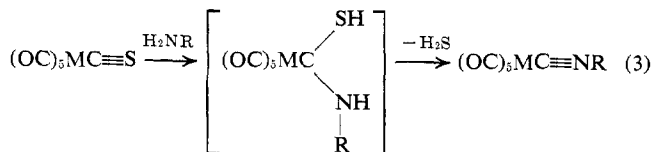


noted in thiocarbamoyl,<sup>11</sup> amidinium,<sup>12</sup> and amino-carbene<sup>13</sup> complexes. Surprisingly the -SH proton occurs at low field and does not exchange with D<sub>2</sub>O in acetone at 35° over a 20-min period.

Primary amines also react with the M(CO)<sub>5</sub>(CS) complexes. These reactions may proceed through a complex similar to those isolated from the secondary amine reactions. Hydrogen sulfide is rapidly lost with formation of isocyanide complexes.



Methyl isocyanide complexes were produced in essentially quantitative yield within 10 min when the M(CO)<sub>5</sub>(CS) compounds were allowed to react with methylamine in pentane solution at room temperature. The substituted complex *trans*-W(CO)<sub>4</sub>(CS)(PPh<sub>3</sub>) reacted more slowly, yielding the expected *trans* isocyanide compound after several hours. This lower reactivity probably results from a slower rate of amine attack on the thiocarbonyl carbon atom, which has a higher electron density than in the W(CO)<sub>5</sub>(CS) derivative.

An unusual isocyanide complex, W(CO)<sub>5</sub>CNCH<sub>2</sub>-COOCH<sub>3</sub>, was produced when W(CO)<sub>5</sub>(CS) in methanol was treated with glycine methyl ester. Aniline, hydrazine, and ammonia do not react with W(CO)<sub>5</sub>(CS) at room temperature. The complex C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub>(CS)<sup>+</sup> was previously reported to react with methylamine, giving a thiocarbamoyl complex<sup>14</sup> rather than a coordinated isocyanide.

The amine reactions reported here clearly indicate that the CS ligand is much more susceptible to nucleophilic amine attack than is CO. Milder nucleophiles such as alcohols and water did not react with W(CO)<sub>5</sub>(CS). Likewise, attempts to alkylate the S atom with Et<sub>3</sub>O<sup>+</sup>BF<sub>4</sub><sup>-</sup> gave no reaction.

**Acknowledgment.** We are grateful for support of this research through a National Defense Education Act (Title IV) Fellowship to B. D. D.

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### Formation of an Unstable Silicon-Carbon Double Bond in the Photodecomposition of Trimethylsilyldiazoacetate

Sir:

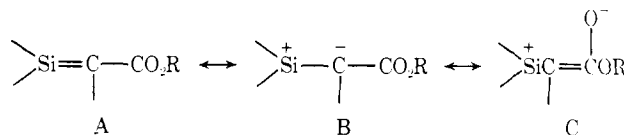
Recently, reports were published on the photochemical reactions of disilane<sup>1</sup> and silacyclobutane.<sup>2</sup> It was

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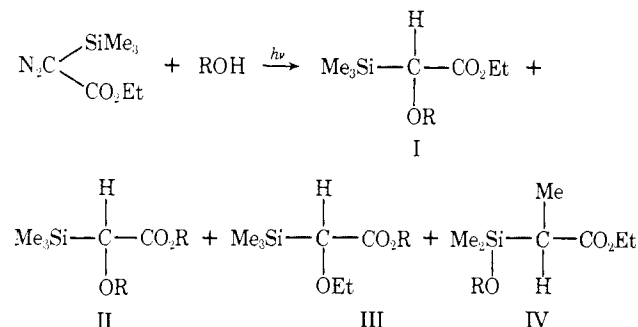
(2) P. Boudjouk and L. H. Sommer, *J. Chem. Soc., Chem. Commun.*, **54** (1973).

shown that an unstable intermediate with a silicon-carbon double bond is important in these reactions and that it reacts with alcohol to form an alkoxysilane.

We have initiated an investigation of the photochemical decomposition of ethyl trimethylsilyldiazoacetate<sup>3</sup> in alcohols, and we have established the formation of intermediate A which may be resonance stabilized by the contribution of structures B and C.



