Cleavage of Co-C bond in allyl cobaloximes with arenesulphenyl chloride

B D Gupta, Vandana Dixit, Veena Singh & V Vijai Kanth
Department of Chemistry, I.I.T. Kanpur, India 208 016

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Arenesulphenyl chlorides (ArSCI, Ar = Ph, C6H5, 2,4(NO2)2C6H4) are reacted with allylcobaloximes, RCo(dmglH)Py (R = allyl), under thermal and photochemical conditions to obtain the corresponding sulphides as the major organic products. α-Pinanyl cobaloxime forms the ring opened product as well. The homolytic as well as heterolytic cleavage of the Co-C bond is considered.

The ease with which organometallic complexes participate in free radical reactions is quite remarkable. In particular, organobis(dimethylglyoxime)cobalt(III) pyridine complexes, trivially known as organocobaloximes, have been successfully utilized in organic synthesis by many groups. Recently, we have shown that alkyl and arylalkyl sulphides can easily be synthesised using such precursors. Both homolytic as well as heterolytic pathways were considered to explain the results.

In this paper we report the reactions of allyl and substituted allylcobaloximes (1-5) (see Table 1 for numbering) with arenesulphenyl chloride, ArSCI, (Ar = Ph, C6H5, 2,4(NO2)2C6H4) under thermal and photochemical conditions. The choice of the three arenesulphenyl chlorides is made simply because these can react as free radicals and/or as electrophiles depending upon the reaction conditions and the substituent on the aren ring. The present study, therefore, has been undertaken to understand the Co-C bond cleavage process in organocobaloximes.

Material and Methods

Allyl cobaloximes10,19, benzene sulphenyl chloride26 and penta chlorobenzenesulphenyl chloride21,22 were synthesized as described earlier. α-Pinanyl bromide was prepared26 from (1R)-(-)-myrtenol (Aldrich), pyridine and phosphorous tribromide at 0°C (97%, b.p. 70-72 °C/2mm), 1H NMR (CDCl3): 0.80, 1.28 (s, gem Me), 1.09(d), 1.25(m), 1.83-2.62(m) cycloalkyl), 3.82 (s, CH3), 5.60 (bd, vinyl). It is unstable and is used fresh to make α-pinanyl methyl cobaloxime, 1H NMR (CDCl3): 0.72; 1.24 (6H gem Me), 0.80-2.02 (m, 12H cy-alk), 2.12 (s, 12H, dmglH), 2.31 (s, 2H, CH2-Co), 5.40 (s, 1H,=CH), 7.30,7.63,8.61(m, 5H Py). 2,4-Dinitrobenzenesulphenyl chloride, purchased from Aldrich Chemical Company USA, was used as such without any further purification. 1H NMR spectra (see Table 2) were recorded on Jeol JNM-PMX 60 and Varian XL 400 spectrometers. The elemental analysis was done at RSIC, Lucknow. The UV-vis spectra were recorded on a Shimadzu 160A spectrophotometer. Melting points were measured on a Fischer John’s melting point apparatus and are uncorrected.

Reaction of arenesulphenyl chloride with allylcobaloximes: General procedure

1. Reaction of arenesulphenyl chloride with allylcobaloxime

PI condition: All reactions were carried out in a specially designed all-glass apparatus with external cooling system. Organocobaloxime (1mmol) and aren sulphenyl chloride (1 mmol) were added to the deoxygenated dichloromethane (25 ml). The solution was irradiated with 2×200 W tungsten lamps placed 10 cm apart from the reaction vessel, while the temperature was maintained at 0°C with a Julabo refrigerator circulator. The progress of the reaction was monitored for cobaloxime with TLC on silica gel using ethyl acetate as the eluent. On completion of the reaction, the mixture was concentrated in vacuo and was flash chromatographed using dichloromethane as the eluant. Once the organic product had eluted out, the solvent was changed to ethyl acetate when organocobaloxime, if any, was eluted out. Finally, the inorganic cobaloxime was eluted out with acetone. The organic product was further purified on the silica gel column.

