A NEW REARRANGEMENT REACTION OF 1-CHLORO-2-HYDROXYALKYL PHENYL SULFOXIDES

Isao Kuwajima and Yutaka Fukuda

Aoyama Gakuin University, Chitosedai, Setagaya-ku, Tokyo (Received in Japan 2 December 1972; received in UK for publication 2 January 1973)

We have recently reported that treatment of the %-hydroxyaldehyde diphenylmercaptals (I) with methyl- or n-butyllithium leads to the formation of the corresponding phenylthiomethyl ketone in high yield. This reaction is considered to proceed through an initial formation of the dilithiated intermediate (II), which decomposes into the corresponding enolate anion of the phenylthiomethyl ketone (III) via removal of phenylthiclate anion followed by rearrangement of hydride ion to the neighboring carbon atom as shown in the following scheme.

In the present study, as one of the extension of this type of the rearrangement reaction, we have examined a similar reaction of 1-chloro-2-hydroxy-alkyl phenyl sulfoxide with alkyllithium under the assumption that the corresponding phenylsulfinylmethyl ketone would be formed through a similar decomposition

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of the dilithiated intermediate (IV) followed by the rearrangement reaction. Verification of this hypothesis has been obtained as follows.

Lithiation of chloromethyl phenyl sulfoxide was carried out by the method of Durst² and the solution was treated with n-hexanal at -78° in THF under a nitrogen atmosphere. To the resulting solution was added an equimolar amount of methyllithium in situ and the mixture was kept stirring for 1 hr at 0°, which was shown to yield the corresponding hydrogen rearrangement product, 1-phenyl-sulfinyl-2-heptanone as shown in the following equation. Similarly, n-octanal and n-decanal also gave the corresponding phenylsulfinylmethyl ketone by the same procedure.

All of the products obtained above were confirmed by comparison with the authentic samples prepared by oxidation of the corresponding phenylthiomethyl ketones with hydrogen peroxide in acetic acid. Similar to the case of the rearrangement reaction of V-hydroxyaldehyde diphenylmercaptals, another rearrangement product resulted from alkyl group migration was little observed in any case.

It was also shown that decrease of the formation of (V) was generally observed along with the formation of the chlorine-butyl exchange product when

the similar reaction was attempted by the use of n-butyllithium in place of methyllithium in the above experiment.

On the other hand, it was found that the product, resulted from removal of phenylsulfinyl group of (V), was also formed in some case. For example, when a similar reaction was attempted with benzaldehyde under similar reaction conditions, the formation of acetophenone was observed in 43% yield along with phenylsulfinylacetophenone (36%).

$$c_{6}H_{5}$$
-CH=0 $\xrightarrow{1)} c_{6}H_{5}$ -SO-CHClLi $\xrightarrow{2)} c_{6}H_{5}$ -CO-CH₃ + $c_{6}H_{5}$ -SO-CH₂-CO-C₆H₅

Further, treatment of benzophenone under similar reaction conditions was shown to lead to the exclusive formation of this type of product, desoxybenzoin and the corresponding phenylsulfinyl ketone (VI) was obtained little in this case.

$$(c_{6}H_{5})_{2}c=0 \xrightarrow{1) c_{6}H_{5}-so-chclli} c_{6}H_{5}-co-ch_{2}c_{6}H_{5} \qquad \qquad c_{6}H_{5}-co-ch_{2}c_{6}H_{5} \qquad \qquad c_{6}H_{5}-so-ch-co-c_{6}H_{5}$$

Now, we have little data for discussing about the formation of these products, but we have considered they are formed through an initial formation of the corresponding phenylsulfinyl ketone followed by removal of the sulfinyl group.

References

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