Journal of Organometallic Chemistry, 67 (1974) C7—C9

Preliminary communication

REACTIONS OF CARBOALKOXYCARBENES WITH ALKYLSILANES

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(Received November 30th, 1973)

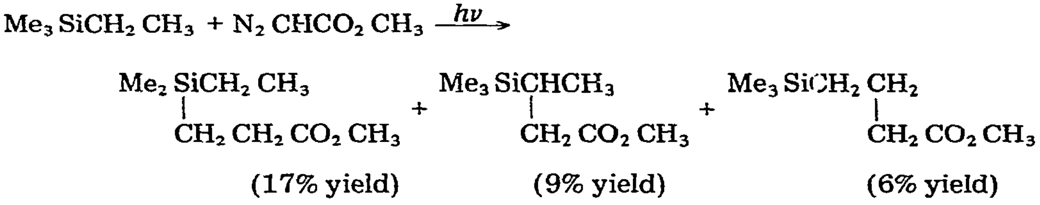
Summary

Carboalkoxycarbenes react readily with alkylsilanes to give α-C—H and β-C—H insertion products of the carbene. Carboalkoxycarbenes also insert into Si—C bonds, as well as into the C—H bonds of a disilacyclobutane.

Insertion into carbon—hydrogen bonds is a well-known reaction in the chemistry of carbenes [1]. Seyferth and coworkers have found that dichlorocarbene, generated by pyrolysis of phenyl(bromodichloromethyl)mercury, selectively inserts into β-C—H bonds of alkylsilanes, and proposed a β-activating effect of the silicon atom on the C—H insertion [2]. However, Gaspar and coworkers [3] recently have reported that the silicon atom activates α-C—H bonds of alkylsilicon compounds toward insertion of CH_2 (via CH_2N_2/CuCl).

This communication describes our results which show that the C—H insertion of carboalkoxycarbenes also occurs at both α- and β-C—H bonds, and which demonstrate that the inductive and steric effect of the trimethylsilyl group must be considered in order to correlate relative insertion rates.

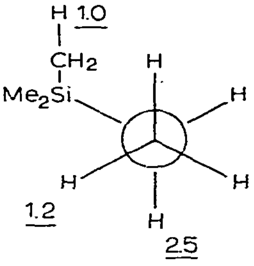
The photolysis of methyl diazoacetate in trimethylethylsilane was carried out with a high pressure mercury lamp to give three major products on analysis of gas chromatography. These were found to be the β-C—H insertion (6%), α-methyl C—H insertion (17%) and α-methylene C—H insertion (9%) products of carbomethoxycarbene. The structures of these products were characterized by infrared, NMR and elemental analyses. This result is in contrast to what was observed in the dichlorocarbene reactions. Lower selectivity of $H\ddot{C}CO_2CH_3$ vs. $:CCl_2$ could be explained in terms of similar reactivities of the former for primary and secondary C—H bonds [1]. The relative rate per bond showed that an α-secondary C—H bond (2.5) is more reactive than a primary α-C—H bond (1.0), and a primary α-C—H bond seems somewhat less reactive than a primary β-C—H bond (1.2). The difference is small, but may be explained by steric hindrance to carbene insertion.

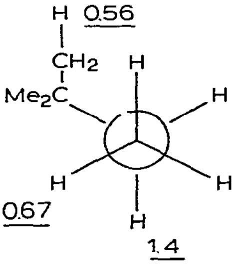


$$Me_3SiCH_2CH_3 + N_2CHCO_2CH_3 \xrightarrow{h\nu}$$

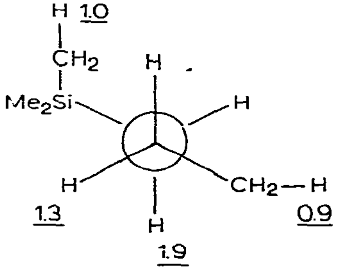
$$\begin{array}{l} Me_2SiCH_2CH_3 \\ \quad | \\ \quad CH_2CH_2CO_2CH_3 \\ \quad\quad (17\%\ \text{yield}) \end{array} + \begin{array}{l} Me_3SiCHCH_3 \\ \quad\quad | \\ \quad\quad CH_2CO_2CH_3 \\ \quad\quad (9\%\ \text{yield}) \end{array} + \begin{array}{l} Me_3SiCH_2CH_2 \\ \quad\quad\quad | \\ \quad\quad\quad CH_2CO_2CH_3 \\ \quad\quad\quad (6\%\ \text{yield}) \end{array}$$

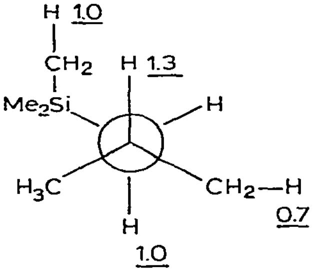
A competition reaction of trimethylethylsilane with 2,2-dimethylbutane shows that the reactivities of C—H bonds towards carbomethoxycarbene insertion are higher in trimethylethylsilane than in 2,2-dimethylbutane [*k*(Si)/*k*(C)=1.8], possibly as a result of the inductive effect of the silicon substituent.