TI condition: A procedure similar to that of PI was
Table 1—Organic products and their yield from the reaction of arene sulphenyl chloride with allyl cobaloximes (1-5)

<table>
<thead>
<tr>
<th>RCo III</th>
<th>ArSCl</th>
<th>Reaction condition/ time (min)</th>
<th>Organic product (product no.)</th>
<th>Yield (%)</th>
<th>Isolated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allyl (1)</td>
<td>A</td>
<td>P1/10</td>
<td>PhSCH2CH=CH2 (6)</td>
<td>68</td>
<td></td>
</tr>
<tr>
<td>3-Methylallyl (2)</td>
<td></td>
<td>P1/10</td>
<td>MeCH(SPh)CH=CH2 (7)</td>
<td>72</td>
<td></td>
</tr>
<tr>
<td>3,3-Dimethylallyl (3)</td>
<td></td>
<td>P1/10</td>
<td>Me2C(SPh)CH=CH2 (8)*</td>
<td>82</td>
<td></td>
</tr>
<tr>
<td>3-Phenylallyl (4)</td>
<td></td>
<td>P1/5</td>
<td>PhCH(SPh)CH=CH2 (9)</td>
<td>78</td>
<td></td>
</tr>
<tr>
<td>Allyl (1)</td>
<td>B</td>
<td>P1/20</td>
<td>ClC6H4SCH2CH=CH2 (11)</td>
<td>68</td>
<td></td>
</tr>
<tr>
<td>3-Methylallyl (2)</td>
<td></td>
<td>P1/25</td>
<td>MeCH(ClC6H4S)CH=CH2 (12)</td>
<td>68</td>
<td></td>
</tr>
<tr>
<td>3,3-Dimethylallyl (3)</td>
<td></td>
<td>P1/35</td>
<td>Me2C(ClC6H4S)CH=CH2 (13)*</td>
<td>81</td>
<td>60</td>
</tr>
<tr>
<td>3-Phenylallyl (4)</td>
<td></td>
<td>P1/15</td>
<td>PhCH(ClC6H4S)CH=CH2 (14)</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>Allyl (1)</td>
<td>C</td>
<td>T1/90</td>
<td>(NO2)2C6H5SCH2CH=CH2 (16)*</td>
<td>37</td>
<td>54</td>
</tr>
<tr>
<td>3-Methylallyl (2)</td>
<td></td>
<td>T1/90</td>
<td>MeCH(NO2)2C6H5SCH=CH2 (17)*</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>3,3-Dimethylallyl (3)</td>
<td></td>
<td>T1/180</td>
<td>Me2C(NO2)2C6H5SCH=CH2 (18)*</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td>3-Phenylallyl (4)</td>
<td></td>
<td>T1/240</td>
<td>PhCH(NO2)2C6H5SCH=CH2 (19)*</td>
<td>32</td>
<td></td>
</tr>
</tbody>
</table>

# The reaction with PhSBr is very slow and forms (8) and (8') in 1:1 ratio (see Materials and Methods).
* In addition, a side product, O-allyl derivative of dimethylglyoxime, is also formed in each case.
+ The same reaction under irradiation by a 400W mercury lamp forms (13) and (13'), MeC=C-CH3SCCI5 in 9:1 ratio. The lamp emits radiation predominantly at 365-366 nm, with smaller amounts in the UV region at 297, 303, 313 and 334 nm, as well as significant amount in the visible region at 404-408, 436, 546 and 577-579 nm.

followed except that the reaction mixture was heated at around 70°C under diffused light. The work-up procedure was similar to that in P1 condition.

Reactions of benzene sulphenyl bromide with 3,3-dimethylallyl cobaloxime: An equimolar mixture of (3) and PhSBr in benzene-dichloromethane (1:1) was heated at 55°C for 24 h. On work-up, it afforded a 1:1 mixture of 3-methylbut-2-enyl sulphide (8') and 1,1-dimethylallylphenyl sulphone (8) as characterized by NMR.

Results and Discussion

Pentachlorobenzensulphenyl chloride (B) reacts with 3-methylallylcobaloxime (2) in 1:1 molar ratio under anaerobic and photochemical conditions (P1 conditions, see Materials and Methods). A smooth reaction occurred and was complete within 25 min to give the corresponding sulphide (12) in 68% yield. The thermal reaction was very slow and afforded lower yields. The similar observations were made in the reaction of (A) or (B) with other allylcobaloximes (1-4). However, the reaction of (C) with allylcobaloximes required high temperature and the yields of the organic sulphides were consistently lower in each case. In addition, a side product, o-allyl derivative of dimethylglyoxime was also formed in each case. The photochemical reaction, on the other hand, gave a mixture of products that could not be characterized. The reaction of cyclohexylmethyl cobaloxime with (A), (B) or (C) afforded a complicated mixture of products that could not be characterized.

o-Pinanyl cobaloxime (5) is very reactive under P1 conditions, for example, the reaction of (5) with (A), (B) or (C) is complete within 5 min. In fact, the addi-
Table 2—Characteristics of allyl aryl sulphides (6-20)\# 

