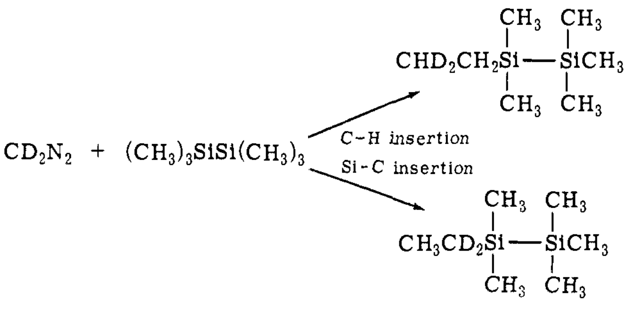
methyldisilane but otherwise under identical conditions, no products of reaction of diazomethane with these substances were detected. Since these substrates are quite reactive toward photochemically generated methylene, it is clear that no photogenic methylene was produced under the conditions used for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

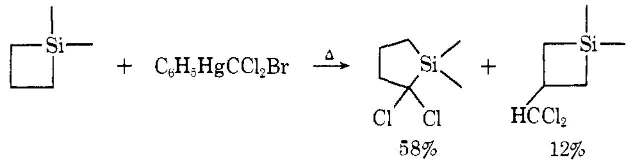
Carbon–hydrogen insertion was established as the reaction leading to the observed product by experiments with diazomethane-d_2. The reaction product



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).

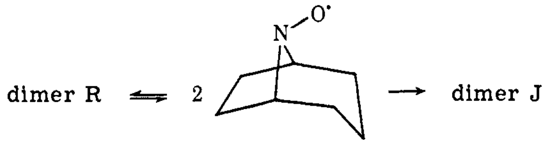
(3) J. Bredt, *Justus Liebigs Ann. Chem.*, **437**, 1 (1924).

(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.

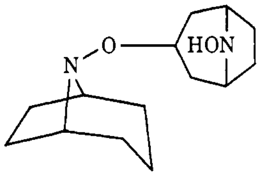
(6) E. G. Rozantsev and V. P. Ivanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (6) 1416 (1970).

of which are diamagnetic) was synthesized for studies of the *reversible* dimerization in solution of unhindered nitroxides to yield diamagnetic dimers (dimer R). During the course of these studies it was discovered that **1** also underwent an *irreversible* dimerization in the solid state and in some solvents. This change was accelerated by heat but occurred fairly readily at room temperature in CCl_4 (80% in 12 days).

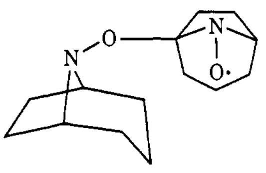


1

The irreversible dimer (J) is a white, microcrystalline material, mp 156° (decomposition at high temperatures), the infrared spectrum of which indicated no significant features other than hydrogen-bonded OH. Dimer J is diamagnetic both in the crystal form and in solution, but is readily oxidized by Ag_2O in benzene to give a solution whose spectrum showed splitting constants (a_N = 16 G, additional fine structure) similar to but not identical with those from **1** (a_N = 17 G, a_H (1 H) = 4 G).[7] The nmr spectrum showed an absorption at δ 4.4 suggesting an R_2CHOR group, consistent with structure **2**.[8] Catalytic reduction of dimer J (5% Pd/C, 95% EtOH, 5 hr, 50° (760 mm)), however, afforded 0.24 equiv of nortropane, but no norpseudotropine (or nortropine) could be detected among the oily reduction products by tlc.[9]



2



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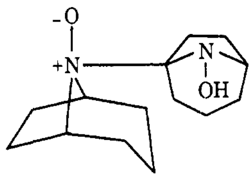
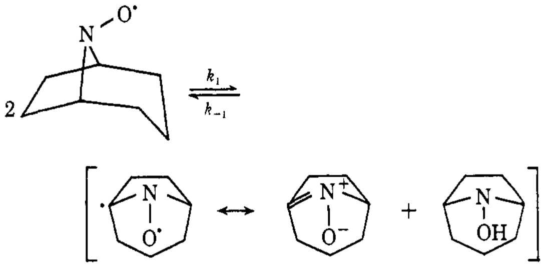


