Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

PHOTOLYSIS OF DODECAMETHYLCYCLOHEXASILANE. GENERATION OF DIMETHYLSILYLENE AND SOME OF ITS INSERTION REACTIONS

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(Received March 20th, 1972)

SUMMARY

The UV photolysis of dodecamethylcyclohexasilane (I) in cyclohexane at ca. 45° proceeds readily with loss of dimethylsilylene species to give two of the lower homologs, *viz.*, decamethylcyclopentasilane and octamethylcyclotetrasilane. Prolonged photolysis leads to the formation of a significant amount of 1,4- dihydrohexamethyltetrasilane, which can be ascribed to homolytic scission of the silicon–silicon bond of the cyclotetrasilane. The photochemically generated dimethylsilylene species readily insert into silicon–hydrogen or silicon–methoxy bonds of appropriate monosilane derivatives. However, photolysis of (I) in dimethyldichlorosilane affords several products whose formation may be best explained in terms of a direct reaction of photochemically excited polysilanes with chlorosilanes. Other evidence for this comes from the photolysis of tetradecamethylhexasilane in dimethyldichlorosilane.

INTRODUCTION

The photochemical behavior of monosilane and its derivatives has been studied by mercury sensitized photolysis[1–4], flash photolysis[5,6] and vacuum ultraviolet photolysis[7–9]. However, no interest had been shown in the photolysis of organopolysilanes, which exhibit characteristic absorptions in the ultraviolet region[10], until 1969, when we initiated a series of studies on the photolysis of permethylated derivatives of cyclic[11,12] and acyclic polysilanes[12,13] and of cyclic silahydrocarbons containing silicon–silicon linkages in the ring[14].

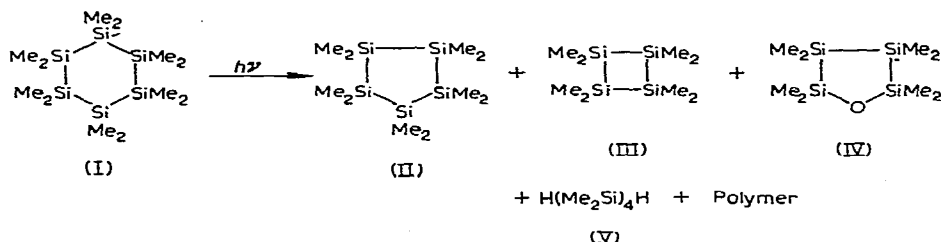
In preliminary accounts[11,13], we reported briefly that dodecamethylcyclohexasilane (I) and some of the permethylated linear and branched-chain polysilanes undergo contraction of their skeletal silicon–silicon chain with loss of divalent silicon species, when irradiated with ultraviolet light. In this paper, we describe a detailed photochemical study of permethylated cyclopolysilanes and insertions of the dimethylsilylene intermediate generated during photolysis into some heteropolar single bonds.

RESULTS AND DISCUSSION

Photolysis of dodecamethylcyclohexasilane

Dodecamethylcyclohexasilane (I)[15–17] has been found to undergo photolysis

readily when its solution in cyclohexane under bubbling dry nitrogen at ca. 45° is irradiated for 20–40 h with ultraviolet light (2537 Å), giving rise to several products. These include two of the lower permethylated cyclopolysilanes *viz.*, decamethylcyclopentasilane (II)[18,19] and octamethylcyclotetrasilane (III), and also rather unexpected compounds, *viz.* 2,2,3,3,4,4,5,5-octamethyl-1-oxa-2,3,4,5-tetrasilacyclopentane (IV), 1,4-dihydrooctamethyltetrasilane (V)[20–22], and a nonvolatile polymer. Except for the polymer these products were isolated by preparative GLC and identified by mass, IR and ^{1}H NMR spectroscopic studies (see Experimental). The photolysis of (I) affords a novel and very convenient route to (II) and particularly to (III), the latter, a fairly air-sensitive snow-white crystalline solid melting at 105–106°, is the lowest member of the homologous series of permethylated cyclopolysilanes to have been isolated and fully substantiated*.