When ethyl trimethylsilyldiazoacetate is photolyzed with a high-pressure mercury lamp in alcohols, four products, I-IV, are obtained in approximately 60-90%



yield. All four products were structurally characterized by ir, nmr, and elemental analyses. Product I may be rationalized in terms of a trimethylsilyl(carbethoxy)-carbene reaction, and product III has been explained by a Wolff rearrangement, probably not involving carbene intermediate.<sup>4,5</sup> Product II may be derived *via* both carbene and ion pair<sup>4,5</sup> paths. The formation of IV, with a methyl migration, is quite interesting and is the main concern of the present communication. This reaction is quite general since rearranged products were formed in each system studied. The efficiency of migration varies with respect to solvent alcohol in the order *t*-BuOH > *i*-PrOH > EtOH > MeOH, in contrast with O-H insertion products (I and II) (Table I).

**Table I.** Photolysis of Ethyl Trimethylsilyldiazoacetate in Alcohols

Alcohol	Relative product yields, %			
	I	II	III	IV
MeOH	64	14	12	10
EtOH <sup>a</sup>	87			13
<i>i</i> -PrOH <sup>b</sup>	35	22	22	21
<i>t</i> -BuOH	40	17	8	35

<sup>a</sup> Products I, II, and III are all identical in ethanol. <sup>b</sup> Relative yields of I and II are obtained by nmr.

This implies that when the carbene does not show sufficient reactivity toward an oxygen atom (formation of products I and II *via* oxygen ylide), probably owing to steric hindrance of a neighboring bulky group,<sup>6</sup> then

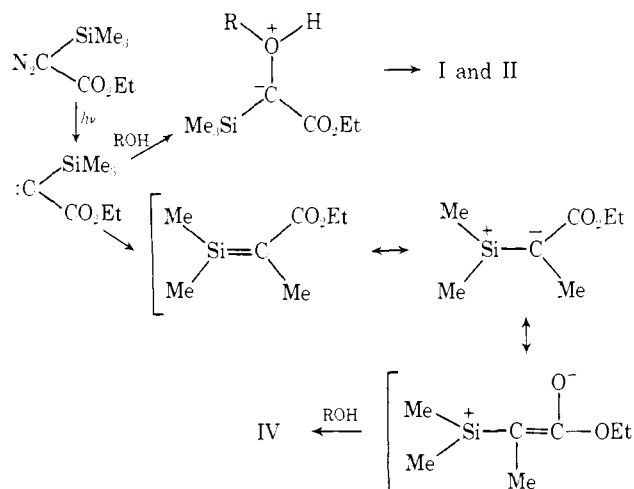
(3) U. Schöllkopf and N. Rieber, *Angew. Chem.*, **79**, 905 (1967).

(4) O. P. Strausz, T. DoMinh, and H. E. Gunning, *J. Amer. Chem. Soc.*, **90**, 1660 (1968).

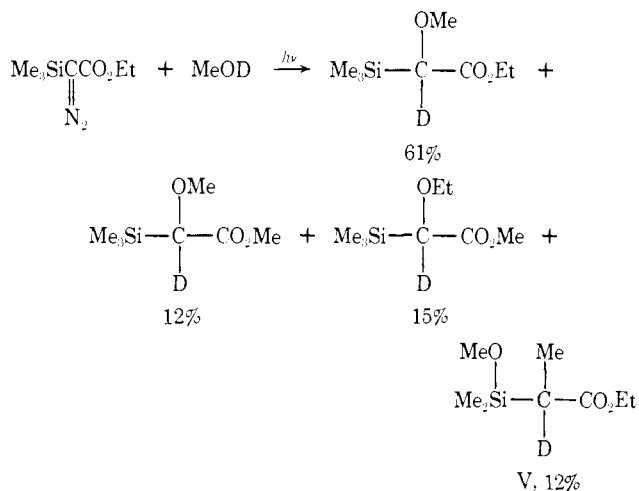
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the methyl migration proceeds more rapidly. We rationalize the formation of IV from the diazo compound as shown below.<sup>7,8</sup>



The possibility of the intervention of a silacyclopropane intermediate *via* 1,3 insertion of the carbene<sup>9,10</sup> was tested. Ethyl trimethylsilyldiazoacetate in methanol-*d*<sub>1</sub> was subjected to photodecomposition. These results indicate a very low probability for a silacyclopropane intermediate; the deuterium from methanol was only found on the  $\alpha$  carbon and not in the migrating methyl group. The structure of the methyl migration product V was deduced from its <sup>1</sup>H nmr spectrum [7



5.95 (2 H, q, CO<sub>2</sub>CH<sub>2</sub>), 6.58 (3 H, s, SiOCH<sub>3</sub>), 8.77 (3 H, t, CO<sub>2</sub>CCH<sub>3</sub>), 8.83 (3 H, br s, SiCCH<sub>3</sub>), and 9.87 (6 H, s, Si(CH<sub>3</sub>)<sub>2</sub>), and its exact parent peak (found, *m/e* 191.1023; calcd, *m/e* 191.1083). The isotopic purity of V was found to be higher than 99% from the relative peak heights.

