2. This scheme reflects the framework of biocatalytic proposals (devoid of absolute configurational considerations) which were presented at the C.I.C.-A.U.G. Conference in Toronto, May, 1970; cf. also T. Keszeg, "Biogenic-Type Synthesis of Terpenes", Progress in Organic Chemistry, Vol. 8, in press.


4. Synthetic routes to 2-b-cyanine, 5,6-epi-2-cyanine, 5,6,7a and 6-2-cyanine 7a-8a have previously been reported.


11. We are grateful to Pritschke, Dodge & Olesick, Inc., New York for generous samples of epoxy alkenes oil and 55-


14. We are grateful to Professor S. Piers of this department for providing us with an authentic sample, g.c. and spectral characteristics of caproptopyr (cf. E. Piers, R.J. Britton, M.J. Kenzie and R.S. Bill, Chem. J. Chem. Soc., 49, 2660 (1974)) and for providing us with spectral data on synthetic ylangocyp carving prior to publication.

Recent publications on the alkylation of benzene and toluene by the WCl₆-O₂H₂AlCl₂ system prompt us to report our observations stressing the difference between the behaviour of this metathesis catalyst and that of a simple Lewis acid such as C₂H₅AlCl₂ for the alkylation of benzene.

C₂H₅AlCl₂ alone is indeed an effective alkylation reagent (A), but it gives a mixture of mono-, di- and higher alkylation products, while the WCl₆-containing catalyst promotes the formation of monosubstituted derivatives (B); on the other hand, a small but definite difference is observed in the distribution of monosubstituted isomers. Moreover, the catalyst is a highly active species: in most cases, the reaction is complete in a matter of seconds.

Interestingly, small amounts of dialkylated products (7%) which could be detected after a few seconds disappeared very rapidly. This prompted us to treat, with the metathesis catalyst in benzene, a mixture of mono- and polyalkylated benzenes (prepared from oct-1-one and benzene with C₂H₅AlCl₂ alone as catalyst): the di- and polyalkylated products disappeared rapidly to form exclusively monosubstituted products (C).

A common feature of these reactions is the subsequent isomerization of the monosubstituted products to give a constant isomeric composition, obtained from oct-1-one as well as from oct-4-one; this behaviour is also illustrated by the conversion, under the same conditions, of 2-phenylhexane into a 60:40 mixture of 2- and 3-phenylhexane.
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Time (minutes)</th>
<th>Monoalkylated Products (x-Phenylcyclohexanes) (%)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Diaalkylated Products (%)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Polyalkylated Products (%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;AlCl&lt;sub&gt;2&lt;/sub&gt; (A)</td>
<td>1-1440</td>
<td>22 18 24</td>
<td>29</td>
<td>7</td>
</tr>
<tr>
<td>WCl&lt;sub&gt;6&lt;/sub&gt;-C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;AlCl&lt;sub&gt;2&lt;/sub&gt; (B)</td>
<td>0.5</td>
<td>31 32 30</td>
<td>7</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>37 29 34</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>10-1440</td>
<td>42 27 31</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>WCl&lt;sub&gt;6&lt;/sub&gt;-C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;AlCl&lt;sub&gt;2&lt;/sub&gt; (C)</td>
<td>0</td>
<td>18 17 20</td>
<td>33</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>21 17 27</td>
<td>25</td>
<td>7</td>
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<tr>
<td></td>
<td>24</td>
<td>29 20 33</td>
<td>16</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>33 24 35</td>
<td>8</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>40 29 31</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>44 30 26</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

<sup>a</sup> Experimental Conditions: Benzene, 2·10<sup>-1</sup> mole; oct-4-ene, 10<sup>-2</sup> mole, WCl<sub>6</sub> 1·5·10<sup>-3</sup> mole; C<sub>2</sub>H<sub>5</sub>AlCl<sub>2</sub>, 6·10<sup>-3</sup> mole; 7 = 25°C.

<sup>b</sup> % of products calculated versus the initial amount of octene, using an internal g.l.c. standard; the different types of alkylation products mentioned in this table account for a quantitative conversion of the initial olefin; the corresponding values were standardized to 100 %.

<sup>c</sup> In this experiment, oct-4-ene was replaced by alkylated products isolated after 24 hrs from former experiment involving oct-4-ene and C<sub>2</sub>H<sub>5</sub>AlCl<sub>2</sub> alone.

**References:**

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**STABLE CYCLIC SULFENOCARBOXYLIC ACID ANHYDRIDES DERIVATIVES OF 1,2-OXATHIOLE-5-ONE**

Curt-Eric Hagberg, Ove Bohman and Carin Engdahl

Institute of Chemistry, University of Uppsala,

P.O. Box 581, S-751 21, Uppsala 1, Sweden

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Previously Field and collaborators<sup>1</sup> have given evidence for the unstable cyclic o-sulfenobenzoic acid anhydride (I), which also has been proposed as an intermediate by D’Sylva<sup>2</sup> and Daniely<sup>3</sup>.

We now wish to report two stable 3-substituted 4-carboxy-1,2-oxathiole-5-ones (IIa,b), whose structures have been determined by spectroscopic data, elemental analysis and by means of chemical reactions.

![Diagram](image-url)

**I**

**II**

The compounds (II) have been prepared by treatment of the corresponding benzylicsulfinylmalonic acids (III)<sup>3</sup> in a mixture of acetic and hydrochloric acid at 45°C. Under these conditions the compounds (III) underwent a benzylic carbon-sulfur bond cleavage according to Scheme 1.

![Scheme](image-url)

**Scheme 1**

The benzylic part was isolated and identified as benzylic chloride, benzylic alcohol and benzylic acetate.

The other part (III) was isolated as white crystalline solids. The product derived from IIa was shown to be the most stable one and could be kept at room temperature for several months. The proposed structures (III) are supported by the following data.

The mass spectrum of IIa gave a M<sup>+</sup>-peak at m/e (rel int) 222(98), M<sup>+</sup>+1 (11.4); M<sup>+</sup>+2 (5.6) and for IIb m/e: M<sup>+</sup> 160(82), M<sup>+</sup>+1 (5.3), M<sup>+</sup>+2 (4.5). IR-spectrum of the crude product IIa shows two strong bands within the carbonyl region at 1786 and 1675.