The relative rate of the photolysis is rather strongly dependent upon the initial concentration of (I), and the relative yields of the products are also dependent upon the duration of reaction. Typical results are summarized in Table 1. At a high concentration (Run 1), although the major product after 20 h irradiation was the cyclopentasilane (II), a relatively large amount of the unchanged starting substance (I) remained. At a lower concentration (Run 4), the starting cyclohexasilane (I) was converted completely to two of the lower homologs, but a small amount of the open-chain product (V) was also formed. Prolonged irradiation of the same dilute solution (Run 5) led to an increased yield of the cyclotetrasilane (III), but the amount of the open-chain product (V) also increased.

The formation of compound (IV) may be ascribed to accidental oxidation of the cyclotetrasilane (III) by oxygen which could not be excluded completely during photolysis and/or the subsequent work-up; (III) is, as mentioned above, fairly air-sensitive.

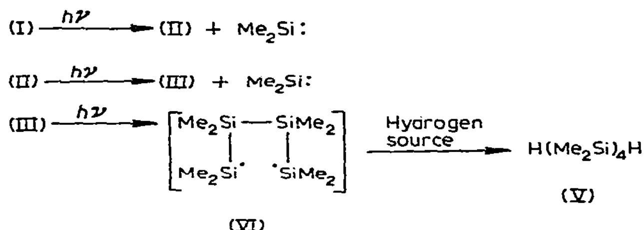
The photochemical degradation of (I) to (II) to (III) is pictured as involving loss of the dimethylsilylene intermediate[25], Me_2Si: (for evidence, see below).

Recently, Narula[24] has briefly reported that hexamethyldisilane undergoes photolysis upon irradiation with ultraviolet light (236 nm) to produce trimethylsilyl radicals as intermediates. In our case, the formation of the open-chain 1,4-dihydrotetrasilane in significant amounts upon prolonged irradiation (Run 5) suggests that

* Russian chemists[23] reported that the cyclotetrasilane (III) was obtained as crystals melting at 194–197° from pyrolysis of "polydimethylsilane" (prepared by lithium coupling of dimethyldichlorosilane in tetrahydrofuran). However, no elemental analyses or molecular weight data were given, although the IR spectrum was shown. Judging from the melting point reported, it seems likely that their product was the cyclopentasilane (II), and not the cyclotetrasilane (III).

the cyclotetrasilane (III) undergoes homolytic scission of the silicon–silicon bond to give a diradical (VI), which then abstracts hydrogen atoms from the solvent or methyl groups of the polysilanes present in the reaction system. Doubtless, the formation of a small amount of the 1,3-dihydrotrisilane[21] in Run (5) can be ascribed to further photolysis of (V).

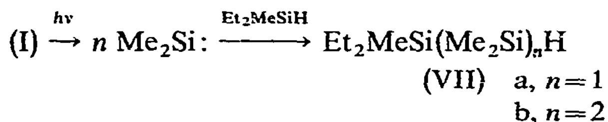
Summarizing these results, we can best represent the mode of photolysis of (I) by the following scheme:



The silylene species generated during photolysis are thought to polymerize in the absence of a trapping agent. The IR spectrum of the solid polymeric material obtained in Runs (1) and (2) showed a weak absorption at 2090 cm^{-1} due to the Si–H stretching vibration, while the spectra of the liquid polymers produced in Runs (4) and (5) exhibited a strong Si–H absorption band in the same region. All the polymeric materials from Runs (1) through (5) reacted with bromine very violently, suggesting the presence of silicon–silicon bonds[10a].

Insertion of dimethylsilylene into some heteropolar single bonds

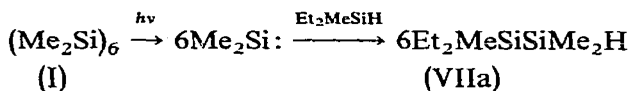
(*a*). *Insertion into Si–H bonds.* The dimethylsilene species has been shown by several research groups[20,25a,26] to insert readily into a silicon–hydrogen bond. Using this "trapping" technique, we have now established that the dimethylsilylene intermediate is generated during the photolysis. Thus, the irradiation of the cyclohexasilane (I) in the presence of a large excess of diethylmethylsilane in cyclohexane for 20 h gave 1,1-diethyl-1,2,2-trimethyldisilane (VIIIa)* and 1,1-diethyl-1,2,2,3,3-pentamethyltrisilane (VIIb)* in the ratio of 2.5/1, along with some amounts of (II) and (III), in high total yield. Here, polymeric material was produced only in traces.



