on MO calculations and are thus tentative. The large upfield shifts of all the aromatic protons except the meta ones are noteworthy. More significantly, $H_{5,6}$ are equivalent in $\mathbf{3}^{2-}$ but not in $\mathbf{2}^{2-}$. Each of the two dianions can be obtained free of the other if the reaction vessel and later the nmr tube are kept close to −78°.

Two alternate, convenient, highly stereoselective syntheses of $\mathbf{2}^{2-}$ have also been achieved. Reaction of *o*-dibenzylbenzene with excess butyllithium in MTHF at room temperature gives, along with smaller amounts of the monoanion, mainly $\mathbf{2}^{2-}$ as shown by methyl iodide quenching and reaction with dichlorodimethylsilane (83% **10**, 17% **11**). Similarly, reaction of diether **12** with potassium in MTHF at 0° gives $\mathbf{2}^{2-}$. Quenching with silane again gives 87% **10** and 13% **11**. These experiments strongly suggest that $\mathbf{2}^{2-}$ is more stable than $\mathbf{3}^{2-}$ despite steric factors. Presumably the greater attractions between the two contact metal gegenions and the more proximate negative charge on an inside phenyl substituent engender this interesting order of stabilities.

Conrotation is in accord with orbital symmetry analysis,[4,5] but neither this approach nor the experiment is consistent with a simplified frontier orbital analysis. The odd electron in a diphenyl-*o*-xylylene anion radical occupies an s orbital, leading to an expectation of disrotation, according to the latter analysis. This appears to be the first instance in which the frontier orbital approach has been shown to lead to an erroneous prediction. In general, *cycloreversions of anion radicals can only be ideally "allowed" for that rotational mode allowed for their neutral precursors, and then only when the orbitals occupied by the odd electron also correlate.* In many cases, therefore, neither mode will be ideally allowed,[6] though some preference may still exist.

Acknowledgment. We thank the National Science Foundation (GP-17596) for support.

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[4] H. C. Longuet-Higgins and E. W. Abrahamson, *J. Amer. Chem. Soc.*, **87**, 2045 (1965).

[5] R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 395, 2046, 2511 (1965); *Angew. Chem.*, **81**, 787 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

[6] The cyclobutene anion radical → 1,3-butadiene anion radical cycloreversion is not ideally allowed in either rotational sense.

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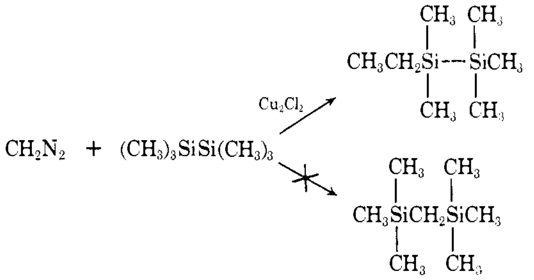
Carbon–Hydrogen Insertion in the Copper-Catalyzed Decomposition of Diazomethane in Hexamethyldisilane. A Silicon α Effect

Sir:

The possibility that silylene SiH_2 might insert into a silicon–silicon bond[1-3] led us to investigate the analogous methylene insertion. In order to be able to carry out experiments without rigorously excluding oxygen, we chose hexamethyldisilane as the reaction substrate. This compound has the advantage of not containing silicon–hydrogen bonds. In addition to high reactivity toward oxygen, silicon–hydrogen bonds have been shown to be 8.9 times as reactive as carbon–hydrogen bonds toward photochemically generated methylene.[4] Therefore, the replacement of silicon–hydrogen bonds by methyl groups was expected to diminish the importance of side reactions which might compete with silicon–silicon insertion.

To maximize the selectivity among competing reaction pathways, the relatively impotent carbenoid species resulting from the copper-catalyzed decomposition of diazomethane[5,6] was chosen for the initial experiments. Diazomethane was swept in a nitrogen stream from a cooled decalin reservoir into a magnetically stirred suspension of 500 mg of cuprous chloride in 2 ml of hexamethyldisilane over a 5-hr period. The reaction mixture was maintained at room temperature and shielded from light. A condenser cooled to 14° retarded evaporation of the reaction mixture.

Vapor chromatographic analysis using several stationary phases detected only a single product formed in *ca.* 5% yield (based on diazomethane). Upon isolation the product proved to be ethylpentamethyldisilane rather than the hoped-for 2,4-disila-2,2,4,4-tetramethylbutane.



