Homolytic bimolecular displacement at carbon in organocobaloximes: intramolecular cyclizations

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The reactions of hex-5-enyl-, 2-allyloxyethyl- and 5-phenylpent-4-ynyl- cobaloximes with arene sulphonyl chlorides under visible light photolysis at 0°C give the corresponding cyclized products. The results are interpreted in terms of $S_n2'$ mechanism.

The ease with which organometallic compounds participate in free radical reactions is quite remarkable. In particular, the free radical chemistry of sigma bonded organobis(dimethylglyoximato)(pyridine)cobalt(III) complexes, trivially known as organocobaloximes, has been very well documented in the literature. The main feature of all these complexes is the weak Co-C bond, and the homolytic displacement of a paramagnetic cobaloxime(II) species by the attack of a C, S or N centered electrophilic radical on the organic ligand of the organocobaloxime is the key step. The reactions not only provide mild protocols for important organic intermediates but also delineate complex organometallic mechanism involving low spin metal radicals.

In this paper we report the reactions of hex-5-enyl-, 2-allyloxyethyl- and 5-phenylpent-4-ynyl-cobaloximes with arenesulphonyl chloride under visible light photolysis at 0°C.

Materials and Methods

Most of the chemicals were Aldrich reagents and were used as such without any further purification. Melting points were measured on a Fischer John's melting point apparatus and are uncorrected. $^1$H NMR spectra were recorded on 80 and 100 MHz NMR spectrometers. The electronic spectra were recorded on Shimadzu UV 160A spectrophotometer.

The organocobaloximes (1,7,11) (see Scheme 1 and Table 1 for numbering) were synthesized according to the literature procedures. Thiophene-2-sulphonyl chloride was prepared by the chlorosulphonation of thiophene at -15°C [b.p. 90°C/1mm, $^1$H NMR (CCl$_4$): 7.20 (m), 7.93 (m)].

| Table 1—Organic products from the reaction of hex-5-enyl (1), 2-allyloxyethyl (7) and 5-phenylpent-4-ynyl cobaloxime (11) with ArSO$_2$Cl (A1-A6) under photochemical conditions |
|----------------|--------------|----------------|------------------|----------------|
| RCo            | ArSO$_2$Cl  | Prod. No.      | Reaction time (h) | Yield %        |
| (1)            | (A1)        | (2)            | 30               | 39             |
| (A2)           | (3)         | 26             | 31               |
| (A3)           | (4)         | 28             | 75               |
| (A4)           | (5)         | 26             | 61               |
| (A5)           | (6)*        | 26             | 46               |
| (A6)           | (9)         | 22             | 54               |
| (7)            | (A5)        | 20             | 48               |
| (A6)           | (10)        | 22             | 62               |
| (11)           | (A6)        | (12)**         | 22               | 93             |

*A mixture of two isomers (6) and (6') [CH$_2$=CH(CH$_2$)$_4$SO$_2$C$_6$H$_5$Br-4] in the ratio 60:40

** A mixture of two isomers (12) and (12') [PhC=CH$_2$CH$_2$CH$_2$SO$_2$-Th] in the ratio 60:40.
Table 2—Characteristics of organosulphones (2-10)