$$\text{(I)} \xrightarrow{h\nu} n\ Me_2Si: \xrightarrow{Et_2MeSiH} Et_2MeSi(Me_2Si)_nH$$

(VII) a, $n=1$; b, $n=2$

With the intention of determining how much dimethylsilylene would insert into Si–H bonds, we photolyzed (I) in diethylmethylsilane in a sealed quartz tube for 60 h**. From this run, (VIIa) as the overwhelming major product was obtained in 46% yield, based on the following stoichiometric equation:



$$\underset{\text{(I)}}{(Me_2Si)_6} \xrightarrow{h\nu} 6Me_2Si: \xrightarrow{Et_2MeSiH} \underset{\text{(VIIa)}}{6Et_2MeSiSiMe_2H}$$

* For identification, see the succeeding paper[27].

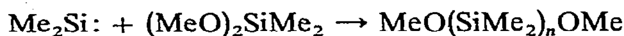
** Detailed description of this technique is given in ref. 27.

In this reaction, although small amounts of another insertion product (VIIb) and of the cyclic siloxane (IV) were also formed, none of the cyclotetrasilane (III) and cyclopentasilane (II) was detected.

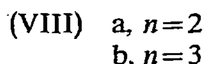
In another related study[27] we observed that diethylmethylsilane can trap 69% of dimethylsilylene generated by photolysis of decamethyltetrasilane under similar conditions. Therefore, the quantity of dimethylsilylene actually generated from (I) must be considerably larger than that corresponding to the above observed yield of (VIIa). Dimethylsilylene species which are not trapped by the silicon–hydrogen compound or some other reactive species composed of a few Me_2Si units (such as free silyl radicals) are thought to give polymeric materials by complex, and not yet understood, routes.

(*b*). *Insertion into Si–OMe and Si–Cl* bonds. Several examples of silylenes reacting with alkoxy- or halo-substituted polysilanes have been reported to date. The insertion of silylenes into the silicon–oxygen or silicon–halogen bonds in polysilanes is rather general[25e,f]. However, several attempts to effect the related reactions with monosilane derivatives have been unsuccessful. Silicon tetrafluoride did not react with difluorosilylene[28], and the reaction of dimethylsilylene with dimethyldimethoxysilane has been shown to be kinetically unimportant in the thermolysis of the corresponding disilane[25d]. These observations prompted us to investigate the reaction of photochemically generated dimethylsilylene with methoxy- and chloro-derivatives of monosilane.

The insertion of dimethylsilylene generated by photolysis of (I) into dimethyldimethoxysilane did proceed smoothly to give, in good yield, 1,2-dimethoxytetramethyldisilane (VIIIa) and 1,3-dimethoxyhexamethyltrisilane (VIIIb) in the ratio of 1.6/1.

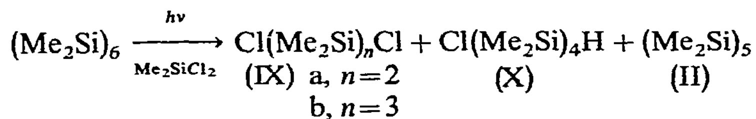


$$Me_2Si: + (MeO)_2SiMe_2 \rightarrow MeO(SiMe_2)_nOMe$$



(VIII) a, $n=2$
b, $n=3$

On the other hand, the photolysis of (I) in dimethyldichlorosilane gave rise to unexpected results; 1,2-dichlorotetramethyldisilane (IXa), 1,3-dichlorohexamethyltrisilane (IXb), 1-chloro-4-hydrooctamethyltetrasilane (X) and the cyclopentasilane (II) were formed in the ratio of 1/3.6/1.6/2.5, respectively.