<table>
<thead>
<tr>
<th>Product No.</th>
<th>M.P. (°C)</th>
<th>(^1)H NMR chemical shifts, (\delta), (ppm), multiplicity, (J)= Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>(6)</td>
<td>liq</td>
<td>H1: 3.4 (d) [6], H2: 5.4-5.98 (m), H3: 4.78-5.12 (m), Aromatic: 7.0-7.20 (m)</td>
</tr>
<tr>
<td>(7)</td>
<td>liq</td>
<td>H1: 3.5 (m), H2: 5.3-5.90 (m), H3: 4.51-4.90 (bm), Aromatic: 7.0-7.20 (m)</td>
</tr>
<tr>
<td>(8)</td>
<td>liq</td>
<td>H1: 3.5 (d), H2: 5.34 (m)</td>
</tr>
<tr>
<td>(8')</td>
<td>liq</td>
<td>H1: 5.86-6.04 (m), H2: 4.2-5.08 (m), H3: 4.20-5.08 (m), Aromatic: 7.20-7.30 (m)</td>
</tr>
<tr>
<td>(9)</td>
<td>liq</td>
<td>H1: 3.5 (m), H2: 5.3-5.90 (m), H3: 4.51-4.90 (bm), Aromatic: 7.20-7.30 (m)</td>
</tr>
<tr>
<td>(10)</td>
<td>65</td>
<td>H1: 3.5 (d), H2: 5.4-5.97 (m), H3: 4.76-5.01 (m), Aromatic: 7.20-7.30 (m)</td>
</tr>
<tr>
<td>(12)</td>
<td>69</td>
<td>H1: 3.5 (m), H2: 5.3-5.97 (m), H3: 4.51-4.88 (m), Aromatic: 7.20-7.30 (m)</td>
</tr>
<tr>
<td>(13)</td>
<td>54</td>
<td>H1: 3.5 (d), H2: 5.34 (m)</td>
</tr>
<tr>
<td>(13')</td>
<td>54</td>
<td>H1: 3.48 (d), H2: 5.20 (t)</td>
</tr>
<tr>
<td>(14)</td>
<td>85</td>
<td>H1: 5.94-6.4 (bm), H2: 4.18-5.16 (m), H3: 4.18-5.16 (m), Aromatic: 7.30-7.40 (m)</td>
</tr>
</tbody>
</table>

\# All compounds give satisfactory element (C, H and S) analysis. The UV-vis [CH\(_2\)CN] for compounds (6-9) has a characteristic \(\lambda_{max}\) value of 240-244 with a shoulder at 310 nm and for compounds (11-14), the characteristic \(\lambda_{max}\) value is 216-218 with a shoulder at 253 nm.

* The values of compounds (16-19) match with the reported ones[16]. Some of the \(^1\)H NMR values do not follow the above tabulated form and hence these are given below:

(10): 0.80 (s), 1.26 (s), [CH\(_2\)]\(_2\), 1.8-2.3 (bm) [cycloalkyl], 3.4 (s) [CH\(_3\)], 5.4 (bs) [=CH], 7.0-7.20 (m)[Ar]
(10'): 1.6 (s) [Me], 1.8-2.3 (bm) [cycloalkyl], 3.36 (s) [CH\(_3\)], 4.56 (s) [=CH\(_2\)], 5.4 (bs) [=CH]
(15): 1.6 (s) [Me], 1.78-2.3 (bm) [cycloalkyl], 3.36 (s) [CH\(_3\)], 4.50 (s) [=CH\(_2\)], 5.17 (bs) [=CH]
(20): 0.7 (s), 1.26 (s) [CH\(_2\)]\(_2\), 1.8-2.3 (bm) [cycloalkyl], 4.8-4.93 (dd) [=CH\(_2\)], 4.3 (t) [allylic H], 7.4 (s), 7.66 (s) 8.06 (d), 8.20 (d) [Ar]

Time seems to be the reaction time. The reaction with (A) affords the corresponding sulphide (10) which during the purification over silica gel rearranges to the ring opened product having limonene structure (10'). A slow addition of PhSCI to (5) over a period of 90 min gives a mixture of (10) and (10'). The same observation is made with (B). However, with (C), it forms a stable sulphide (20) that does not rearrange to the ring opened product.

The following independent reactions characterize the reaction further.

(i) No allyl chloride or allyl derivative of dimethylglyoxime is formed in any of the reactions of allylcaloxime with (A) or (B). However, with (C), allyl derivatives of dimethylglyoxime is formed in each reaction.

(ii) A small amount of diaryl disulphide is formed in many reactions. However, its further reaction with the allylcaloximes is very slow. For example, a reaction of diphenyldisulphide with allylcaloxime (1) under refluxing conditions remains incomplete even after 10 hr.

(iii) The reaction of (3) with (B) under P2 conditions forms (13) and (13') in the ratio 9:1 (see footnote, Table 1).

