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SELECTIVE CARBENE INSERTION INTO CARBON-SULFUR BONDS IN THE PHOTODECOMPOSITION OF SILYLDIAZOACETATE. II

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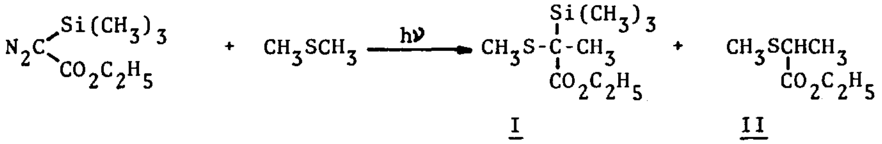
In recent years an increased interest in the reaction of reactive intermediates bearing organo silyl groups[1-7], has been developed. During the course of our study of the chemistry of sulfonium ylides produced by the reaction of carbene with sulfides[8], we have devoted special attention to the reaction of sulfur compounds with trimethylsilylcarbenes. Here, we wish to report a peculiar reaction of the silylcarbene, that is, selective insertion into alkyl carbon-sulfur bonds, which occur even though sulfides bearing β-hydrogens.

Irradiation of ethyl trimethylsilyldiazoacetate in excess dimethyl sulfide was carried out with a high pressure mercury lamp at room temperature(20-25°). Vapor phase chromatographic analysis using several stationary phases detected two products. The major product I (30% yield) was proved to be ethyl α-methylthio-α-trimethylsilylpropionate by nmr (CCl_4 in τ): $Si(CH_3)_3$ group at 9.90(s), $O\text{-}C\text{-}CH_3$ at 8.74(t), $S\text{-}C\text{-}CH_3$ at 8.56(s), $S\text{-}CH_3$ at 8.01(s) and CO_2CH_2- at 5.87(q); the infrared spectrum showed strong bands at 1710, 1250, 1220 and 850 cm^{-1}, and elemental analysis: Calcd for $C_9H_{20}SiSO_2$: C, 49.05; H, 9.15; S, 14.55. Found: C, 49.29; H, 9.39; S, 14.48. The minor product II (7% yield) was identified as ethyl α-methylthiopropionate. Its nmr spectrum (CCl_4 in τ) showed a three-proton triplet at 8.74 ($O\text{-}C\text{-}CH_3$), a three-proton doublet at 8.64 (J=7.0 cps)($S\text{-}C\text{-}CH_3$), a three-proton singlet at 7.92($S\text{-}CH_3$), a one-proton quartet at 6.80(J=7.0 cps)(S-CH-) and a two-proton quartet at 5.85(CO_2CH_2-); its infrared spectrum showed a strong band at 1730 cm^{-1}, and elemental analysis was in agreement with this structure.



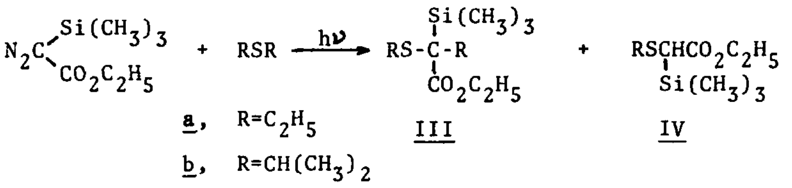
$$N_2C\begin{smallmatrix}Si(CH_3)_3\\ CO_2C_2H_5\end{smallmatrix} + CH_3SCH_3 \xrightarrow{h\nu} CH_3S\text{-}\overset{Si(CH_3)_3}{\underset{CO_2C_2H_5}{C}}\text{-}CH_3 + CH_3S\underset{CO_2C_2H_5}{CH}CH_3$$

I II

This minor product II might have been produced from the product I by action of moisture.[9] Thus, the main reaction occuring was indeed the silylcarbene insertion into the C-S bond between methyl and methylthio group. Also, it should be noticed that no C-H insertion product was found.