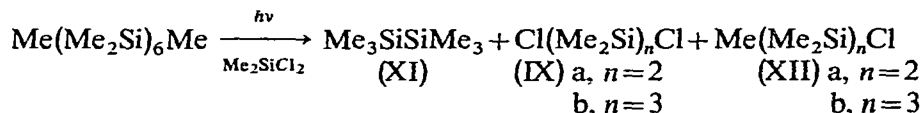
$$(Me_2Si)_6 \xrightarrow[Me_2SiCl_2]{h\nu} Cl(Me_2Si)_nCl + Cl(Me_2Si)_4H + (Me_2Si)_5$$

(IX) a, $n=2$; b, $n=3$ (X) (II)

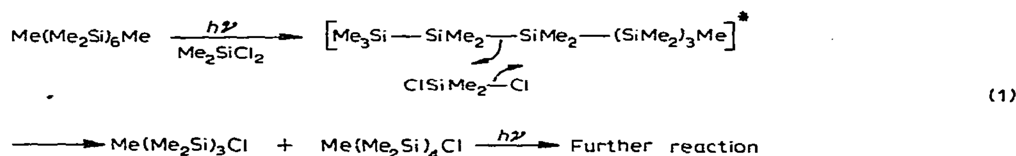
In this case, the trisilane species (IXb) was produced in abundance, in contrast with the insertion into Si–H and Si–OMe bonds, from which the disilane species (VIIa) and (VIIIa), respectively, were formed in abundance. This unusual feature of the photolysis in dimethyldichlorosilane may indicate that a direct reaction of photochemically excited polysilanes with the chlorosilane, to give α,ω-dichloropolysilanes (IX), occurs in competition with the generation of dimethylsilylene.

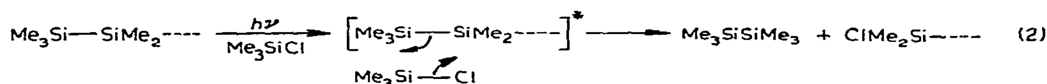
Indeed, convincing evidence for this was afforded by the photolysis of tetradecamethylhexasilane[29] in dimethyldichlorosilane, which gave rise to the formation of hexamethyldisilane (XI), dichlorodisilane (IXa), dichlorotrisilane (IXb), chloro-

pentamethyldisilane (XIIa) and 1-chloroheptamethyltrisilane (XIIb) in the ratio of 1.0/1.6/2.6/2.0/1.3, respectively.



If the above reaction involved only generation of dimethylsilylene from the permethylated polysilanes followed by its insertion into Si–Cl bonds, both octamethyltrisilane (which has been found to be highly resistant to photolysis[27]) and the dichlorodisilane (IXa) should be produced as the main products. In fact, octamethyltrisilane was formed only in a negligible amount. Furthermore, the most abundantly produced compound was the dichlorotrisilane (IXb). The formation of (XI), (XIIa) and (XIIb) may be best explained in terms of the direct reaction of the photo-excited polysilanes with dimethyldichlorosilane, as exemplified below:





The trimethylchlorosilane participating in reaction (1) was probably produced by a reaction analogous to (2).

EXPERIMENTAL

All melting and boiling points reported here are uncorrected. Molecular weights were determined by mass spectroscopic studies.

Materials

Cyclohexane used as solvent was purified by treatment with concentrated sulfuric acid and refluxing over sodium. The distillate was dried over lithium aluminum hydride and distilled from it just before use. Diethylmethylsilane[30], dimethyldimethoxysilane[31], and dodecamethylcyclohexasilane (I)[16] were prepared by methods described in the literature.

GLC analysis

An Aerograph Model 90-P gas chromatograph with a thermal conductivity detector was used for analysis and separation of the reported products. All the products were easily separated by using a column containing 30% Apiezon Grease L (3/8 in. x 20 ft.).

