Studies on Unstabilized \( \pi \)-Sulfuranes: 
Synthesis of \( \text{trans-1,2-Disubstituted Epoxides} \)
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4-Nitrobenzylidenemethylsulfurane

4-Nitrobenzylidenemethylsulfurane, a semi-stabilized sulfonium ylide has been generated by the attack of methylsulfinyl carbanion in dimethyl sulfoxide and reacted with a series of substituted benzaldehydes, furfural and benzylideneacetophenone to afford \( \text{trans-1,2-disubstituted epoxides} \) in fair to good yields. The structural assignments of the products are based on IR and NMR spectral evidences.

Many routes [1-5] have been devised from time to time to bring about transformation of olefinic as well as carbonyl function [6] into their epoxy derivatives. Two distinct approaches have been utilized for this purpose of which the former involves the controlled oxidation of olefinic systems [7, 8] while latter comprises methylene transfer reaction over carbonyl entities [9]. The former has been proved to be of little worth [7, 8, 10, 11] because of the lower yields of the epoxides possibly due to side reactions. The latter approach, formulated by Corey and Chaykovsky [9] in their attempts to study the reactivity of methylenedimethylsulfurane towards carbonyl compounds was restricted to the synthesis of monosubstituted epoxides i.e. styrene oxides. In the subsequent years, arsnyl ylides have also earned the distinction of being epoxidation reagents as investigated by Trippett and Walker [12]. Unlike preceding method, these ylides, though yielded 1,2-diphenylethylene oxides, failed to offer a generalised method as the formation of epoxides was reported to be controlled by the nature of groups present on the ylidal carbanion as well as on the nature of solvent and base [13]. And it was reported that epoxides could only be formed if ylide carbanion carried electron donating groups otherwise olefins were the exclusive products of the reaction and, therefore, idea of synthesizing 1,2-diphenylethylene oxide containing electron attracting groups could not be realised. Taking the advantage of the fact that the \( \pi \)-sulfuranes were the exclusive epoxidation reagents, it was thought to be of interest to enable the synthesis of nitro containing 1,2-diphenylethylene oxides through the interaction between a new semi-stabilized \( \pi \)-sulfurane, i.e. 4-nitrobenzylidenemethylsulfurane and carbonyl compounds.

Results and Discussion

4-Nitrobenzyl bromide with dimethyl sulfide at room temperature afforded 4-nitrobenzylidemethylsulfonium bromide (1). Solution of 4-nitrobenzylidenemethylsulfurane (2) was prepared successfully by addition of solution of 4-nitrobenzylidemethylsulfonium bromide in dimethylsulfoxide with stirring to a solution of methylsulfinyl carbanion in equimolar amount under \( \text{N}_2 \) at low temperature (0–10 °C in DMSO containing enough THF to prevent freezing) because of the marked thermal instability of 2.

The reaction of 2 with a range of carbonyl compounds (3a–j) were carried out at low temperatures to afford \( \text{trans-1,2-disubstituted epoxides} \) (4a–j) in 50–65% yields (Scheme 1).

\begin{align*}
&\text{4a: } \text{Ar} = \text{C}_6\text{H}_5; R = \text{H} \\
&\text{b: } \text{Ar} = 4\text{-CH}_3 \cdot \text{C}_6\text{H}_4; R = \text{H} \\
&\text{c: } \text{Ar} = 3,4\text{-OCH}_3 \cdot \text{C}_6\text{H}_4; R = \text{H} \\
&\text{d: } \text{Ar} = 4\text{-CH}(\text{CH}_3) \cdot \text{N} \cdot \text{C}_6\text{H}_4; R = \text{H} \\
&\text{e: } \text{Ar} = 3\text{-OC}_2\text{H}_3\cdot4\text{-OH} \cdot \text{C}_6\text{H}_5; R = \text{H} \\
&\text{f: } \text{Ar} = 4\text{-OH} \cdot \text{C}_6\text{H}_5; R = \text{H} \\
&\text{g: } \text{Ar} = 4\text{-CHO} \cdot \text{C}_6\text{H}_4; R = \text{H} \\
&\text{h: } \text{Ar} = 3\text{-NO}_2 \cdot \text{C}_6\text{H}_4; R = \text{H} \\
&\text{i: } \text{Ar} = 2\text{-C}_6\text{H}_4\text{OH}; R = \text{H} \\
&\text{j: } \text{Ar} = \text{C}_6\text{H}_5\text{CH}=\text{CH}; R = \text{C}_6\text{H}_5 \\
\end{align*}