The photodecomposition of ethyl trimethylsilyldiazoacetate with diethyl sulfide in 1 : 10 molar ratio at room temperature gave ethyl α-ethylthio-α-trimethylsilylbutyrate IIIa as a major (43% yield) product, and other minor product (6% yield), ethyl ethylthio(trimethylsilyl)acetate IVa; the structure was established by comparison of its spectra with those of an authentic sample prepared by the reaction of ethyl trimethylsilyldiazoacetate with ethyl mercaptan. IVa corresponds to a product of β-elimination from intermediate sulfonium ylide[10,11], which is a quite common path in the reaction of ordinary carbene with sulfides bearing β-hydrogens. The nmr spectra of the product IIIa showed (CCl_4 in τ): 9.90(s, 9H), 9.2-8.6(m, 9H), 8.06(q, 2H), 7.47(q, 2H) and 5.87(q, 2H). The infrared spectrum showed a strong band at 1710, 1250 and 840 cm^{-1}. Anal. Calcd for $C_{11}H_{24}SiSO_2$: C, 53.18; H, 9.74; S, 12.91. Found: C, 53.38; H, 9.95; S, 12.64.

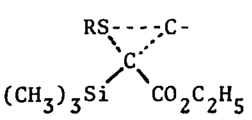
Photolysis of ethyl trimethylsilyldiazoacetate in excess diisopropyl sulfide similarly gave IIIb and IVb in yields of 31 and 25%, respectively.



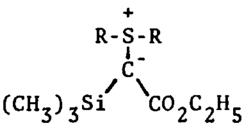
$$N_2C\begin{smallmatrix}Si(CH_3)_3\\ CO_2C_2H_5\end{smallmatrix} + RSR \xrightarrow{h\nu} RS\text{-}\overset{Si(CH_3)_3}{\underset{CO_2C_2H_5}{C}}\text{-}R + RS\underset{Si(CH_3)_3}{CH}CO_2C_2H_5$$

a, $R=C_2H_5$ III IV

b, $R=CH(CH_3)_2$



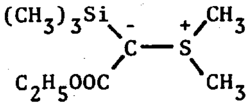
[A]

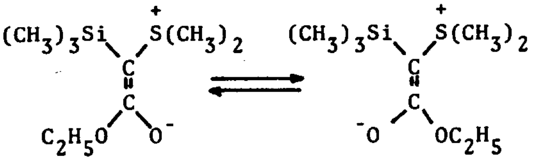


[B]

Although these selective C-S insertions might be direct insertion of carbene via three center transition state[A], the sulfonium ylide intermediate mechanism[B] seems more acceptable, considering our previous results on the reaction of carbenes and sulfides[8,10-15].

The sulfonium ylide mechanism was established by isolation of the corresponding sulfonium ylide in the reaction at low temperature(0°~ -78°), other conditions being identical with those under which the product I was produced. Vapor phase chromatography (10% SF-96 on Celite 545, 1 m x 6 mm, temp. 150°) of the low temperature reaction mixture in dimethyl sulfide gave, in addition to I and II, a volatile solid, m. p. 40° (uncorrected) product, which was identified as dimethylsulfonium carboethoxy(trimethylsilyl)methylide[C] from its infrared and nmr spectra. Its nmr($CDCl_3$ in τ) showed a nine-proton with two singlets at 10.15 and 10.10 ($Si\text{-}CH_3$), a three-proton with two triplets at 8.98 and 8.93 ($O\text{-}C\text{-}CH_3$), a six-proton with two singlets at 7.88 and 7.85 ($\text{-}\overset{+}{S}\text{-}CH_3$) and a two proton with two quartets at 6.20 and 6.14 ($O\text{-}CH_2\text{-}$). Its infrared spectrum showed a strong band at 1620 cm^{-1}, which is characteristic of the ester carbonyl with sulfonium ylide[16,17]. The nmr spectrum reveals two different types of the sulfonium ylide, probably geometrical isomers [C'] and [C"], which rapidly interconvert into each other[16,18].


[C]


[C'] [C"]

The ylide [C] slowly became liquid on exposure to light and air or attempted recrystallisation, and did not give any C-S insertion product.

We have no evidence concerning the nature of silylcarbene insertion process. One may consider that the intermediate sulfonium ylide must be undergoing photochemical and not thermal rearrangement to the observed C-S insertion product in the room temperature reactions. At present we do not understand the role of trimethylsilyl group in this apparent change in the course of rearrangement of sulfonium ylides.

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