Photolysis of dodecamethylcyclohexasilane (I)

The following is typical of the procedures used. A solution of 4.0 g (0.011 mole)

TABLE 1

PHOTOLYSIS OF DODECAMETHYLCYCLOHEXASILANE (I) IN CYCLOHEXANE (200 ml)

Run No.	*(I) used (g)*	*Time (h)*	*Yield of volatile products (%)*[a]					*Residue (g)*
			$(Me_2Si)_4$-O (IV)	*$H(Me_2Si)_4H$ (V)*	*$(Me_2Si)_4H$ (III)*	*$(Me_2Si)_5$ (II)*	*$(Me_2Si)_6$ (I)*	
1	8	20	2		3	55	40	3.0[b]
2	6	20	3		11	67	19	2.3[b]
3	4	20	3	Trace	12	68	17	1.7[b]
4	2	20	8	5	17	70		1.1[c]
5[d]	2	40	11	14	20	52		1.0[c]

[a] Yields were calculated on the basis of peak area ratios obtained by GLC of the distillates. [b] Solid. [c] Liquid. [d] $H(Me_2Si)_3H$ (3% yield) was also detected.

TABLE 2

MELTING POINTS, ^{1}H NMR AND OTHER DATA FOR ISLATED PRODUCTS

Compound No.	*Formula*	*M.p.*[a] *(°C)*	*Mol. wt. found (calcd.)*	*Chemical shifts (τ)*		
				$SiCH_3$	*(H)$SiCH_3$*	*(CH_3)SiH*
(II)	$(Me_2Si)_5$	187–189[b]	290 (290.79)	9.85		
(III)	$(Me_2Si)_4$[c]	105–106	232 (232.63)	9.77		
(IV)	$(Me_2Si)_4$-O[d]	45	248 (248.63)	9.82		
(V)	$H(Me_2Si)_4H$	[e]		9.75	9.80	5.92

[a] In a sealed capillary. [b] Lit.[18a]: m.p. 188–190°. [c] Found: C, 41.04; H, 10.26. $C_8H_{24}Si_4$ calcd.: C, 41.30; H, 10.40%. [d] IR spectrum showed a very strong absorption of ν(SiOSi) at 980 cm^{-1}; Found: C, 38.37; H, 9.76. $C_8H_{24}OSi_4$ calcd.: C, 38.64; H, 9.73%. [e] Liquid, n_D^{20} 1.4935 (lit.[21]: n_D^{20} 1.4922).

of (I) in 200 ml of dry cyclohexane was irradiated for 20 h with a low-pressure mercury lamp (10 watt), fitted with a Vycor filter (2537 Å), under bubbling nitrogen at ca. 45°. Most of the cyclohexane was distilled off under nitrogen, and the residue was distilled under reduced pressure, to give the volatile products boiling up to 140°/1 mmHg a polymer (1.7 g) being left as a residue. The relative yields of the products contained in the distillate were determined by GLC (see Table 1), individual products were isolated by preparative GLC. Melting points, molecular weights and ^{1}H NMR data, together with the results of elemental analysis for isolated products, are listed in Table 2.

Photolysis of (I) in the presence of diethylmethylsilane

A mixture of 6 g (0.017 mole) of (I) and 20 g (0.2 mole) of diethylmethylsilane dissolved in 200 ml of cyclohexane was photolyzed for 20 h. The reaction mixture was concentrated and the residue was distilled under reduced pressure to give 7.8 g of colorless liquid boiling over a range of 49–152°/17 mmHg. GLC analysis of this pro-

duct showed two peaks corresponding to 1,1-diethyl-1,2,2-trimethyldisilane (VIIa)[27] and 1,1-diethyl-1,2,2,3,3-pentamethyltrisilane (VIIb)[27], in an area ratio of 2.5/1, along with much smaller peaks corresponding to the cyclic siloxane (IV), cyclotetra- (III) and -pentasilane (II).

Photolysis of (I) in dimethyldimethoxysilane

(I) (8.0 g, 0.023 mole) in 200 ml of dimethyldimethoxysilane was irradiated for 40 h. The reaction mixture was fractionally distilled to give 8.4 g of 1,2-dimethoxytetramethyldisilane, b.p. 146–148°, n_D^{20} 1.4252 (lit.[32] b.p. 84°/90 mmHg, n_D^{26} 1.4207), 4.8 g of 1,3-dimethoxyhexamethyltrisilane, b.p. 92–93°/20 mmHg, n_D^{20} 1.4587 (lit.[32] b.p. 77°/10 mmHg, n_D^{26} 1.4569) and 2.4 g of residue.

