The Insertion Reaction of $^1CH_2$ into the Silicon–Carbon Bond

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Singlet methylene reacts with 1,1-dimethylsilacyclobutane to yield as well as the expected products formed by C–H insertion some 1,1-dimethylsilacyclopentane which strongly suggests that it can insert in the silicon–carbon bond.

While singlet methylene ($^1CH_2$) is known to insert rapidly into C–H bonds[1] and there is some evidence that it can also insert in C–O bonds, there is none that it can insert in C–C bonds. A recent theoretical calculation[2] suggested that insertion into a *strained* C–C bond as in cyclopropane should occur with a small or zero energy barrier, but this has not been confirmed experimentally.[3] An *upper* limit for such a reaction of 1 in 40000 compared with the insertion into the C–H bonds was found.

The silicon analogue of methylene, silylene (silanediyl; $^1SiH_2$) appears to be slightly less reactive than methylene,[4—6] and although silylene and its dimethyl derivative $^1SiMe_2$ insert readily into Si–H bonds they apparently do not insert into either C–H or Si–C bonds.[7,8] (Interestingly however there is some evidence that silylene can insert into Si–Si bonds.) It did, however, seem possible to us that $^1CH_2$, being more reactive than $^1SiH_2$, might insert into an Si–C bond. Somewhat surprisingly, the less reactive dichlorocarbene, CCl_2 is known to insert into a strained Si–C bond,[9] but there are no published results of similar work for $^1CH_2$.† We have therefore

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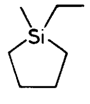
† Note added in proof. Unpublished studies of $^1CH_2$ with silacyclopentane have been carried out by M. Jones Jr. (Ph.D. Thesis, Yale University, New Haven, Conn., U.S.A., 1963).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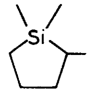
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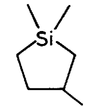
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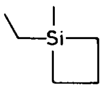
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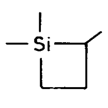
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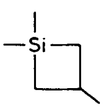
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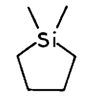
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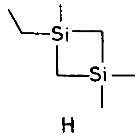
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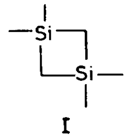
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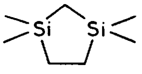
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investigated this possibility with a variety of organosilane substrates and report the results here.

Methylene was produced by the photolysis of ketene at 313 nm. In some experiments oxygen was added to eliminate reactions of $^3CH_2$ but it was found that the reaction products of interest were unaffected by the presence or absence of oxygen. In all cases argon was added to bring the total pressure of the system to 350 Torr. Products were analysed by gas chromatography using a 4 m column packed with 10% OV 101 on Chromosorb W.

Photolysis of mixtures of ketene and trimethyl-t-butylsilane in the ratio of 1:5 produced only two major g.c. peaks in the ratio of 1.4:1 (independent of photolysis time and of the presence or absence of O_2). These products were not individually characterised but neither peak coincided with that of an authentic sample of $Me_3SiCH_2CMe_3$. Thus there was no evidence for insertion into the Si–C bond. The observed peaks almost certainly arise from the C–H insertion processes giving $Me_2(Et)SiCMe_3$ and $Me_3SiC(Et)Me_2$. It is interesting to note that these products are not formed in the statistical ratio of 1:1, thus suggesting an activating (or steric) effect of the silicon.‡[10]

A similar set of experiments was carried out using 1,1-dimethylsilacyclopentane as the reactant. The three products expected as a result of methylene insertion in the various C–H bonds, *viz*. **A**—**C**, were found. Their relative yields were 1.7:1.5:1 as against statistical expectations of 1.5:1:1, (though there is evidence that even in hydrocarbon systems methylene does react a little more rapidly with secondary C–H bonds than primary ones). Again the experimental ratios suggest an activating effect of the Si atom. In most experiments no chromatographic peak was present corresponding to the retention time of an authentic sample of 1,1-dimethylsilacyclohexene, the compound expected to be formed as a result of Si–C insertion. However on prolonged photolysis a *very small peak* with this retention time was detected. Assuming that this peak does indeed correspond to the Si–C insertion product then we can set a maximum relative rate constant of a little less than 1% of that into a C–H bond (note there are 2 equivalent Si–C 'ring' bonds as against 14 C–H bonds). Thus about 99.9% of the observed products arise from C–H insertion.

Photolysis of ketene, 1,1-dimethylsiletane mixtures gave *4 products*. These were identified as **D**—**G**, formed in the ratios 17:14:8:1.

The observation of 1,1-dimethylsilacyclopentane **G** provides the first reliable evidence for insertion by $^1CH_2$ into the Si–C bond, leading to ring expansion (the C–C bond is assumed unreactive as in cyclobutane[3]). The remaining compounds almost certainly all arise *via* C–H insertion. (From the experiments with trimethyl-t-butylsilane it seems unlikely that any of the 1-ethyl-1-methylsiletane **D** comes *via* an Si–C insertion pathway). While the insertion into the various C–H bonds is not exactly statistical (and the same trends are observed as with the other reactants studied) we can take an average value for them. Hence we find that the insertion into the (strained) Si–C bond is about 7 times slower than the average rate of insertion into the C–H bond.

In a final set of experiments, mixtures of ketene and 1,1,3,3-tetramethyl-1,3-disiletane were photolysed. Three products were observed and tentatively identified as **H**—**J**. The ratio of **H** to **I** was approximately 2.5:1. The relative yield of **J**, the product resulting from Si–C insertion, proved difficult to determine since it eluted with a retention time close to that of **H**. However by using a 2.5 m column of silicon oil (DE 117) on Chromosorb (in addition to the 4 m column of OV 101) appreciably better resolution of these peaks was obtained. The yield of **J** was about 4% of the combined yields of **H** and **I**. From this we calculate that in 1,1,3,3-tetramethyldisilacyclobutane the insertion of $^1CH_2$ into a Si–C bond was about 6 times slower than into a C–H bond. Within experimental error this does not differ significantly from the ratio of 1:7 in the case of the 1,1-dimethylsilacyclobutane.

We conclude that $^1CH_2$ does insert into a strained Si–C bond as found in the 4-membered ring. It may insert, though at a considerably slower rate, in the 5-membered ring. We have no evidence for insertion in a 'normal' Si–C bond. These results parallel the older work of Seyferth *et al.*[9] on $^1CCl_2$, in which the only example of an Si–C insertion process was with 1,1-dimethylsiletane.

We thank Maitland Jones for helpful correspondence.

Received, 10th February 1988;§ Com. 8/05016C

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‡ One possibility here is that of the β-activating effect.[9] It is known that the β C–H bond in trimethyl-t-butylsilane is weakened by *ca.* 12 kJ mol^{-1} relative to normal C–H bonds.[10]

§ Received in revised form 7th November 1988.