<table>
<thead>
<tr>
<th>Prod.</th>
<th>CH₂SO₂</th>
<th>Cycloalkyl</th>
<th>Aromatic</th>
<th>Others</th>
<th>UV-VIS (MeOH) λmax (nm)</th>
<th>M.P. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>(2)</td>
<td>3.19</td>
<td>0.94-2.56</td>
<td>7.56,</td>
<td>2.44</td>
<td>219,249,254,257,269</td>
<td>oil</td>
</tr>
<tr>
<td>(3)</td>
<td>3.13</td>
<td>0.94-2.56</td>
<td>7.34,</td>
<td>2.44</td>
<td>224,254,260,265,273</td>
<td>52</td>
</tr>
<tr>
<td>(4)</td>
<td>3.06</td>
<td>0.91-2.44</td>
<td>6.97,</td>
<td>3.88</td>
<td>238,265,275</td>
<td>oil</td>
</tr>
<tr>
<td>(5)</td>
<td>3.14</td>
<td>0.78-2.63</td>
<td>7.48,</td>
<td>7.78</td>
<td>229,245,265,273</td>
<td>oil</td>
</tr>
<tr>
<td>(6)</td>
<td>3.13</td>
<td>0.81-2.53</td>
<td>7.75</td>
<td></td>
<td>233,250,273</td>
<td>66</td>
</tr>
<tr>
<td>(8)</td>
<td>3.06</td>
<td>0.95-2.80</td>
<td>7.63</td>
<td></td>
<td>231,249</td>
<td>oil</td>
</tr>
<tr>
<td>(9)</td>
<td>3.30</td>
<td>0.73-2.70</td>
<td>7.20,</td>
<td>7.70</td>
<td>230,247</td>
<td>oil</td>
</tr>
<tr>
<td>(10)</td>
<td>3.36</td>
<td>3.66-4.05</td>
<td>7.25</td>
<td>7.58</td>
<td>231,249</td>
<td>oil</td>
</tr>
</tbody>
</table>

1°HNMR of (6'), CDCl₃, δ: 3.81-4.20 (m), 2.09, 2.34 (m), 4.87 (s), 5.08 (d), 5.53-6.09 (m), 7.75 (d), UV-VIS (MeOH) λmax (nm) 233, 254, 262, 274, m.p. 111°C.

2°HNMR of (12), CDCl₃, δ: 1.31-2.36 (m, CH₃), 2.50-2.86 (t, CH₃SO₂), 2.93-3.26 (t, CH₂SO₂), 7.00, 7.66 (m, Th), 7.23 (bs, Ph); λmax (nm) (MeOH) 249, 298, m.p. 134°C.

3°HNMR of (1'), CDCl₃, δ: 1.73-2.25 (m, CH₂), 2.56-3.06 (t, CH₂SO₂), 6.85 (m, Th), 7.03-7.50 (m, Ph); λmax (MeOH) (nm) 248, 260, m/z 290 (100), 225 (22), 78 (56.5), m.p. 134°C.

The results are in line with our earlier observations. The amount of work reported on the homolytic substitution at the olefinic carbon center is still small. It is reported in the literature that hex-5-enyl radical, generated by the homolysis of hex-5-enyl cobaloxime, when trapped by radical trapping agents like PhSSPh, PhSeSePh and CCl₄ leads to the formation of both cyclized and uncyclized products. The ratio of the two products is a function of the concentration of the trapping agent. The mechanism is believed to be a unimolecular process. Bipolaric homolytic displacement at carbon, the examples of which are available, has been invoked to explain the formation of 1,1,1-trichloroethylcyclopentane in the reaction of hex-5-enyl cobaloxime with a low concentration of CCl₄ under thermal conditions.

In the present studies, the exclusive formation of cyclopentylmethyl sulphones and the complete absence of the corresponding chloride under the photochemical conditions support the bimolecular displacement process. The variation in concentration and molar ratios (Table 3) does not have remarkable effect except on the reaction time. The exclusive formation of the cyclized product (10) in the reaction of allyloxyethyl cobaloxime (7) with (A6) supports the same viewpoint further. The results are in line with our earlier observations.

Metal mediated intramolecular radical cyclization involving an acetylenic appendage has matured into...
an area of gainful importance leading to the synthesis of complex carbocyclic framework. The formation of the cyclized product (12) in the reaction of (11) with (A6) is novel and supports our previous results. However, the formation of additional uncyclized product (12') suggests that thiophene-2-sulphonyl chloride (A6) has lesser selectivity as compared to the 4-substituted benzenesulphonyl chloride. The latter react with (11) and form exclusively the cyclized products.

The present study, once again, demonstrates the ability of the organocobaloxime complexes to participate as stoichiometric reagents in free radical reactions.

Acknowledgement

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References