Photolysis of (I) in dimethyldichlorosilane

(I) (12 g, 0.034 mole) in 400 ml of dimethyldichlorosilane was irradiated for 40 h. Products from two runs were combined and fractionally distilled under reduced pressure to give 2.2 g of 1,2-dichlorotetramethyldisilane, b.p. 46°/18 mmHg, n_D^{20} 1.4541 (lit.[33] b.p. 146–148°, n_D^{20} 1.4545), 8.0 g of 1,3-dichlorohexamethyltrisilane, b.p. b.p. 94–95°/18 mmHg, n_D^{20} 1.4848 (lit.[29] b.p. 82–83°/11 mmHg, n_D^{20} 1.4852), 3.5 g of 1-hydro-4-chlorooctamethyltetrasilane, b.p. 114–116°/18 mmHg, n_D^{20} 1.4972 (lit.[34] b.p. 59°/0.8–1.0 mmHg, n_D^{20} 1.4986) (Found: mol. wt., 268. $C_8H_{25}ClSi_4$calcd., mol. wt., 269.1), 5.5 of crude cyclopentasilane (II) and 11 g of residue.

Photolysis of tetradecamethylhexasilane in dimethyldichlorosilane

Tetradecamethylhexasilane[29] (4 g, 0.011 mole) in 100 ml of dimethyldichlorosilane was irradiated for 40 h. The mixture was distilled under reduced pressure to give 5.5 g of a colorless liquid boiling over a range of 33–98°/13 mmHg, consisting of hexamethyldisilane, chloropentamethyldisilane[33], 1,2-dichlorotetramethyldisilane[33], 1-chloroheptamethyltrisilane[21] and 1,3-dichlorohexamethyltrisilane[29] in the ratio already mentioned. Each of these products was identified by comparison of its GLC retention time with that of an authentic sample.

ACKNOWLEDGEMENT

The cost of this research was defrayed in part from Grant-in-Aid for Scientific Research of the Ministry of Education, to which the authors' thanks are due. The authors are also greatly indebted to the Tokyo-Shibaura Electric Co., Ltd. for support of this work.

REFERENCES

1 H. J. Emeleus and K. Stewart, *Trans. Faraday Soc.*, 32 (1936) 1577.
2 D. G. White and E. G. Rochow, *J. Amer. Chem. Soc.*, 76 (1954) 3897.
3 H. Niki and G. J. Mains, *J. Phys. Chem.*, 68 (1964) 304.
4 M. A. Nay, G. N. C. Woodall, O. P. Strausz and H. E. Gunning, *J. Amer. Chem. Soc.*, 87 (1965) 179.
5 G. Herzberg and R. D. Verma, *Can. J. Phys.*, 42 (1964) 395.
6 I. Dubois, G. Herzberg and R. D. Verma, *J. Chem. Phys.*, 47 (1967) 4246.
7 O. P. Strausz, K. Obi and W. K. Duholke, *J. Amer. Chem. Soc.*, 90 (1968) 1359.
8 K. Obi, A. Clement, H. E. Gunning and O. P. Strausz, *J. Amer. Chem. Soc.*, 91 (1969) 1622.