Since the isomerization of (13) to (13') is well known to occur in the presence of ArS radicals under thermal conditions, a few more observations are made from independent experiments

(a) The \(\gamma\) product, once formed, is quite stable and does not isomerize to the \(\alpha\) isomer, for example, a pure sample of (13) is stable up to 10 days when kept...
at room temperature under diffused light. No isomerization is observed.

(b) Though the reaction of (2) with (A) under P1 is complete within 10 min, yet even if the reaction mixture is kept under these conditions for 4h, γ product (7) is the only product isolated. This indicates that once (7) is formed, it does not isomerise to α isomer although the reaction mixture has excess PhSCI and cobaloxime (II) in solution.

(c) A mixture of 3-methylallyl cobaloxime (2) and (A) in the ratio 1:2 under P1 conditions affords MeCH(SPh)CH=CH₂ (7) after 2 hr (NMR inference). This solution is heated to 35°C under irradiation for 12h, chloroform is added and the solution is further heated at 70°C for 10h. Only (7) is observed in solution. No rearrangement of any kind is noticed.

(d) A reaction mixture (obtained after the ether work-up of the reaction of (3) with (B) under (P2) containing [13, 13′ (9:1)] and a trace of (C₆Cl₃S)₂ was kept at room temperature under diffused light. The subsequent ¹H NMR spectra showed that the amount of (13′) started increasing after 10d and became predominant after 30d. No further change occurred after this (see Fig. 1).

It is well established that the Co-C bond in organocobaloximes is cleaved by both homolytic as well as heterolytic pathways depending upon the nature of R, the reaction conditions and the substrate with which it reacts. The complications, however, arise because of the possibility of a variety of reaction sites in the organometallic substrate, for example, allylcobaloxime may react with ArSCI in a number of ways (i) free radical addition at the double bond followed by Co-C bond cleavage, (ii) cleavage of Co-C bond and subsequent reactions of allyl radicals, (iii) S₂2 and S₈2′ reactions at the carbon center displacing Co (II), (iv) electrophilic attack of sulphur on the carbon center of RCo(III) with synchronous or subsequent loss of Co (III) and (v) electron transfer from RCo(III) to sulphur followed by decomposition of the intermediate RCo (IV) species. In order to check the nature and mechanism of the cleavage of the Co-C bond, the reactions were carried out under thermal and photolytic conditions.

From the regiospecific nature of products and the free radical nature of these reactions a direct S₈2′ attack of SA₄ at the γ carbon of the allyl cobaloxime (reaction pathway iii) seems to be the most prominent process for reactions with (A) or (B). We believe that the mechanism is similar to the one proposed by us earlier for the reaction of same substrates with arene sulfonyl chloride. However, with (C) the following mechanism, proposed earlier by Johnson et al., seems to operate. It is thought to involve the addition of the electrophile to the double bond to form the electron deficient intermediate like E (which may be written as the corresponding episulphonium ion) followed by heterolytic cleavage of Co-C bond.

\[
\text{CH}_2=\text{CHCH}_2\text{Co (III)} + \text{ArSCI} \rightarrow \text{Co (III)} \text{Co}=\text{Co(dmgH)₃Py}
\]

These reactions parallel the corresponding reactions of allyl tributyl tin compounds with arene sulphonyl chlorides.

The major side reaction with (C) is the formation
of O-allyl derivatives of dimethylglyoxime (RDmgH). Such products have been encountered earlier in the reactions of allylcobaloximes with electrophiles, electrophilic free radicals and oxidising agents.\textsuperscript{3,9,13-15} The mechanism of their formation has already been described.

The formation of (13') in the reaction of (3) with (B) may arise either by a direct Sq2 attack of ArS radical at the \(\alpha\)-carbon of the allyl group or by a rearrangement of the less stable isomer (13) under the reaction conditions as such isomerizations are well known to occur. We have no conclusive evidence to distinguish between the two; however the experimental details do suggest that the isomerization is very slow under the reaction conditions. (13') can also be formed by the reaction of diaryl disulphide, formed as a side product, with (13) but we have ruled out this possibility since such reactions are slow indeed.

The formation of ring opened products in the reaction (A) and (B) with \(\alpha\)-pinenylmethyl cobaloxime is interesting and needs further investigation. Similar ring opened products are known to form in the free radical addition reactions of \(\alpha\)-pinene\textsuperscript{24}. The absence of such ring opened products in (C) further suggests that its mechanism is different with that of (A) or (B). It seems likely that the nitro group present in the \textit{ortho} position in (C) enhances the ionic nature of the sulphonyl sulphur\textsuperscript{25} and therefore changes the reactivity pattern.

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**References**


