

REACTIONS OF PENTAFLUOROPHENYLTRIMETHYLSILANE AND CYANOMETHYLTRIMETHYLSILANE WITH CARBONYL COMPOUNDS CATALYZED BY CYANIDE ANIONS

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Summary

Treatment of pentafluorophenyltrimethylsilane (I) and cyanomethyltrimethylsilane (II) with enolizable ketones in the presence of a catalytic amount of potassium cyanide-18-crown-6 complex gave the corresponding trimethylsilyl enol ethers. The same dehydrogenative silylation of acetylacetone and benzoylacetone with silane I was extended to the preparation of 2,4-bis(trimethylsiloxy)-1,3-pentadiene and 1-phenyl-1,3-bis(trimethylsiloxy)-1,3-butadiene, respectively. The dehydrogenative silylation of acetylacetone and benzoylacetone with dimethylbis(pentafluorophenyl)silane under the same conditions affords novel heterocycles 5-methylene-2,6-dioxa-1-silacyclohex-3-enes. In the reaction studied the silylating ability of the silanes increases in the order $\text{Me}_3\text{SiCN} \approx \text{Me}_2\text{Si}(\text{CN})_2 < \text{Me}_3\text{SiCH}_2\text{CN} < \text{Me}_3\text{SiC}_6\text{F}_5 \approx \text{Me}_2\text{Si}(\text{C}_6\text{F}_5)_2$. On the other hand, potassium cyanide-18-crown-6 complex catalyzed the addition of silane I or II to a carbonyl group of non-enolizable compounds such as benzaldehyde, crotonaldehyde, and methyl(triethylgermyl)ketene.

Introduction

An important role is played by nucleophilic catalysis in the chemistry of organometallic compounds [1,2]. In particular, and of certain interest from the synthetic point of view, are the addition reactions of organosilicon compounds at the carbonyl group of aldehydes and ketones



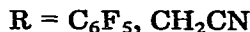
X = H [3,4], CN [5–8], N₃ [5], C≡CPh [9], CH₂CH=CHR [10], CH₂COOR [11–14]
 C(N₂)COOEt [15], SR [16–18]

These reactions are rapidly initiated by anion (e.g. cyanide and fluoride ion) and neutral nucleophiles such as pyridine [18] and triphenylphosphine [16]. Depending on the structure of the carbonyl compound and the nature of the substituent X, reaction 1 may also occur in other directions. For example, Evans et al. have noted that anionic initiators such as potassium cyanide-18-crown-6 or potassium ethylthiolate-crown complex are efficient catalysts for the 1,4-addition of phenylthiotrimethylsilane to α,β -unsaturated ketones and aldehydes [16]. This considerably increases the synthetic possibilities of the reactions discussed.

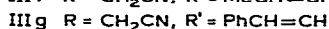
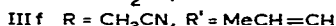
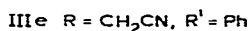
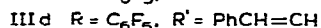
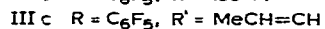
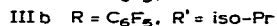
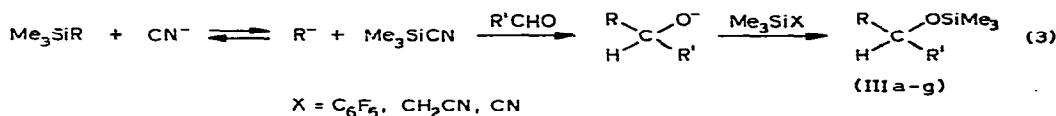
It has been shown by us in the work reported here that pentafluorophenyltrimethylsilane and cyanomethyltrimethylsilane are also related to the organosilicon compounds which react readily with carbonyl compounds under conditions of nucleophilic catalysis.