9 M. A. Ring, G. D. Beverly, F. H. Koester and R. P. Hollandsworth, *Inorg. Chem.*, 8 (1969) 2033.
10 For reviews see, *e.g.*,
(a) M. Kumada and K. Tamao, *Advan. Organometal. Chem.*, 6 (1968) 19;
(b) K. M. MacKay and R. Watt, *Organometal. Chem. Rev. A*, 4 (1969) 137;
(c) B. G. Ramsey, *Electronic Transitions in Organometalloids*, Academic Press, New York and London, 1969.
11 M. Ishikawa and M. Kumada, *Chem. Commun.*, (1970) 612.
12 M. Ishikawa and M. Kumada, *Chem. Commun.*, (1971) 507.
13 M. Ishikawa and M. Kumada, *Chem. Commun.*, (1971) 489.
14 (a) T. Yamanaka, M. Ishikawa and M. Kumada, *24th Annual Meeting of the Chemical Society of Japan, Osaka*, April 1-4, 1971, Abstr. No. 3, p. 1194;
(b) T. Yamanaka, M. Ishikawa and M. Kumada, *Symposium on Organometallic Chemistry, Nagoya (Japan)*, Oct. 15–17, 1971, Abstr. p. 167.
15 C. A. Burkhard, *J. Amer. Chem. Soc.*, 71 (1959) 963.
16 H. Gilman and R. A. Tomasi, *J. Org. Chem.*, 28 (1963) 1615.
17 U. G. Stolberg, *Angew. Chem.*, 75 (1963) 206.
18 (a) E. Carberry and R. West, *J. Organometal. Chem.*, 6 (1966) 582;
(b) E. Carberry and R. West, *J. Amer. Chem. Soc.*, 91 (1969) 5440.
19 M. Kumada, M. Ishikawa, S. Sakamoto and S. Maeda, *J. Organometal. Chem.*, 17 (1969) 223.
20 E. Wiberg, O. Stecher, H. J. Andrascheck, L. Kreuzbichler and E. Staude, *Angew. Chem.*, 75 (1963) 516.
21 M. Kumada, M. Ishikawa and S. Maeda, *J. Organometal. Chem.*, 2 (1964) 478.
22 H. Gilman and D. R. Chapman, *J. Organometal. Chem.*, 5 (1966) 392.
23 O. M. Nefedov, M. N. Manakov and A. D. Petrov, *Dokl. Akad. Nauk SSSR*, 147 (1962) 1376; see also O. M. Nefedov, G. Garzo, T. Szekely, V. I. Shiryaev, *Dokl. Akad. Nauk SSSR*, 164 (1965) 822.
24 S. P. Narula, *J. Indian Chem. Soc.*, 46 (1969) 1067.
25 For dimethylsilylene, see, *e.g.*,
(a)P. S. Skell and E. J. Goldstein, *J. Amer. Chem. Soc.*, 86 (1964) 1442;
(b) O. M. Nefedov and M. N. Manakov, *Angew. Chem.*, 78 (1966) 1039;
(c) W. H. Atwell and D. R. Weyenberg, *J. Organometal. Chem.*, 5 (1966) 594; *J. Amer. Chem. Soc.*, 90 (1968) 3834;
(d) W. H. Atwell, L. G. Mahone, S. F. Hayes and J. G. Uhlmann, *J. Organometal. Chem.*, 18 (1969) 69;
(e) W. H. Atwell and D. R. Weyenberg, *Angew. Chem.*, 81 (1969) 485;
(f) D. R. Weyenberg and W. H. Atwell, *Pure Appl. Chem.*, 19 (1969) 343.
26 K. Yamamoto, H. Okinoshima and M. Kumada, *J. Organometal. Chem.*, 27 (1971) C31.
27 M. Ishikawa, T. Takaoka and M. Kumada, *J. Organometal. Chem.*, 42 (1972) 333.
28 P. L. Timms, R. A. Kent, T. C. Ehlert and J. L. Margrave, *J. Amer. Chem. Soc.*, 87 (1965) 2824; for a review, see J. L. Margrave and P. W. Wilson, *Accounts Chem. Res.*, 4 (1971) 145.
29 M. Kumada and M. Ishikawa, *J. Organometal. Chem.*, 1 (1963) 153.
30 F. P. Price, *J. Amer. Chem. Soc.*, 69 (1947) 2600.
31 (a) W. Simpson, *Brit. Patent*, 635, 726; *Chem. Abstr.*, 44 (1950) 6426;
(b) D. Seyferth and E. G. Rochow, *J. Org. Chem.*, 20 (1955) 250.
32 W. H. Atwell and D. R. Weyenberg, *J. Organometal. Chem.*, 7 (1967) 71.
33 M. Kumada, M. Yamaguchi, Y. Yamamoto, J. Nakajima and K. Shiina, *J. Org. Chem.*, 21 (1954) 1264.
34 H. Gilman and D. R. Chapman, *Chem. Ind. (London)*, (1965) 1788.