Reaction of Stannylcarbene with Sulphides. A Novel C–S Insertion of Stannylcarbene into C–S Bonds

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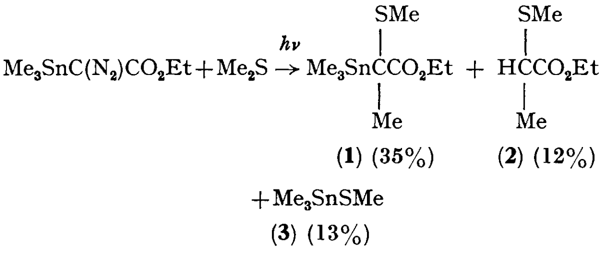
Summary In the photolysis of ethyl trimethylstannyldiazoacetate, trimethylstannyl(ethoxylcarbonyl)carbene is produced which inserts into the C–S bonds of alkyl sulphides.

Recently, the chemistry of organometallic carbenes has attracted interest.[1] We have previously demonstrated selective carbene insertion into carbon–sulphur bonds in the decomposition of ethyl trimethylsilyldiazoacetate.[2] However, hitherto there has been no report of reactions of carbenes derived from stannyl diazo compounds with compounds containing a hetero atom.[3] Here we report the first insertion of a stannylcarbene into C–S bonds of alkyl sulphides, including sulphides which have no β-hydrogen atom.

Ethyl trimethylstannyldiazoacetate (0·9 mmol) was irradiated in an excess of dimethyl sulphide for 6·3 h with a high pressure mercury lamp under nitrogen. Preparative g.l.c. gave three products. The main product (**1**) was proved to be ethyl α-methylthio-α-trimethylstannylpropionate by its n.m.r. spectrum; (CCl_4) δ 0·23 (s, 9H, $SnMe_3$), 1·32(t, *J* 7 Hz, 3H, O–C–Me), 1·63(s, 3H, C–Me), 2·00(s, 3H, SMe), and 4·16 (q, *J* 7 Hz, 2H, OCH_2–); its i.r. spectrum showed strong bands at 1720 and 1220 cm^{-1}; and its mass spectrum showed a peak at *m/e* 312 (M^+, ^{120}Sn). The other two products were identified as ethyl α-methylthiopropionate (**2**), and methylthiotrimethylstannane (**3**) by comparison with authentic samples. The minor product (**2**) may be produced from (**1**) by the action of moisture. When pure (**1**), collected by preparative g.l.c., was allowed to stand, (**2**) was found to be present in addition to unchanged (**1**).



$$\mathrm{Me_3SnC(N_2)CO_2Et + Me_2S \xrightarrow{h\nu} Me_3Sn\underset{Me}{\overset{SMe}{C}}CO_2Et + H\underset{Me}{\overset{SMe}{C}}CO_2Et}$$

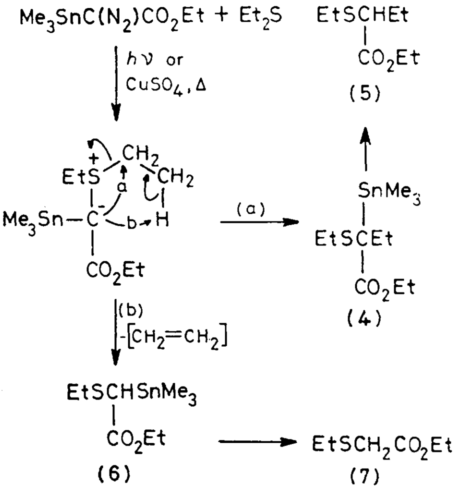
(**1**) (35%) (**2**) (12%)

$$\mathrm{+ Me_3SnSMe}$$

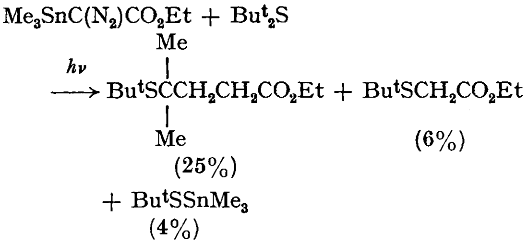
(**3**) (13%)

Thus, the main reaction between ethyl trimethylstannyldiazoacetate and dimethyl sulphide was insertion of the stannylcarbene into one of the C–S bonds of dimethyl sulphide. This selective C–S insertion of the stannylcarbene is similar to that of trimethylsilyl(ethoxy)carbonylcarbene,[2] but is the first example of reaction of a stannylcarbene with a hetero compound. The only reaction of stannylcarbenes so far reported, even when using stannyl diazo compounds, is the reaction with olefins.[4] Although direct insertion of the stannylcarbene into the C–S bond *via* a three centre transition state may be possible, the sulphonium ylide intermediate mechanism seems more probable, considering previous results obtained for reactions of carbenes with sulphides.[5] The stannylcarbene attacks the sulphur atom to give a sulphonium ylide, in which a methyl group probably migrates from the sulphonium centre to the adjacent carbanionic carbon atom *via* a Stevens type rearrangement.

A similar C–S insertion product (**5**) (37%) was obtained when the photolysis of the stannyldiazoacetate was carried out in diethyl sulphide, although the insertion product was destannylated, probably by moisture. Product (**7**) (9%) and ethylthiotrimethylstannane (16%) were also formed as minor products. The former results from β-elimination from the sulphonium ylide, followed by destannylation.[6] Compounds (**4**) and (**6**) were not isolated, and may be very unstable to moisture.



In the photochemical reaction of the stannyldiazoacetate, the main reaction pathway is (a); a process which leads to a C–S insertion product, while in the thermal decomposition, the main path is (b); a process which gives a familiar β-elimination product. Anhydrous copper(II) sulphate-catalysed thermal decomposition of the stannyldiazoacetate gives (**7**) in 25% yield mainly by β-elimination, and the C–S insertion product (**5**) in 3% yield. It should be noted that the reaction path is strongly influenced by the reaction conditions. When di-t-butyl sulphide, which has two bulky groups on the sulphur atom, was used no C–S insertion product was formed. Instead the main product was the C–H insertion product accompanied by a small amount of the β-elimination product. Attack at the sulphur atom of the stannylcarbene becomes unfavourable owing to steric hindrance.



$$Me_3SnC(N_2)CO_2Et + Bu^t{}_2S \xrightarrow{h\nu} \underset{(25\%)}{Bu^tS\underset{Me}{\overset{Me}{C}}CH_2CH_2CO_2Et} + \underset{(6\%)}{Bu^tSCH_2CO_2Et} + \underset{(4\%)}{Bu^tSSnMe_3}$$

It was also found that the stannylcarbene inserts into the weaker C–S bond of a sulphide. Thus, the photolysis of ethyl trimethylstannyldiazoacetate in thioanisole, an unsymmetrical sulphide, gave a product resulting from carbene insertion into the Me–S bond and not the Ph–S bond.

In all cases studied, alkylthiotrimethylstannanes were formed as side products. These may arise from the photolysis of C–S insertion products, probably with intramolecular elimination.[7] When compound (**1**) was photolysed in benzene, methylthiotrimethylstannane (**3**) and the destannylated product (**2**) were obtained in addition to an unidentified polymeric compound.

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