

REACTIONS OF β -HYDROXY SULFOXIDES WITH N-BROMOSUCCINIMIDE

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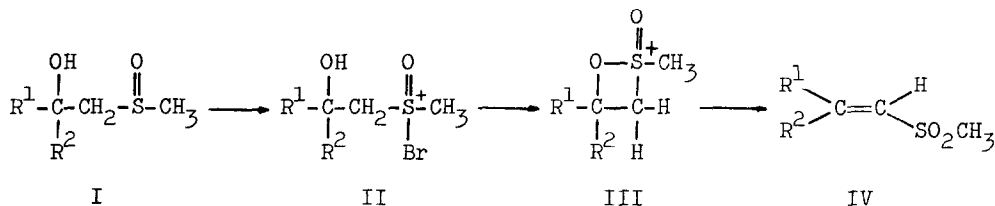
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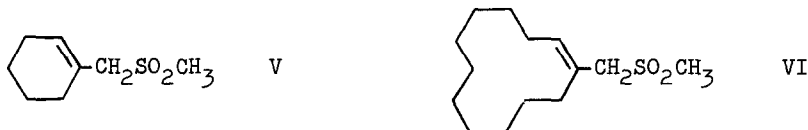
Derivatives of "halosulfoxonium salts" are relatively new class of species which are easily generated by the reaction of sulfoxides with N-bromo- or N-chlorosuccinimide.¹ In this letter, we wish to report a set of new and synthetically useful reactions involving β -hydroxy bromosulfoxonium salt II as a key intermediate.

2-Hydroxy-2,2-diphenylethyl methyl sulfoxide (I, $R^1 = R^2 = \text{Ph}$), readily available from methylsulfinylmethylsodium and benzophenone,² on treatment with N-bromosuccinimide (1.10 equiv) in methylene chloride at -45° for 2 hr, -25° for 1 hr, and 25° for 2 hr, afforded 2,2-diphenylvinyl methyl sulphone (IV, $R^1 = R^2 = \text{Ph}$)³ in 55% yield after thin layer chromatographic purification. The formation of vinyl sulphone can be attributed to a sustained generation of cyclic alkoxysulfoxonium salt III followed by deprotonation.

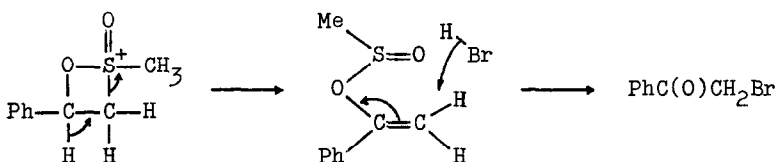


The DMSO^- adducts of enolizable ketones gave the β,δ -unsaturated sulphones in good yields. Thus, (1-hydroxycyclohexyl)methyl methyl sulfoxide (I, $R^1, R^2 = -(\text{CH}_2)_5-$) and (1-hydroxycyclododecyl)methyl methyl sulfoxide (I, $R^1, R^2 = -(\text{CH}_2)_{11}-$) yielded the corresponding β,δ -unsaturated sulphone V (82%)⁴ and VI (74%),⁵ respectively. Although the smooth rearrangement of $\alpha,3$ - to β,δ -

unsaturated sulphone is well known,⁶ alternative pathway involving the direct formation of this product from the intermediate III is also possible



The analogous reactions using the adducts of aldehydes and DMSO⁻ as the starting sulfoxides follows the different course of reaction. Thus, the treatment of 2-hydroxy-2-phenylethyl methyl sulfoxide (I, R¹ = Ph, R² = H) with N-bromosuccinimide produced phenacyl bromide as the major product (66%),⁷ accompanied with a small amount of the corresponding sulphone IV (R¹ = Ph, R² = H, 17%)⁸ This novel reaction would appear to involve initial deprotonation as shown below. Similarly, 2-hydroxydecyl methyl sulfoxide (I, R¹ = n-C₈H₁₇, R² = H) gave a mixture of 1-bromo-2-decanone (12%)⁹ and 2-decenyl methyl sulphone (70%).¹⁰



REFERENCES

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- E. J. Corey and M. Chaykovsky, J. Amer. Chem. Soc., **87**, 1345 (1965).
- Ir (nujol) 1310, 1112 cm⁻¹; δ (CCl₄) 7.07 (s, 1H, olefinic), $\underline{m/e}$ 258 (M⁺)
- Ir (neat) 1315, 1135 cm⁻¹, δ (CCl₄) 5.06 (m, 1H, olefinic); $\underline{m/e}$ 174 (M⁺)
- Ir (neat) 1305, 1136 cm⁻¹, δ (CCl₄) 5.35 (t, 1H, olefinic), $\underline{m/e}$ 258 (M⁺).
- D. E. O'Connor and W. I. Lyness, ibid, **86**, 3840 (1964).
- Identical with an authentic sample.
- Ir (neat) 1310, 1132 cm⁻¹; δ (CCl₄) 7.07 (d, 1H, olefinic), 7.78 (d, 1H, olefinic), $\underline{m/e}$ 182 (M⁺)
- Ir (neat) 1720 cm⁻¹, δ (CCl₄) 3.66 (s, 2H, CH₂Br), $\underline{m/e}$ 234 (M⁺).
- Ir (neat) 1305, 1135 cm⁻¹, δ (CCl₄) 4.24 (m, 2H, olefinic); $\underline{m/e}$ 218 (M⁺)