Tetrahedron Letters No.24, pp. 1983-1986, 1969. Pergamon Press. Printed in Great Britain.

THE THERMAL DECOMPOSITION OF ALKYL, AND ARYLSULFONIUM BIS-CARBOMETHOXYMETHYLIDE

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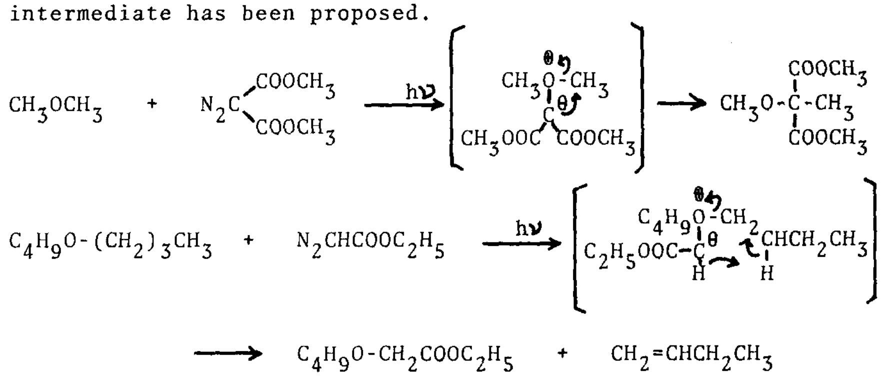
(Received in Japan 1 April 1969; received in UK for publication 20 April 1969)

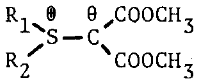
There have been several works reporting that when carboalkoxycarbene was treated with cyclic acetals(1), dimethyl ether(2), and benzyldimethylamine(3), an insertion product of carboalkoxycarbene into carbon-oxygen or carbon-nitrogen bond was obtained. These reactions have been explained by the formation of oxygen- or nitrogen-ylide followed by alkyl migration from onium center to carbanion carbon(Stevens-type rearrangement). Meanwhile, in the reaction of n-butyl ether(4) and triethylamine with carboalkoxycarbene, the formation of 1-butene and ethyl-(diethylamino)acetate has been observed, for which Hofmann-like elimination via the ylide intermediate has been proposed.



However, there is no direct evidence for the mechanism of these rearrangements and eliminations of the ylides(5), especially concerning of the sulfonium ylide(6).

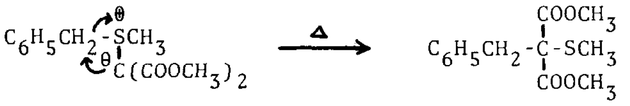
This paper reports some examples which shows that in the thermal decompôsition of stable sulfonium bis-carbomethoxymethylide, the Stevens-type rearrangement and Hofmann-like elimination actually took place.

Stable sulfonium bis-carbomethoxymethylides were prepared by irradiation of dimethyl diazomalonate in sulfides(7). Reactions were carried out on the sample sealed in Pyrex tubes without degassing. After heating in oil bath, the reaction mixtures were analyzed by vapor phase chromatography, and the structures of isolated materials were determined by elemental analysis, n.m.r. and ir spectra.



(I) $R_1=R_2=CH_3$
(II) $R_1=CH_3$, $R_2=C_6H_5$
(III) $R_1=CH_3$, $R_2=CH_2C_6H_5$
(IV) $R_1=R_2=C_2H_5$
(V) $R_1=CH_3$, $R_2=C_2H_5$
(VI) $R_1=CH_3$, $R_2=n\text{-}C_4H_9$
(VII) $R_1=CH_3$, $R_2=t\text{-}C_4H_9$

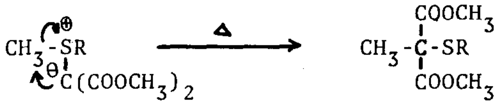
When sulfonium ylide(III) was heated at 200° for 5 hours, the rearranged product(VIII) was obtained in the yield of 90%, which showed four singlet n.m.r. signals at 7.30 ppm($-C_6H_5$), 3.74 ppm($-COOCH_3$), 3.34 ppm($-CH_2-$), and 2.12 ppm($-SCH_3$), in the intensity ratio of 5:6:2:3, and ir absorption maximum at 1735 cm^{-1}. This example represents the Stevens-type rearrangement that involves the migration of an benzyl group from sulfonium center to an adjacent carbanion carbon.



(VIII)

The migration of the methyl group to a carbanionic carbon was not observed. Similar results were obtained in the thermal decomposition of sulfonium ylides(I) and (II) by heating at temperatures above 155° for more than 20 hours, namely, methyl migration products were formed in the yield of 10-16%(8).

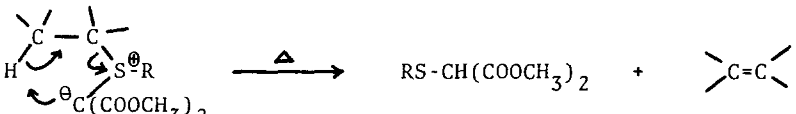
These observations strongly support the argument that " insertion of carboalkoxycarbene into the carbon-oxygen or carbon-nitrogen bond" in the reaction of ether or amine with carboalkoxycarbene actually takes place by the rearrangement of oxygen-, or nitrogen-ylide.



(IX) R=CH_3 16% Yield
(X) R=C_6H_5 10%

When the compounds (V)-(VII) were heated at temperatures above 180° for 4 hours, in all cases dimethyl methylmercaptomalonate was obtained in the yields of 90, 84 and 78%, resepectively, together with olefins. Dimethyl methylmercaptomalonate was identified by the comparison of its physical property with that of authentic sample prepared by the irradiation of dimethyl diazomalonate in methyl mercaptan. It showed the three n.m.r. signals at 3.74 ppm($-COOCH_3$), 2.21 ppm($-SCH_3$), and 3.91 ppm(-CH-), in the intensity ratio, 6:3:1, and ir absorption maximum at 1750 cm^{-1}. Thermal decomposition of compound (IV) at 160° for 5 hours gave dimethyl ethylmercaptomalonate in the yield of 47% together with the formation of ethylene.

These eliminative decomposition of sulfonium ylide is probably cis elimination which requires a 5 membered cyclic transition state.



78-90% Yield

These observations will give a support to the proposed ylide mechanism in the reaction of carboalkoxycarbene with ether and amine bearing β-hydrogen atoms.

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