The product was identified by comparison of its physical properties (vapor chromatographic retention times, and infrared, nuclear magnetic resonance, and mass spectra) with those of an authentic sample prepared by standard techniques.[7]

Since the observed reaction product is also formed upon photolysis of diazomethane in hexamethyldisilane,[8] and since copper-catalyzed decomposition of diazomethane has not previously been observed to give carbon–hydrogen (or silicon–carbon) insertion,[9] it was necessary to preclude stray light as the source of a spurious result, and to differentiate between carbon–hydrogen and silicon–carbon insertion as the pathway leading to the observed product.

When the reaction of diazomethane with hexamethyldisilane was repeated (several times) in the absence of catalyst but otherwise under conditions identical with those which produced ethylpentamethyldisilane, *no* product was detected. With the chromatographic sensitivity employed, a yield as low as 0.25% would certainly have been found. When the catalyzed decomposition of diazomethane was carried out in cyclohexane and methylcyclohexane in place of hexa-

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[1] M. Bowrey and J. H. Purnell, *J. Amer. Chem. Soc.*, **92**, 2594 (1970).

[2] P. P. Gaspar and P. Markusch, *Chem. Commun.*, 1331 (1970).

[3] P. P. Gaspar and B. Jerosch Herold in "Carbene Chemistry," W. Kirmse, Ed., 2nd ed, Academic Press, New York, N. Y., 1971, Chapter 13.

[4] J. Mazac and J. W. Simons, *J. Amer. Chem. Soc.*, **90**, 2484 (1968).

[5] W. von E. Doering and P. P. Gaspar, *ibid.*, **85**, 3043 (1963).

[6] W. von. E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).

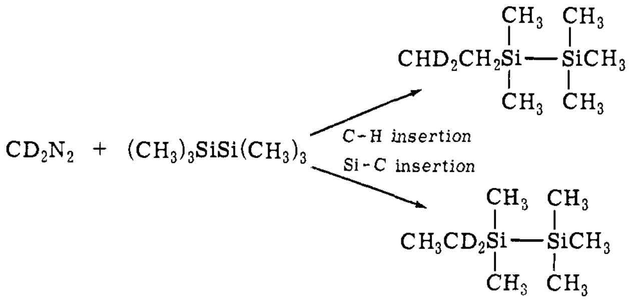
[7] M. Kumada, K. Tamao, T. Takubo, and M. Ishikawa, *J. Organometal. Chem.*, **9**, 43 (1967).

[8] Unpublished work of R. T. Conlin and P. P. Gaspar.

[9] W. Kirmse, "Carbene Chemistry," 2nd ed, Academic Press, New York, N. Y., 1971, p 86.

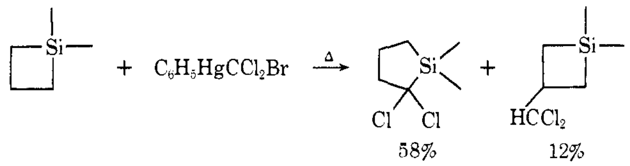
methyldisilane but otherwise under identical conditions, no products of reaction of diazomethane with these substances were detected. Since these substrates are quite reactive toward photochemically generated methylene, it is clear that no photogenic methylene was produced under the conditions used for the copper-catalyzed reaction of diazomethane with hexamethyldisilane.

Carbon–hydrogen insertion was established as the reaction leading to the observed product by experiments with diazomethane-d_2. The reaction product was shown to be the 2,2-dideuterioethylpentamethyldisilane by comparison of its nuclear magnetic resonance spectrum with that of an authentic sample of the specifically labeled compound.[10] An authentic sample of the silicon–carbon insertion product 1,1-dideuterioethylpentamethyldisilane was also prepared.[11] Even with both authentic samples of high isotopic purity available for comparison, the complexity of the ethyl resonance of ethylpentamethyldisilane limits the accuracy to which the isomer ratio can be determined. Nmr spectra determined at 60 MHz indicate that the ratio of the 2,2-dideuterio- to the 1,1-dideuterioethylpentamethyldisilane is greater than 3:1 with none of the latter isomer detected. This lower limit requires further experimental refinement.



