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THE FORMATION OF MERCAPTOACETATE IN THE THERMOLYSIS OF MERCAPTOMALONATE

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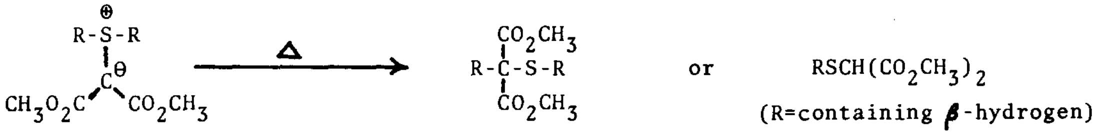
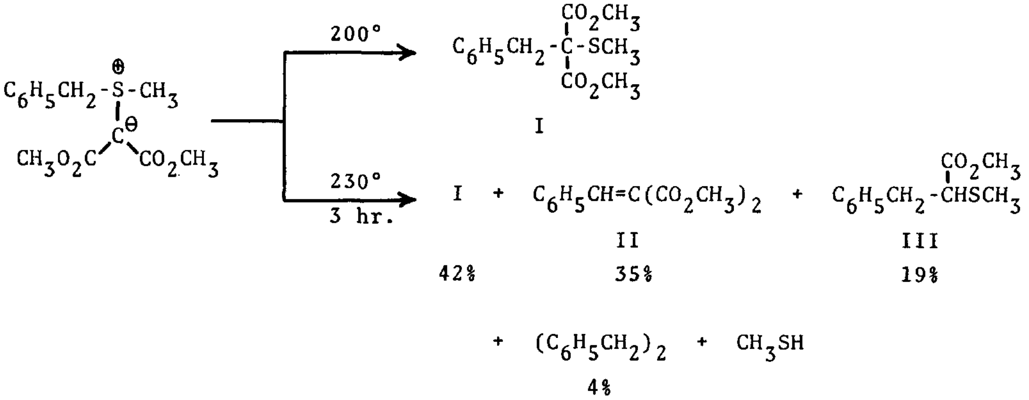
One of the many interesting properties of sulfonium bis-carbomethoxymethylide is the susceptibility to thermal cleavage of the dipolar sulfur-carbon bond to give the product derived from Steavns-type rearrangement or Hofmann-like elimination(1,2). These products are reported to be formed by the migration of alkyl group or β-hydrogen to adjacent carbanion carbon.



During an investigation of the thermal rearrangement of sulfonium ylides, new products, mercaptoacetates, were found together with mercaptomalonates at higher temperatures, and found to be the secondary product from the malonate. No examples known of the acetate formation of the thermolysis of malonic esters have been reported.

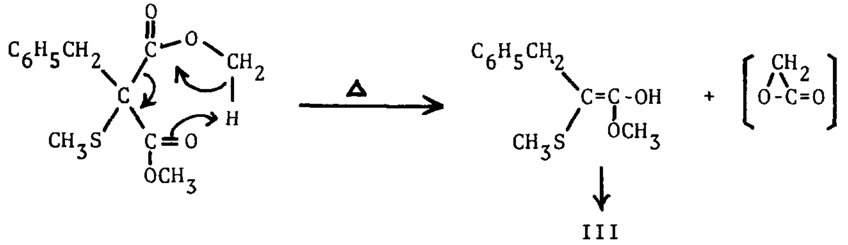
This communication reports some examples in which the thermal rearrangements of sulfonium ylides and mercaptomalonates at higher temperatures give the formation of mercaptoacetates.

We have recently observed the thermolysis of benzyl methylsulfonium bis-carbomethoxymethylide at 200° for several hours to give benzyl methylmercaptomalonate (I) in almost quantitative yield. However, at higher temperatures, benzal malonate (II) and benzyl methylmercaptoacetate (III) were obtained together with I. All the thermolysis were carried out in sealed Pyrex tubes without degassing.



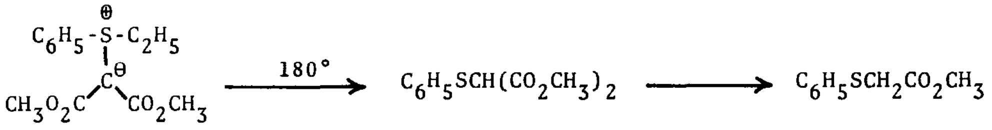
The ratio of the II and III changed with increasing reaction temperature and time, and at 250° for 10 hours, all the malonic ester I disappeared. The structures of these products were determined by independent synthesis (II)(3), and spectra analysis (III)(4).

The above experiments suggest that II and III are formed from the thermolysis of I. In order to test this, the compound I was collected by glpc, and heated under the above conditions. It was found to thermolyze rapidly and to give a quantitative yield of II and III. Although we have no supporting evidence, we suggest that the conversion of I to III involves a elimination through the 7-member cyclic transition state(5).



