani et al. procedure<sup>10</sup> using glucose as an energy source (Scheme 2). We thus obtained a mixture of expected ketosulfone **6a** and of its C-1 epimer in 64% yield. Careful column chromatography of this mixture allowed us to isolate pure **6a** in 40% yield. Under the same conditions, **5b**, prepared in 83% yield by alkylation of **5a**,<sup>11</sup> led to **6b** (71%). Compounds **6** were then transformed as previously into the corresponding diazo compounds **7** which were submitted to cyclisation conditions<sup>12</sup> to give **8a** and **8b** in satisfactory yields.



	R	6	7	8
<b>a</b>	H	40%	65%	74% (95/5)
<b>b</b>	CH <sub>3</sub>	71%	69%	66% (90/10)

Scheme 2.

We then explored some synthetic potentialities of the 3-oxo-tetrahydrofurans **4** (Scheme 3).<sup>13</sup> Reductive desulfonylation<sup>14</sup> of **4c** in free radical conditions (Bu<sub>3</sub>SnH, AIBN)<sup>15</sup> gave known 5-phenyl-3-oxo-tetrahydrofuran **9**<sup>16</sup> in 80% yield. Sodium borohydride reduction of **4c** led to the alcohol **10** (73%) as a mixture (80:20) of two diastereomers.<sup>17</sup> When the mesylate **11** prepared from **10** was submitted to the action of potassium *tert*-butoxide it gave 5-phenyl-2-phenylsulfonyl-3,4-dihydrofuran **14** in 88% yield. We then examined the possibility to convert **10** into the dihydrofuran **15**. For this purpose **10** was first converted into the acetate **12** which was submitted to the SmI<sub>2</sub> mediated<sup>18</sup> reductive elimination conditions of β-acetoxysulfones to give **15** in 46% yield. This compound was obtained in a slightly higher yield (52%) by submitting the thioester **13**, obtained quantitatively from **10**, to radical generating conditions.<sup>19,20</sup>



Scheme 3. (a)  $\text{Bu}_3\text{SnH}$ , AIBN cat.,  $\text{PhCH}_3$ ,  $\Delta$ . (b)  $\text{NaBH}_4$ , EtOH. (c)  $t\text{-BuOK/THF}$ . (d)  $\text{SmI}_2/\text{HMPA}$ , THF

In conclusion we report in this note that the  $\text{Rh}_2(\text{OAc})_4$  catalysed intramolecular insertion reaction of  $\alpha$ -diazo- $\beta$ -keto- $\delta$ -hydroxy-phenylsulfones proceeds in satisfactory yields providing an entry to some furan derivatives. Since starting materials can be prepared in two steps from easily obtained non racemic  $\beta$ -hydroxy esters the methodology should allow optically active compounds to be readily prepared.

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- All new compounds gave spectral and analytical data in full agreement with proposed structures.
- To test the feasibility of the insertion reaction we selected the more commonly used rhodium(II) acetate as the catalyst. We did not yet try to improve the yield by using other rhodium(II) derivatives or reaction conditions.
- Typical procedure: to a solution of **3c** (2.0 g, 6 mmole) in  $\text{CH}_2\text{Cl}_2$  (50 mL; freshly distilled from  $\text{P}_2\text{O}_5$ ) was added, under  $\text{N}_2$  atmosphere, rhodium(II) acetate (15 mg, 0.5 mol%). The reaction mixture was stirred at room temperature for 4 h until disappearance (TLC; pentane:AcOEt, 70:30) of starting material. After evaporation of the solvent the crude product was chromatographed on silica gel ( $\text{CH}_2\text{Cl}_2$ ) to give **4c** (1.30 g, 70%) as a solid (mixture of diastereomers). IR ( $\text{CCl}_4$ ):  $1770\text{ cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ): major isomer  $\delta$  7.99–7.31 (m, 10H); 5.93 (dd, 1H,  $J=7.0$ ,  $J=9.2$ ); 5.08 (s, 1H); 3.18 (dd, 1H,  $J=7.0$ ,  $J=18.7$ ); 2.64 (dd, 1H,  $J=9.2$ ,  $J=18.7$ ). Minor isomer  $\delta$  7.99–7.31 (m, 10H); 5.30 (dd, 1H,  $J=6.4$ ,  $J=10.9$ ); 4.95 (s, 1H); 2.97 (dd, 1H,  $J=6.4$ ,  $J=17.7$ ); 2.79 (dd, 1H,  $J=10.9$ ,  $J=17.7$ ).  $^{13}\text{C NMR}$ : major isomer  $\delta$  203.1; 139.0; 136.7; 134.8; 129.5; 128.9; 126.1; 93.0; 80.7; 44.2. Minor isomer  $\delta$  202.3; 138.8; 136.5; 134.8; 129.8; 129.5; 129.3; 129.1; 126.8; 92.4; 80.1; 44.7. Anal. calcd for  $\text{C}_{16}\text{H}_{14}\text{O}_4\text{S}$ : C, 63.56; H, 4.67. Found: C, 64.10; H, 4.70.
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12. In the case of **7b** the reaction mixture was refluxed for 1 h.
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17. The reduction of the mixture of the two diastereomers of **4c** led to only two diastereomers of **10**, among four possible. This result is in accordance with the well documented high *cis* diastereoselectivity of sodium borohydride reduction of  $\beta$ -ketosulfones. Since it was quite unlikely that the success of the chemistry planned to transform **10** into dihydrofuran derivatives, would significantly depend on the *cis* or *trans* relationship between the hydroxy-phenylsulfonyl moiety and the phenyl group, at this stage of our work we did not try to assign the stereochemistry of the major and of the minor diastereomer. We further used the former compound obtained in larger amount.
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