Copper-catalyzed decomposition of diazomethane in tetramethylsilane was carried out under conditions identical with those employed in the hexamethyldisilane experiments except for the use of a condenser cooled to −78°. Ethyltrimethylsilane formed in *ca.* 10% yield was the sole product detected. This result indicates that only one silicon atom is required to activate a molecule toward attack by the carbenoid species and that the carbon atoms α to the silicon are activated.

The formation of ethylpentamethyldisilane from hexamethyldisilane is of some interest as the first example of carbenoid carbon–hydrogen insertion in the copper-catalyzed decomposition of diazomethane. More significant is the indication that a silicon atom exercises an activating effect on α carbon–hydrogen bonds toward carbenoid insertion. It should be recalled that Seyferth and coworkers have found a strong β activating influence of silicon atoms toward carbon–hydrogen insertion by dichlorocarbene CCl_2 generated by pyrolysis of phenyl(bromodichloromethyl)mercury.[12] Seyferth found no reactivity toward dichlorocarbene at the α carbon–hydrogen bonds, but in a highly strained cyclic organosilane, silicon–carbon as well as β carbon–hydrogen insertions were observed.[13,14]



We intend to compare α and β insertions in the metal-catalyzed reactions of diazomethane with organosilicon compounds in order to elucidate the role of the silicon atom in the transition state for carbenoid insertion. Preliminary results indicate that carbenoid insertion occurs in the β as well as α carbon–hydrogen bonds of *n*-propyltrimethylsilane upon copper-catalyzed decomposition of diazomethane.[15]

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[10] For the synthesis of 2,2-dideuterioethylpentamethyldisilane by the method of ref 7, 2,2-dideuterioethyl bromide was required. This was prepared by the method of H. J. Ache and A. P. Wolf, *J. Amer. Chem. Soc.*, **88**, 888 (1966), from 2,2-deuterioethanol, itself obtained from the lithium aluminum hydride reduction of 2-bromo-2,2-dideuterioacetic acid according to the procedure of E. L. Eliel, C. Herrmann, and J. T. Traxler, *ibid.*, **78**, 1195 (1956).

[11] The synthesis of 1,1-dideuterioethylpentamethyldisilane from 1,1-dideuterioethanol was identical with the synthesis of the 2,2 isomer outlined in ref **10**. The 1,1-dideuterioethanol was obtained by lithium aluminum deuteride reduction of acetyl chloride.

[12] D. Seyferth, S. S. Washburne, C. J. Attridge, and K. Yamamoto, *J. Amer. Chem. Soc.*, **92**, 4405 (1970).

[13] D. Seyferth, R. Damrauer, and S. S. Washburne, *ibid.*, **89**, 1538 (1967).

[14] D. Seyferth, R. Damrauer, S. B. Andrews, and S. S. Washburne, *ibid.*, **93**, 3709 (1971).

[15] The product distribution differs markedly from that obtained in the photolysis, again indicating that different intermediates are involved in the two processes.

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Dimerization of Nortropane-*N*-oxyl[1]

Sir:

Stable dialkyl nitroxide radicals that were not sterically hindered di-*tert*-alkyl nitroxides were unknown until 1966. In that year, Dupeyre and Rassat[2] made use of Bredt's rule[3] in a most ingenious fashion and synthesized a bicyclic nitroxide, norpseudopelletierine-*N*-oxyl. The epr spectra of a number of similar stable, but unhindered, bicyclic nitroxides have been observed since that time.[4-6]

The pioneering work of Dupeyre and Rassat was followed in this laboratory by the preparation of nortropane-*N*-oxyl (**1**).[4] This compound (single crystals

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[1] Issued as N.R.C.C. No. 12811.

[2] R. M. Dupeyre and A. Rassat, *J. Amer. Chem. Soc.*, **88**, 3180 (1966).

[3] J. Bredt, *Justus Liebigs Ann. Chem.*, **437**, 1 (1924).

[4] K. Adamic, D. F. Bowman, T. Gillan, and K. U. Ingold, *J. Amer. Chem. Soc.*, **93**, 902 (1971), and references cited therein.

[5] A. Rassat and J. Ronzaud, *ibid.*, **93**, 5041 (1971), and references therein.

[6] E. G. Rozantsev and V. P. Ivanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (6) 1416 (1970).