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# CONCERNING THE REACTION OF SULFONIUM METHYLIDES WITH CONJUGATED CARBONYL COMPOUNDS

E. J. Corey and Michael Chaykovsky
Department of Chemistry, Harvard University
Cambridge, Massachusetts

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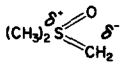
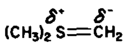
SOME time ago we described the reaction of dimethyloxosulfonium methylide (I) with certain carbonyl compounds to give oxiranes by methylene transfer and also observed that conjugated carbonyl compounds which are receptive to Michael addition afford cyclopropyl derivatives instead of oxiranes with this reagent.[1] More recently we reported that the much more reactive dimethylsulfonium methylide (II) could also be utilized for oxirane synthesis from aldehydes and ketones and that this was the preferred course of methylene transfer even with Michael acceptors which give cyclopropanes with (I)[2]. For example, as we have reported, benzalacetophenone with (I) gives pure

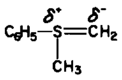


I



$\overset{\delta^+}{(CH_3)_2S}{=}\overset{\delta^-}{CH_2}$

II



$C_6H_5{-}\overset{\delta^+}{\underset{CH_3}{S}}{=}\overset{\delta^-}{CH_2}$

III

1-phenyl-2-benzoylcyclopropane (95% yield) whereas with (II) pure 2-phenyl-2-styryloxirane is formed in 87% yield; no cyclopropane is detectable. It

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[1] E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.* **84**, 867 (1962).

[2] E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.* **84**, 3782 (1962).

was therefore surprising to note in a paper by Franzen and Driessen,[3] which appeared in the interval between our publications on (I) and (II), the statement that dimethylsulfonium methylide (II) and also phenyl-methylsulfonium methylide (III) convert benzalacetophenone to 1-phenyl-2-benzoylcyclopropane in 88% yield.

We have repeated the reactions of (II) and (III) with benzalacetophenone under the conditions specified by Franzen and Driessen in order to resolve this sharp discrepancy. Our original conditions involved essentially complete formation of the ylide (II) from trimethylsulfonium iodide in dimethyl sulfoxide-tetrahydrofuran (using methylsulfinylcarbanion as base) at 0° under nitrogen and subsequent addition of the carbonyl compound; those of Franzen and Driessen entailed the gradual addition of potassium-t-butoxide in dimethyl sulfoxide to a solution of the carbonyl compound and the sulfonium bromide or perchlorate. We obtained in several runs under the latter conditions results which are strictly comparable to those which were found earlier under the former conditions. With either ylide (II) or (III), generated from the sulfonium iodide or perchlorate, the product from benzalacetophenone was the oxirane (86-98% yield); 1-phenyl-2-benzoylcyclopropane could not be detected in the crude product by either infrared or NMR spectroscopy. Since the physical and chemical properties of the isomeric oxirane and cyclopropyl ketone are extremely characteristic and since the former allow quantitative analysis of mixtures to better than ± 1%, there can be no doubt that our results are correct.

A second instance of cyclopropane formation from sulfonium methylides reported by Franzen and Driessen is the conversion of ethyl cinnamate to ethyl 2-phenylcyclopropylcarboxylate in 54% yield. In our hands the appli-

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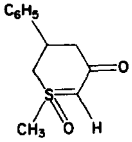
[3] V. Franzen and H-E. Driessen, <u>Tetrahedron Letters</u> No. 15, pp. 661-662 (1962).

cation of their procedure in this case using 1.2 equivalents of ylide gave only 10-12% of the cyclopropyl ester along with 23-25% unreacted ethyl cinnamate and 55% cinnamic acid. The last product was obtained from the aqueous phase resulting from dilution of the reaction mixture with cold water, immediate extraction and acidification. We surmise that it probably is formed from some reaction with the ylide involving the carboethoxyl group, since ethyl cinnamate does not undergo appreciable hydrolysis under these conditions. Thus, even in this case, it would appear that cyclopropane formation is not a dominant reaction course.

It might be noted that the reaction of ethyl cinnamate with the ylide (I) in tetrahydrofuran affords the cyclopropyl ester in 32% yield along with a crystalline product containing sulfur which from analytical date (found: C, 64.76; H, 6.29; S, 14.38) and spectroscopic analysis appears to be the cyclic ylide (IV). The NMR spectrum in particular exhibits an aromatic signal at 7.1-7.3 (ppm downfield from tetramethylsilane) corresponding to five protons, a peak at 4.42 (one proton), a sharp peak at 3.30 (3 protons, unsplit methyl) and broad signals at 3.4-3.6 (2 protons), 2.5-2.7 (2 protons) and 1.8-1.9 (1 proton).



IV

Our previous distinction between the ylides (I) and (II) with regard to their respective tendencies to undergo 1,4- and 1,2- addition would seem justified despite the conflicting report by Franzen and Driessen.[3]