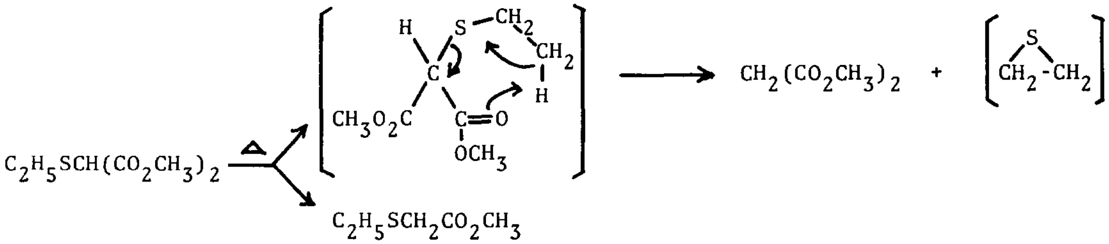
The formation of II is less easily explained as the results of methyl mercaptan elimination. The mechanism of mercaptan elimination may involve one-stage four member cyclic process as seen in usual Ei mechanism(6).

The thermal decomposition of ethyl phenylsulfonium bis-carbomethoxymethylide (IV) was also investigated. At 180°, dimethyl phenylmercaptoacetate (VI) was formed together with ethylene detected by glpc. The structure VI was identified by comparison with the sample synthesized independently(7). The formation of the product VI may be explained by Hoffmann-like elimination followed by the elimination reaction analogous to the transformation of I→III. There was a evidence indicating that phenylmercaptomalonate (V) may be the intermediate to the formation of VI. Thus, V was prepared from the reaction of thiophenol and dimethyl diazomalonate, and it was found to thermolyze rapidly at temperature around 160° to give VI quantitatively.



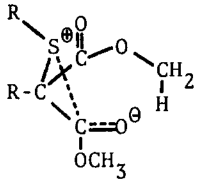
IV V VI

The thermolysis of dimethyl ethylmercaptomalonate (VII), however, yielded methyl ethylmercaptoacetate (VIII) and dimethyl malonate in the ratio of 5:4 at 230° for 5 hrs.. The observation is a further example showing that mercaptomalonate undergoes the thermolysis involving 7-membered cyclic transition state. In this case the carbonyl oxygen abstracts not only hydrogen on the other carbomethoxy group (formation of VIII), but also β-hydrogen on the ethylmercapto group (formation of dimethyl malonate)(8). The sulfur may be eliminated as ethylene sulfide(9).



VII VIII

It will be quite interesting to compare the behavior of mercaptomalonate with alkylmalonate which is stable under the conditions. We might expect such a sulfur atom as in benzyl methylmercapto-, or phenylmercaptomalonate behaves the special roles in the thermal decomposition, that is, the possibility of the neighboring-group interaction(10) of sulfur atom with the carbonyl group, likely representation being IX.



IX

In our reaction, the participation of the neighboring sulfur atom on the carbony carbon would enhance the proton abstraction by carbonyl oxygen and hetelolysis of carbon-carbonyl bond. Further studies on the nature of the reaction mechanism and th effect of the neighboring groups are now in progress.

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4) Product III showed three singlet nmr signals [128 cps(-SCH_3), 218 cps(-CO_2CH_3) anc 431 cps(-C_6H_5)] and multiplet [165-202 cps(-CH_2-CH-)] in the intensity ratio of 3:3:5 and 3, ir absorption maximum at 1735 cm^{-1}(C=O), Anal. Calcd for $C_{11}H_{14}O_2S$; C, 62.84, H, 6.71: Found; C, 63.79, H, 6.55.

5) Formally, α-lactone is eliminated, but no attempt was made to identity it.

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7) The photolysis of methyl diazoacetate in thiophenol gave the product showing the same nmr and ir spectra to those of VI., nmr signals at 212 cps(singlet, -SCH_2-), 220 cps(singlet, -CO_2CH_3) and 428-446 cps(multiplet, -C_6H_5) in the intensity ratio of 2:3:5; ir absorption maximum at 1745 cm^{-1}, Anal. Calcd for $C_9H_{10}O_2S$; C, 59.33, H, 5.53, Found; C, 60.34, H, 5.66.

8) Hydrogen abstraction from α-carbon on the ethylmercapto may not involve because dimethyl benzylmalonate was not formed in the thermolysis of I.

9) We have no special evidence for the formation of ethylene sulfide. Similar sulfur elimination was observed for β-ketosulfide under photolysis; R.H.Fish, L.C.Chow and M.C.Caserio, Tetrahedron Letters, 1259 (1969).

10) E.S.Gould, "Mechanism and Structure in Organic Chemistry" Holt, Rinehart and Winston, N.Y. 1959, p-570.