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SYNTHESIS OF VINYLCYCLOPROPANE

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Synthetic applications of methylsulfinyl carbanion(I), dimethyloxosulfonium methylide(II) and dimethylsulfonium methylide(III) have been studied extensively by Corey and Chaykovsky[1].

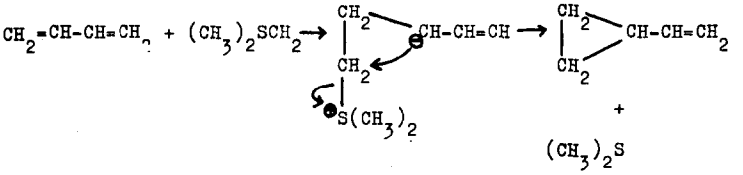
CH_3-SO-$\bar{C}H_2$ $(CH_3)_2SOCH_2$ $(CH_3)_2SCH_2$

(I) (II) (III)

These nucleophiles react with various carbon-carbon double bonds. Argabright et al.[2] have reported that the carbanion I reacts with butadiene to form 1,3-pentadiene. Since ylides II and III also possess carbanionic features, similar reactions of II or III with butadiene are expected. König et al.[3] have confirmed the formation of a trace amount of cyclopentene by the reaction of the ylide II with butadiene.

Formation of intermediates which give several different products is expected, when butadiene is allowed to react with I, II, or III. Therefore, it is of considerable interest to compare the course of the reactions of these three nucleophiles with butadiene. In the present communication, we wish to report the reaction of the ylide III with butadiene.

Reaction of the ylide III with butadiene gave vinylcyclopropane. In a typical experiment, liquid butadiene (10 ml.) was added to 0.03 mol. of III in a mixture of dimethyl sulfoxide (50 ml.) and tetrahydrofuran (45 ml.) at 0°. Stirring was continued for 10 min. at -5 ~ 0° and subsequently for 1.5 hr. at room temperature. Benzene (0.5 ml., as an internal standard) and water (10 ml.) were added and a gas chromatographic analysis (2m., benzyl cyanide + $AgNO_3$ column, 40°) showed the presence of vinylcyclopropane (ca. 30% yield based on III), which was identified by infrared and mass spectroscopy with an authentic sample. Formation of a small amount of 1,3-pentadiene was confirmed but no cyclopentene was detected. Formation of vinylcyclopropane can be explained by the 1,2-addition of III to butadiene, followed by direct elimination of dimethyl sulfide as shown below :



1,3-Pentadiene was probably formed by the reaction of butadiene with the carbanion I, which is considered to be present in the reaction mixture.

References

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