CHEMISTRY LETTERS, pp. 163-166, 1989. © 1989 The Chemical Society of Japan

Selectivities of α-Halosulfinyl Carbanions towards Enones

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The reactions of lithio α-chloromethyl and α,α-dichloromethyl phenyl sulfoxides with enones gave 1,2 and 1,4 adducts respectively. The reaction of the latter carbanion with enones provides a useful synthesis of novel substituted cyclopropanes.

Carbanions stabilized by adjacent sulfur atoms can undergo both 1,2 and 1,4 additions to α,β-unsaturated carbonyl compounds.1) The selectivity of these reactions depends on the nature of each substrate (carbanion and enone) and on reaction conditions (temperature and solvent).2) The organosulfur mediated carbanions which have been reported to undergo conjugate additions include α-sulfenyl,3) α-sulfinyl,4) and α-sulfonyl5) carbanions; sulfonium6) and sulfoximine ylides.7)

The reaction of stabilized sulfinyl carbanion with enones has been shown to have tremendous synthetic potential.3) In spite of intensive studies in this area, the number of good Michael donors of this type is still quite limited. As part of our continuing effort to gain further insight into the reactivity and chemistry of α-halomethyl phenylsulfinyl carbanions,8) the reactions of lithio chloromethyl phenyl sulfoxide8) 1 and lithio dichloromethyl phenyl sulfoxide9) 2 with enones were examined. The preliminary results of these studies are the content of this letter. To the best of our knowledge, this represents the first report on the subject. The enones employed in these studies were 2-cyclohexen-1-one 3, 2-cyclopenten-1-one 4 and 3-pent-en-2-one 5.

The reaction of the carbanion 1 with enones 3, 4, and 5 in THF at -78 °C for 2 h, with or without the addition of HMPA, gave only the 1,2 addition product.10) The results are summarized in Eq.1 and Table 1.

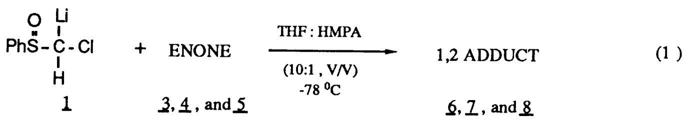
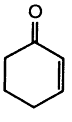
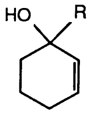
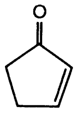
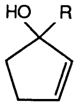
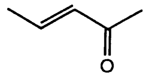
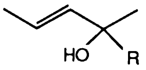
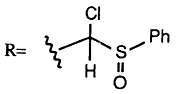
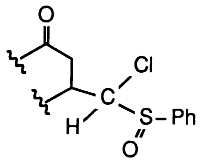


Table 1.

Ketone	Adduct14), % Yield
 3	 , 63 6
 4	 ,62 7
 5	 ,73 8



When the reaction indicated in Eq.1 was warmed up to room temperature before quenching, no adducts 6, 7, and 8 were isolated, and only complex mixtures were obtained. Attempts to equilibrate the isolated adducts 6, 7, and 8 with lithium diisopropylamide (LDA)/THF/HMPA/-78 °C → 0 °C were also unsuccessful,11) neither the 1,4 adduct 9 nor the epoxide11) 10 was isolated.



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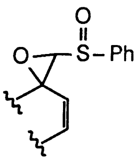

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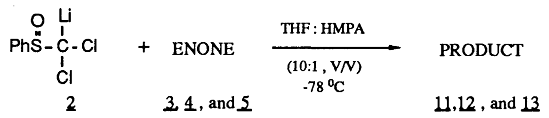
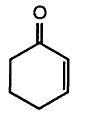
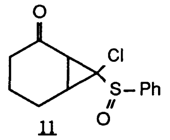
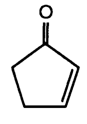
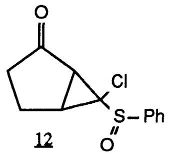
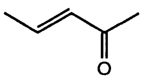
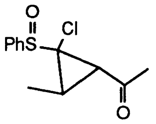
In contrast to the above results, lithio dichloromethyl phenyl sulfoxide 2 undergoes 1,4 addition reaction with enones 3 and 4 to give the cyclopropane products 11 and 12 in high yields. The reaction of carbanion 2 with enone 5 was quite complex and the cyclopropane 13 was isolated in low yield. The results are summarized in Eq.2 and Table 2.

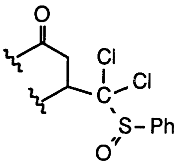


(2)

Table 2 .

Ketone	Product[14], % Yield
 3	 11 , 66
 4	 12 , 79
 5	 13 , 14

It is interesting to note that no acyclic product 14 was isolated from the reaction shown in Eq.2. Apparently this type of Michael initiated ring closure reaction occurs quite readily.[12)]



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The reaction provides a facile entry to this novel class of cyclopropanes. The presence of the second chlorine atom in the carbanion 2 causes to α-carbon bearing the negative charge to become sufficiently soft to undergo the conjugate addition.[13)] Exploratory work on the reactions of these carbanions (1 and 2) with other α,β-unsaturated compounds is in progress.

One of us (B.M.R.B.) thanks the International Seminar in Physics and Chemistry, Sweden for financial support.

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10) Cf. Refs. 2 and 3.

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14) Products were characterized by their spectral data.

(Received November 4, 1988)