Finally the evidence against the role of trimethylsilyl(carbomethoxy)carbonium ion intermediate which might be formed by protonation of the diazo compound was also obtained. Ethyl trimethylsilyldiazoacetate in methanol in the presence of a catalytic amount of hydrochloric acid did not produce a methyl migration

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product, but did produce ethyl methoxyacetate quantitatively.<sup>11</sup> This reaction indicates that the carbonium ion is not implicated in the photoreaction, at least not in the formation of methyl migration product.

Further evidence against any role of trimethylsilyl(carbomethoxy)carbonium ion intermediate comes from the irradiation of ethyl trimethylsilyldiazoacetate in a methanol solution of lithium bromide.<sup>12</sup> The photolysis did not produce the expected bromoacetate and the original product distribution was not affected by the lithium bromide.

We are currently investigating other silicon-containing diazo compounds as sources for different Si=C species as part of our study.

**Acknowledgment.** We thank the Shinetsu Chemical Co. for providing trimethylchlorosilane.

(11) One-thirtieth millimole of acid decomposed 1 mmol of the diazo compound in 2 ml of methanol at room temperature, and the product was identified by comparison with an authentic sample.

(12) One millimole of lithium bromide was used for the photolysis of 1 mmol of the diazo compound in 2 ml of methanol.

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### A Novel One-Step Synthesis of [8]Paracyclophanes. Cycloaddition of Dispiro[2.2.2]deca-4,9-diene with 1,3-Butadienes

Sir:

In spite of the considerable interest in the chemistry of the lower homologs of [*m*]paracyclophanes, only a few preparation methods have been available.<sup>1-3</sup> We report here the cycloaddition of dispiro[2.2.2]deca-4,9-diene (**1**)<sup>4</sup> with a variety of substituted 1,3-butadienes, which provides a convenient preparation method of [8]paracyclophanes and whose reaction mechanism is of considerable interest.

In a general procedure, 200 mg (1.51 mmol) of **1** and 2 equiv of diene in 8 ml of benzene were heated at 160°C for 5 hr in a sealed glass ampoule under argon. The reaction products were isolated either by preparative vpc or column chromatography on silica gel and their structures were confirmed by elemental analysis and mass, nmr, uv, and ir spectroscopies.<sup>5</sup> The reaction was quite general and with both 1-substituted and 1,4-disubstituted 1,3-butadienes afforded [8]paracyclophanes in 60–90% yields as shown in Table I. In nmr spectra of *trans*-[8]paracycloph-4-enes (**3**), the characteristic

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(5) For example, **3b**: *m/e* 244 (P<sup>+</sup>); nmr (100 MHz, CCl<sub>4</sub>, TMS)  $\delta$  0.9–2.5 (br m, 9 H), 3.02 (m, 2 H), 3.43 (s, 3 H), 3.95 (d of d, *J* = 8 and 15 Hz, 1 H), 4.00 (d of d, *J* = 9 and 15 Hz, 1 H), 6.90 (m, 4 H); uv (in EtOH)  $\lambda_{\max}$  ( $\epsilon$ ) 222 (7300), 266 (sh, 320), 271 (400), 278 nm (360). **4b**: *m/e* 244 (P<sup>+</sup>); nmr (100 MHz, CCl<sub>4</sub>, TMS)  $\delta$  1.35 (m, 4 H), 2.30 (m, 5 H), 2.95 (m, 2 H), 3.43 (s, 3 H), 4.50 (d of d, *J* = 9 and 11 Hz, 1 H), 4.70 (d of d, *J* = 9.5 and 11 Hz, 1 H), 6.94 (s, 2 H), 7.00 (s, 2 H); uv (in EtOH)  $\lambda_{\max}$  ( $\epsilon$ ) 226 (6200), 277 (370), 284 nm (330).