4

An attempt to remove traces of hydroxylamine **6** from **1** (0.75 g) by stirring for 24 hr with freshly prepared silver oxide (0.15 g) and hexane (70 cm^3) gave on fractional sublimation a residue of dimer J, recovered **1**, and dark red crystals (2%, mp 99–102°), shown by X-ray crystallography[10] to have structure **3**. This strongly suggested that dimer J was the corresponding hydroxylamine, **3**-H, but the esr spectrum of **3** (a_N = 19.3 G, a_H (1 H) = 7 G) was not identical with that obtained by oxidizing dimer J with Ag_2O. Preparative scale attempts to obtain **3** from dimer J and various oxidants were also unsuccessful. We again resorted to X-ray methods,[10] which showed dimer J (as the hydrochloride) to have structure **4**.[11]

The simplest mechanism to account for the dimerization of **1** involves a hydrogen abstraction by one molecule of **1** on a second to give a reactive intermediate, **5**, which is trapped within the solvent cage to give **4** directly.



5 **6**

$$5 + 6 \xrightarrow{k_2} \text{dimer J } (4)$$

nitroxide 1, $k_{dec} = 1.3 \times 10^{-5}\ M^{-1}\ \sec^{-1}$
$(CH_3CH_2)_2NO\cdot$, $k_{dec} = 1.36 \pm 0.32 \times 10^4\ M^{-1}\ \sec^{-1}$

A possible alternative route to dimer J is one in which **5** is trapped by a third molecule of **1**, followed by hydrogen transfer from **6**. However, this mechanism seems unlikely because formation of the polar amine oxide **4** is favored over formation of **3** even in nonpolar solvents.[12] Perhaps **3** arises from a small amount of **5** that is not trapped by **6** and escapes from the solvent cage. In the presence of silver oxide, **6** is apparently oxidized to regenerate **1** before it can reduce **3**.

A colorimetric study of the disappearance of **1** (initially 0.8 M in benzene, 30°) shows that the decay of **1** follows second-order kinetics[13] with k_{dec} (equivalent to k_1k_2/k_{-1} in our scheme) = $1.3 \times 10^{-5}\ M^{-1}\ \sec^{-1}$. For comparison, the second-order decay of diethyl nitroxide[4] proceeds with a rate constant of $(1.36 \pm 0.32) \times 10^4\ M^{-1}\ \sec^{-1}$ (benzene, 25°). This difference of 10^9 must presumably result from the decreased overlap between the π nitroxide orbitals and the bridgehead orbital in **5**, *i.e.*, Bredt's rule. In connection with the formation of **4** it is worth noting that **1** is more reactive in hydrogen abstractions than are stable, sterically hindered nitroxides. For example, **1** oxidizes aqueous hydrogen peroxide rapidly at room temperature with copious gas evolution, though 2,2,6,6-tetramethylpiperidine-1-oxyl is inert to these conditions.

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[7] We assign the secondary splittings in **1** and in **3** to the exo 3-H protons. This splitting in the product from dimer J is perhaps obscured by the presence of other radicals.

[8] The irreversible dimerization of 2,2,6,6-tetramethyl-4-piperidone-1-oxyl yields an analogous product: Y. Takeo, S. Morimura, and K. Murayama, *Bull. Chem. Soc. Jap.*, **44**, 2207 (1971).

[9] A small amount of an unstable solid, mp 113–116°, was also obtained whose mass spectrum was consistent with an isomer of nortropine, possibly 1-hydroxynortropane (4-aminocycloheptanone).

[10] E. J. Gabe, private communication. The X-ray structures of **3** and **4**·HCl were refined to agreement factors, R, of 5.8 and 5.4%, respectively.

[11] The unique bridgehead C–H in **4** is apparently downshifted to δ 4.4 by remote interaction with the nitrogen in the amine oxide group.

[12] Formation of **5** and **6** may actually proceed from dimer R or through ion pairs $[R_2NO^+R_2NO^-]$.

[13] There is some downward curvature in the plot of $[R_2NO]^{-1}$ *vs.* time beyond about 70% decomposition, but the reaction is complicated by precipitating dimer J and formation of colored by-products.

[14] N.R.C.C. Postdoctoral Fellow, 1971–1972.

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