THE DIELS-ALDER REACTION OF PHENYL SULFONYLACETYLENE AND FURAN DERIVATIVES. NORMAL VS. TANDEM 'PINCER' REACTIONS

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Abstract- The Diels-Alder reaction between some furan derivatives and phenylsulfonylacetylene has been studied along the normal and 'pincer' pathways. The ring opening of some of the resulting products has been also examined.

The ring opening of 7-oxanorbornenic derivatives constitutes a key step in the synthetic use of these compounds (Diels-Alder adduct of furan). On the other hand, we have considered that phenylsulfonyl functionality has been proved to be an interesting auxiliary in order to achieve the ring opening of 7-oxanorbornene system via base-induced, strain-directed $S_N2'$ reaction or Michael addition followed by $\beta$-elimination reaction. On these basis, the use of phenylsulfonylacetylene (I) as dienophile component in the reaction with furan derivatives appears to be an interesting possibility.

In this communication, we aim to lay out account of the behaviour of 1 in the Diels-Alder reaction with some furan derivatives and also of the application of our ring opening methodology to the resulting adducts. Furthermore, to the best of our knowledge, there is no precedent in the literature for the use of this dienophile in Diels-Alder reactions of furan.

The reaction of furan (2) with 1 affords compounds (3), (4) and (5) (Scheme 1) depending on the reaction conditions (Table 1). It should be pointed out that bis-adducts (4) and (5) are the products resulting of the tandem 'pincer' Diels-Alder reaction. According to these results, single cycloadduct (3) can be obtained selectively using 20 eq. of furan and short reaction times (Table 1, Entry 2). On the other hand, the best conditions in order to synthesize the 'pincer' cycloadducts were found using 600 eq. of furan.

\[
\begin{align*}
\text{PhSO}_2\text{C} &= + \text{C}_4\text{H}_4 \rightarrow \text{C}_8\text{H}_{14} + \text{C}_9\text{H}_{14}\text{O} + \text{C}_{10}\text{H}_{14}\text{O} \\
\text{Scheme 1}
\end{align*}
\]
Table 1

Distribution of products in the reaction between furan and phenylsulfonylacetylene

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ratio 2:1</th>
<th>Solvent</th>
<th>Reaction time (^a)</th>
<th>Isolated yields (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>1</td>
<td>114:1</td>
<td>Furan</td>
<td>3 days</td>
<td>36</td>
</tr>
<tr>
<td>2</td>
<td>20:1</td>
<td>CH(_2)Cl(_2)(^b)</td>
<td>6 days</td>
<td>32(^c)</td>
</tr>
<tr>
<td>3</td>
<td>15:1</td>
<td>CH(_2)Cl(_2)(^d)</td>
<td>4 days</td>
<td>25(^e)</td>
</tr>
<tr>
<td>4</td>
<td>600:1</td>
<td>Furan</td>
<td>17 days</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^a\) The reactions were conducted at room temperature. All compounds were isolated by column chromatography on SiO\(_2\) using hexane:ethyl acetate (5:1) as eluant. \(^b\) Furan was gradually added in small amounts. \(^c\) 45% of 1 was recovered. \(^d\) Furan was added in all at once. \(^e\) 6% of 1 was recovered.

The reaction was also applied to 2-methylfuran (6), 2-hydroxymethylfuran (7) and 2-benzylxoxymethylfuran (8)\(^7\) (Schemes 2 and 3). In the first case (ratio 6:1=8:1, CH\(_2\)Cl\(_2\), rt, 4 days) single adducts (9a) and (9b) were obtained as main products in 28 and 25% isolated yields respectively, together with a 6% of the 'pincer' adduct (10). However, the use of longer reaction times (41 days) and larger amounts of furan (ratio 6:1=38:1) improve the yield of bis adducts. In this case, adduct (10) was obtained in 23% isolated yield, together with an inseparable mixture (41%) of cycloadducts (11) and (12) in ratio 11:12=2:1. Small amounts of single adducts were also recovered (12% of 9a, 11% of 9b) (Scheme 2).

\[ \text{Furan} + \text{PhSO}_2\equiv \rightarrow \text{9a} + \text{9b} + \text{10} + \text{11} + \text{12} \]

Scheme 2

On the other hand, the reaction of furan (7) with 1 (ratio 7:1=8:1, CH\(_2\)Cl\(_2\), rt, 3 days) afforded 'pincer' adducts (13) and (14) as main products (49% overall yield) together with 11% of single adduct (15). For the benzyl derivative (8), the reaction with 1 (ratio 8:1=9:1, CH\(_2\)Cl\(_2\), rt, 6 days) gave the single cycloadduct (16) as major product (30% isolated yield) together with 5% of 'pincer' adduct (17). In this case, 30% of 1 was recovered. In both cases, adducts (18) and (19) were not observed in any reaction conditions. For 8, the 'pincer' adduct related to 14 was also not detected (Scheme 3).
The ring opening reaction of some of these cycloadducts was also separately investigated in different conditions. Compound (5), in desulfonylation conditions (6 % Na-Hg, NaHPO₄, MeOH, -20 °C) afforded compound (20) in 65 % isolated yield (Scheme 4).

In summary, the behaviour of phenylsulfonylacetylene (1) as dienophilic component in the Diels-Alder cycloaddition with furan derivatives has been studied along the normal and 'pincer' pathways. The ring opening of some of these compounds has been also examined in order to explore the synthetic utility of the reaction. Active research in order to delimitate the scope of these reactions are now in progress.

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REFERENCES AND NOTES


5. The structure of all new compounds has been determined by NMR techniques (300 MHz $^1$H and 75 MHz $^{13}$C) using selective decoupling and nOeId experiments. All compounds give satisfactory analytical and spectroscopical data according to the proposed structures. Full details will be published elsewhere.

6. The tandem 'pincer' Diels-Alder reaction consists in "two consecutive Diels-Alder cycloadditions between two dienes and an acetylenic dienophile, which acts as a bis-dienophile". For a recent account on the synthetic use of this process, see: M. Lautens and E. Fillon, *J. Org. Chem.*, 1997, 62, 4418.

7. In the case of furan (21), the reaction with 1 gave 71 % of the Michael adduct (22).

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