Formation of α-Dimethylamino-α-methylthio-carbene. Carbene-induced Isomerization of Dimethyl Maleate

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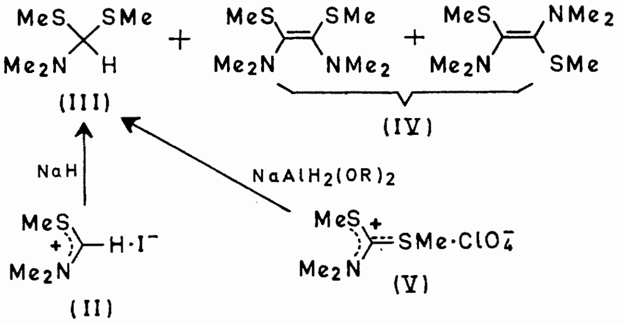
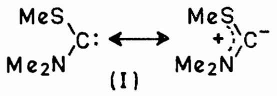
Summary Deprotonation of $(Me_2N)(MeS)CH^+I^-$ with NaH produces an *N,S*-carbene: dimethyl maleate undergoes isomerization during the carbene-forming reaction.

CARBENES containing two α-hetero-atoms have been receiving increasing attention in recent years.[1] To our knowledge, there is no report in the literature on *N,S*-carbenes except for thiazolium carbenes.[2] In connection with our study on carbonium ions stabilized by three α-hetero-atoms,[3] we attempted to produce α-dimethylamino-α-methylthio-carbene (I) by the deprotonation of methyl *NN*-dimethylthioformimidate iodide (II).

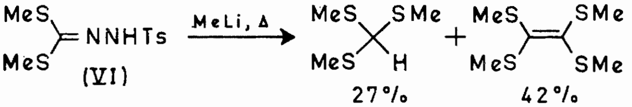




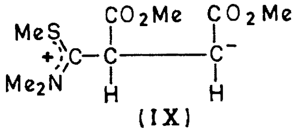
When the salt (II) was treated with NaH in tetrahydrofuran at 0—5°, a rapid evolution of hydrogen ensued and the thioacetal (III), b.p. 55—57° (3 mm Hg), and (IV), b.p. 70—72° (0·25 mm Hg), were obtained in 52% and 20% yields, respectively.

The n.m.r. spectrum (CCl_4) of the product (III) showed δ 2·07 (s, SMe), 2·35 (s, NMe), and 4·61 (s, CH). The n.m.r. and i.r. spectra of (III) were in agreement with those of an authentic sample obtained by the hydride reduction of tri(hetero)carbonium salt (V).[4] The n.m.r. spectrum (CCl_4) of the product (IV) showed δ 1·90—2·10 (complex d, SMe) and 2·55—2·70 (complex d, NMe). The nonequivalence of the *S*- and *N*-methyls suggests that (IV) is a mixture of *cis*- and *trans*-isomers.

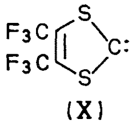
The product (IV) is best explained as the result of a base-induced deprotonation of (II) affording the *N,S*-carbene (I) which then reacts as a nucleophile toward additional carbonium ion (II), finally yielding compound (IV). The mechanism for the formation of (III) remains unsettled; however, the formation of compounds such as (III) has been observed in the carbene-decomposition of the tosylhydrazone (VI).[5]



The nucleophilic carbene (I) can react with electron-deficient olefins. The reaction of (II) (10 mmol), NaH (10 mmol), and dimethyl maleate (VII) (60 mmol) under the above conditions gave dimethyl fumarate (VIII) (52 mmol) along with (III) and (IV). Control experiments demonstrated that neither (II) nor NaH cause isomerization of (VII) under these reaction conditions. It seems reasonable that the carbene (I) undergoes reversible Michael-type addition to the olefin to give zwitterion (IX) which is sufficiently long lived for bond rotation to occur. Recently, Harzler reported that the maleate (VII) underwent isomerization during the reaction forming the 1,3-dithiolium carbene (X).[6]

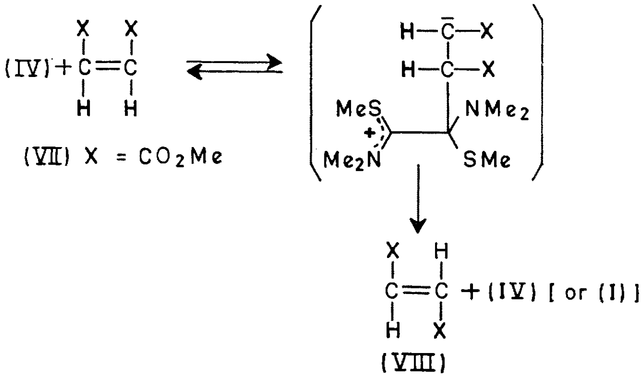


(IX)



(X)

However, the following experimental results suggest the occurrence of isomerization catalysed by compound (IV); (i) when a fivefold excess of the maleate (VII) was added to the mixture obtained from the reaction of (II) with NaH, (VII) was almost completely converted into the fumarate (VIII); (ii) the thioacetal (III) did not cause isomerization; and (iii) compound (IV) caused quantitative isomerization of a fivefold excess of (VII). The suggested mechanism for the isomerization catalysed by (IV) is shown below.



The probable mechanism closely resembles that suggested for the reactions of tetrakis(amino)ethylene with electrophiles;[7] however, a mechanism involving a charge-transfer complex between (VII) and (IV) cannot be ruled out.

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