

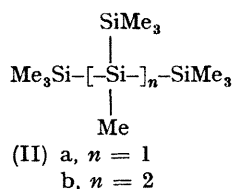
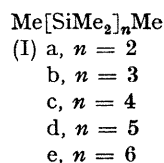
## Photolysis of Permethylated Linear and Branched-chain Polysilanes

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**Summary** Permethylated linear polysilanes  $\text{Me}[\text{SiMe}_2]_n\text{Me}$  ( $n = 3-6$ ) and branched-chain polysilanes  $\text{Me}_3\text{Si}[(\text{Me}_3\text{Si})\text{SiMe}_2]_n\text{SiMe}_3$  ( $n = 1,2$ ) undergo photolysis at room temperature with loss of dimethylsilylene  $\text{Me}_2\text{Si}$ : in the former case and (trimethylsilyl)methylsilylene  $\text{Me}_3\text{SiSiMe}$ : in the latter.

The recently discovered<sup>1</sup> photolysis of dodecamethylcyclohexasilane  $(\text{Me}_2\text{Si})_6$  to produce two of the lower homologues of permethylated cyclopolysilanes  $(\text{Me}_2\text{Si})_n$ , ( $n = 4, 5$ ) with simultaneous generation of dimethylsilylene prompted the photolysis of some permethylated linear (I)<sup>2</sup> and branched-chain polysilanes (II).<sup>3,4</sup>



The photolysis of the linear polysilanes (tetra to hexa) (Ic-e) always gave rise to octamethyltrisilane (Ib) as the sole volatile product, and unidentified polymeric material. The generation of dimethylsilylene during the photolysis, which may be largely responsible for the formation of the polymeric material, could be confirmed by its isolation in good yield as an insertion product (1,1-diethyl-1,2,2-trimethyldisilane<sup>1</sup>) into the silicon-hydrogen bond of diethylmethylsilane (Table).

Of interest is the photolysis of the permethylated branched-chain polysilanes (II) which is believed to proceed with generation of a novel bivalent silicon intermediate, (trimethylsilyl)methylsilylene. Thus the photolysis of

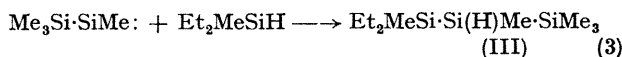
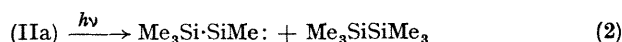
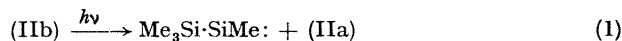
2,3-bis(trimethylsilyl)octamethyltetrasilane (IIb)<sup>4</sup> (4.0 g) in presence of diethylmethylsilane (20 g) in cyclohexane for 15 h gave 1,1-diethyl-1,2,3,3,3-pentamethyltrisilane (III)

TABLE

Compound	Photolysis of linear permethylpolysilanes (I) <sup>a</sup>			
	Time (h)	Yield (%)		
(Ic)	40	0	86	105
(Id)	40	0	94	101
(Ie)	40	0	74	109
(Ib)	65	24	67	59
(Ic) <sup>b</sup>	15	87 <sup>c</sup>	66	Trace

<sup>a</sup> Photolysis was carried out in cyclohexane at room temperature with a low-pressure mercury lamp (2537 Å). <sup>b</sup> Photolysis in presence of a large excess of diethylmethylsilane. <sup>c</sup>  $\text{Et}_2\text{MeSiSiMe}_2\text{H}$ .

(3.4 g) and 2-(trimethylsilyl)heptamethyltrisilane (IIa) (1.1 g), along with a small amount of hexamethyldisilane. Similarly, (IIa) was photolysed in presence of diethylmethylsilane to give (III) and hexamethyldisilane as the main products. The structure of (III) was verified by its <sup>1</sup>H n.m.r., i.r., and mass spectra. It can be concluded that the predominant reaction path for the photolysis of the branched-chain polysilanes and formation of (III) is represented by equations (1-3).



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<sup>1</sup> M. Ishikawa and M. Kumada, *Chem. Comm.*, 1970, 612.

<sup>2</sup> M. Kumada, M. Ishikawa, and S. Maeda, *J. Organometallic Chem.*, 1966, 5, 120.

<sup>3</sup> H. Gilman and R. L. Harrel, *J. Organometallic Chem.*, 1966, 5, 199.

<sup>4</sup> M. Ishikawa and M. Kumada, to be published.