Scheme 1.
The success of the reaction contrasted to the failure to form olefins or cyclopropanes suggested the low potential formation of a sulfur-oxygen bond and high nucleophilicity of the ylidic carbanion. It was found that the electron withdrawing substituents on the carbonyl group facilitated the reaction as is evident from the yields of 4a-j. The trans geometry of the epoxide derivatives (4a-j) was confirmed on the basis of NMR spectra in which the trans coupling constants observed were in the range 2 cps to 4 cps.

All the epoxides (4a-j) synthesized in the present investigations gave satisfactory elemental analysis and all products except 4a [14] were new. The NMR spectra (CDCl₃) in general exhibited epoxy protons in the range of δ 3.0–4.52, aromatic protons at δ 6.45–8.5. In IR spectra (KBr) of the products νNO₂ and νOH were exhibited in the expected range (Table II).

**Experimental**

Melting points were determined on a Gallen Kamp apparatus and are uncorrected. The NMR spectra (CDCl₃) were run on a Varian A-60 spectrometer using tetramethylsilane as an internal standard and are reported in (ppm) values. All products were

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### Table I. Structure and physical properties of trans-1,2-disubstituted epoxides (4a–j).

<table>
<thead>
<tr>
<th>Product</th>
<th>Yield [%]</th>
<th>Recryst. solvent</th>
<th>m.p. [°C]</th>
<th>Elemental analysis [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Found/(Calcd)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>4a</td>
<td>52</td>
<td>Ethanol–ether</td>
<td>126–127*</td>
<td>69.74</td>
</tr>
<tr>
<td>4b</td>
<td>50</td>
<td>Chloroform–benzene</td>
<td>110–112</td>
<td>70.52</td>
</tr>
<tr>
<td>4c</td>
<td>65</td>
<td>Chloroform–benzene</td>
<td>151–152</td>
<td>63.20</td>
</tr>
<tr>
<td>4e</td>
<td>51</td>
<td>Benzene</td>
<td>65–66</td>
<td>63.81</td>
</tr>
<tr>
<td>4f</td>
<td>51</td>
<td>Chloroform–benzene</td>
<td>100–101</td>
<td>65.32</td>
</tr>
<tr>
<td>4g</td>
<td>53</td>
<td>Chloroform–methanol</td>
<td>95–96</td>
<td>66.89</td>
</tr>
<tr>
<td>4h</td>
<td>58</td>
<td>Chloroform–pet. ether</td>
<td>140–141</td>
<td>58.77</td>
</tr>
<tr>
<td>4i</td>
<td>58</td>
<td>Benzene–pet. ether</td>
<td>130–131</td>
<td>62.31</td>
</tr>
<tr>
<td>4j</td>
<td>60</td>
<td>Chloroform–benzene</td>
<td>150–151</td>
<td>76.91</td>
</tr>
</tbody>
</table>

*a Lit. [14] 126 °C.*

The course of the reaction seems to have proceeded via the intermediacy of sulfonium betaine (1), involving displacement by the oxyanion on the carbon carrying the onium group. Secondly the formation of a sulfur-oxygen bond is not sufficient and thus is unable to provide a considerable driving force for a variety of reactions (Scheme 2). The dimethylsulfide group is known to be an excellent leaving group and this factor also may tend to favour epoxide formation from the betaine 1.