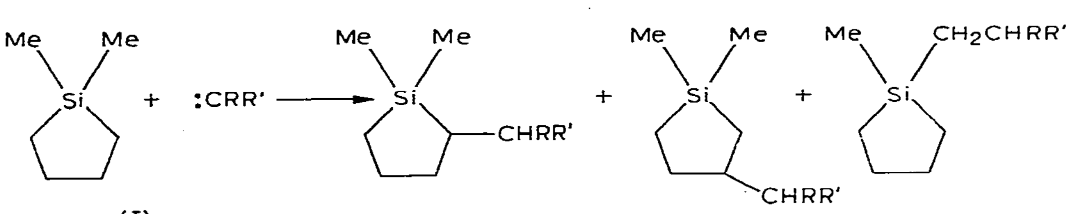


Photodecomposition of methyl diazoacetate in trimethyl(n-propyl)silane and in trimethyl(iso-butyl)silane gave the insertion products of the carbene into α, β and γ-C—H bonds in total yield of 40—50%. The relative rate of the carbene insertion into the primary γ-C—H bond in these compounds showed it to be less reactive than that of the primary β-C—H bond of trimethylethylsilane, probably because of the diminished effect of the silyl group.





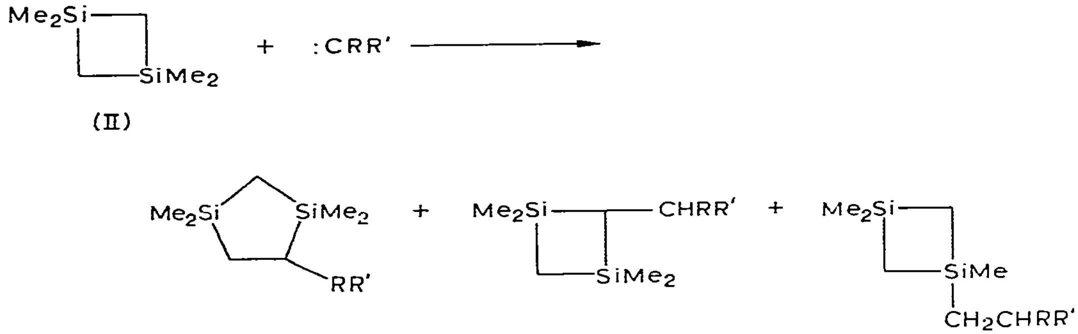
The photolysis of methyl diazoacetate and dimethyl diazomalonate in 1,1-dimethyl-1-silacyclopentane (I) gave carbene insertion products into the secondary α and β-C—H bonds as well as into primary C—H bonds in comparable extent.



(I)

Ratio per bond			
$R = H, R' = CO_2CH_3$	1.6	2.0	1.0
$R = R' = CO_2CH_3$	7.0	11.9	1.0

Also of interest was the reaction of 1,1,3,3-tetramethyl-1,3-disilacyclobutane(II) where we observed carbene insertion into the Si—C bond, as has previously been observed with dichlorocarbene [4]. as well as insertion into primary and secondary C—H bonds in comparable rates.



(II)

Relative yield			
$R = H$ $R' = CO_2CH_3$	14%	33%	53%
$R = R' = CO_2CH_3$*	5%	50%	45%

Acknowledgement

We wish to thank the Shinetsu Chemical Co. for a gift of trimethylchlorosilane.

References

1 W. Kirmse, "Carbene Chemistry", 2nd ed., Academic Press, New York, N.Y., 1971.
2 D. Seyferth, S.S. Washburne, C.J. Attridge and K. Yamamoto, J. Amer. Chem. Soc., 92 (1970) 4405; D. Seyferth, Y.M. Cheng and D.D. Traficante, J. Organometal. Chem., 46 (1972) 9.
3 R.T. Colin, P.P. Gaspar, R.H. Levin and M. Jones, Jr., J. Amer. Chem. Soc., 94 (1972) 7165.
4 D. Seyferth, R. Damrauer, S.B. Andrews and S.S. Washburne, J. Amer. Chem. Soc., 93 (1971) 3709; D. Seyferth, H.-M. Shih, J. Dubac, P. Mazerolles and B. Serres, J. Organometal. Chem., 50 (1973) 39.

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*Reaction in benzene solution.