

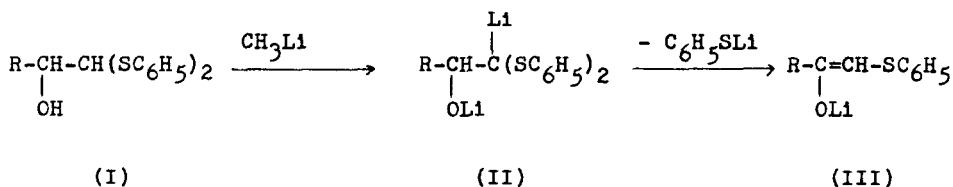
A NEW REARRANGEMENT REACTION OF 1-CHLORO-2-HYDROXYALKYL PHENYL SULFOXIDES

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We have recently reported that treatment of the  $\alpha$ -hydroxyaldehyde diphenylmercaptals (I) with methyl- or n-butyllithium leads to the formation of the corresponding phenylthiomethyl ketone in high yield.<sup>1</sup> 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 phenylthiolate anion followed by rearrangement of hydride ion to the neighboring carbon atom as shown in the following scheme.

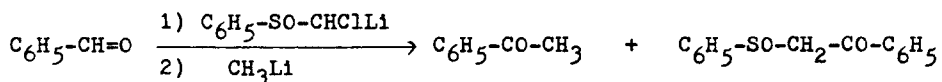


In the present study, as one of the extension of this type of the rearrangement reaction, we have examined a similar reaction of 1-chloro-2-hydroxyalkyl phenyl sulfoxide with alkyllithium under the assumption that the corresponding phenylsulfinylmethyl ketone would be formed through a similar decomposition

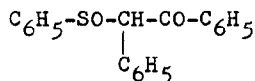
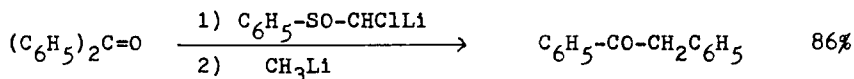


the similar reaction was attempted by the use of n-butyllithium in place of methyllithium in the above experiment.

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%).



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.



(VI)

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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K. Ogura, Bull. Chem. Soc. Japan, 45, 2023 (1972).
- 3) M. Nishio, Chem. Pharm. Bull. Japan, 11, 1669 (1967).