With carbonyl compounds (3a–j), 2 led exclusively to epoxides (4a–j). In no case were olefins or cyclopropanes obtained.

![Schema 2](image-url)
Table II. IR and NMR spectral data of trans-1,2-disubstituted epoxides (4a-j).

<table>
<thead>
<tr>
<th>Product</th>
<th>IR data [KBr]</th>
<th>(\nu) [cm(^{-1})]</th>
<th>Spectral data</th>
<th>NMR data (CDCl(_3)) (\delta) ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CH stretching vibrations</td>
<td>C-C asymmetric ring stretching</td>
<td>(\nu)NO(_2)</td>
<td>Aliphatic H</td>
</tr>
<tr>
<td>4a</td>
<td>832</td>
<td>848</td>
<td>1340</td>
<td>-</td>
</tr>
<tr>
<td>4b</td>
<td>820</td>
<td>848</td>
<td>1340</td>
<td>-</td>
</tr>
<tr>
<td>4c</td>
<td>856</td>
<td>860</td>
<td>1350</td>
<td>-</td>
</tr>
<tr>
<td>4d</td>
<td>820</td>
<td>856</td>
<td>1350</td>
<td>-</td>
</tr>
<tr>
<td>4e</td>
<td>820</td>
<td>840</td>
<td>1330</td>
<td>-</td>
</tr>
<tr>
<td>4f</td>
<td>832</td>
<td>848</td>
<td>1340</td>
<td>-</td>
</tr>
</tbody>
</table>

Preparation of 4-nitrobenzylidemethylsulfonium bromide (1)

1 was prepared by mixing 4-nitrobenzylbromide (21.6 g, 0.1 mol) and dimethylsulfide (6.2 g, 0.1 mol) in benzene solution (30.0 ml). After stirring for 12 h at room temperature, the reaction mixture was filtered to give a whitish grey solid (hygroscopic). Repeated washings of the residue with acetone afforded the pure product 1, m.p. 140-141 °C, yield 22 g (92%).

Analysis for \(\text{C}_12\text{H}_{12}\text{BrNO}_2\text{S}\)

Found C 38.80 H 4.32 N 5.10,
Calcd C 38.84 H 4.31 N 5.03.

IR spectra (KBr) \(\nu\) max. 3380 (ArH), 1600 (C=O), 1350 cm\(^{-1}\) (NO\(_2\)).

Preparation of 4-nitrobenzylidenedimethylsulfurane (2)

Sodium hydride (0.58 g of 50% mineral oil dispersion, 12 mmol) was freed of mineral oil by three washings and decantings with petroleum ether (b.p. 40-60 °C) under atmosphere of nitrogen. After the last washing, the system was evacuated to remove the last traces of the petroleum ether. The vacuum was broken by introduction of nitrogen and 100 ml of dimethylsulfoxide (distilled from calcium hydride at 64 °C at 4 mm) was added. An aliquot of this solution was diluted with an equal volume of tetrahydrofuran (distilled from lithium aluminium hydride) and cooled in an ice-salt bath. A solution of 4-nitrobenzylidenedimethylsulfonium bromide in dimethylsulfoxide (800 ml of solvent per mole of salt), equivalent to the sodium hydride, was added portion wise at such a rate that the internal temperature did not exceed 5 °C. After the addition of the salt was complete, the mixture of 2 was stirred an additional minute longer before adding the acceptor.

Preparation of trans-1,2-disubstituted epoxides (4a-j)

A solution of 0.03 mole of 2 and 0.025 mole of substituted benzaldehydes, furfural and benzylideneacetophenone in 20 ml of DMSO was stirred for 1 h at 0 °C. The stirring was continued for 30-60 min at room temperature and then 1 h at 60 °C. The reaction mixture was then diluted with three volumes of water and the product extracted with benzene, washed with water and dried over anhydrous sodium sulfate. Evaporative distillation of the product after column chromatography over neutral alumina yielded the substituted epoxides (4a-j) in 50-65% yields as shown in Table I.

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