Results and discussion

Webb, Sethi and Gilman have shown [19] that pentafluorophenyltrimethylsilane (I) adds to benzaldehyde at 165–170°C over 4 days to give phenyl(pentafluorophenyl)trimethylsiloxymethane. It is of interest that on the basis of this evidence, Reutov has postulated a nucleophilically-assisted mechanism, $S_{E1}(N)$, for reactions of this type [1]. The addition of cyanomethyltrimethylsilane (II) to both aliphatic and aromatic aldehydes (e.g. benzaldehyde) occurs at 160–180°C when catalyzed by sodium hydroxide and related compounds [20]



In preliminary communications [21,22] we reported that the addition of I and II to the carbonyl group of aldehydes (cf. eq. 2) is dramatically catalyzed by the potassium cyanide-18-crown-6 complex. For example, benzaldehyde reacted completely with silane I in ether in the presence of catalytic amount of this complex in less than 5 h at room temperature. These results are consistent with Reutov's conclusions [1]. Moreover, it may be assumed that reaction 2 occurred with the intermediate formation of C_6F_5^- and $^-\text{CH}_2\text{CN}$ carbanions according to eq. 3 (cf. [5,15]). The anion-initiated reaction of enolisable 2-methylpropanal [23] with silane I proceeds analogously.



When α,β -unsaturated aldehydes such as crotonaldehyde or cinnamaldehyde were used, only 1,2-adducts were formed. Similarly, 1-pentafluorophenyl-1-tri-

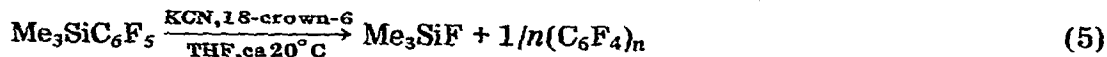
methylsiloxy-2-triethylgermyl-1-propene (IV) was obtained when methyl(triethylgermyl)ketene was treated under the same conditions with silane I



However, attempts to prepare the adduct by treating silane I with highly hindered di-tert-butyl ketone under the influence of KCN, 18-crown-6 catalyst failed.

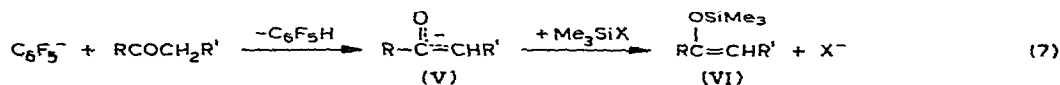
The structure of the adducts IIIa–d and IV is supported by infrared spectra. The spectra of IIIa, b are quite similar. Significantly there are absorption bands at 1660–1650, 1518–1500, 1130–1115 (C_6F_5), 1210–1100 ($\text{Si}-\text{O}-\text{C}$), 1260–1255, and 860–850 cm^{-1} (Me_3Si), and there are no bands attributable to carbonyl absorption. Moreover, the adduct IV shows absorption bands at 1627 ($\text{C}=\text{C}$) and 580 cm^{-1} ($\text{Ge}-\text{C}$). Further evidence for the structure by IIIb–e was provided by acid hydrolysis of IIIb–e and isolation of the corresponding alcohols.

In contrast, the action of the silane I on enolizable ketones such as acetophenone, cyclohexanone, tert-butyl methyl ketone and diisopropyl ketone in Et_2O and in the presence of KCN, 18-crown-6 catalyst gives the corresponding trimethylsilyl enol ether along with pentafluorobenzene. However, when THF was used instead of Et_2O in the above reaction, a polymeric product was formed, which has the empirical formula $(\text{C}_6\text{F}_4)_n$ (cf. [24]). This product may be formed via the by-reaction depicted in eqn. 5



A variety of enolizable ketones are susceptible to this new dehydrogenative condensation. For example, of great interest was the success of a similar reaction of silane I or II with 1-hexyn-3-one which did indeed give the expected 3-trimethylsiloxy-3-hexen-1-yne (VI d) in yields of 70% and 33%, respectively.

The mechanism of the formation of silyl enol ethers is thought to involve initial formation of the carbanion C_6F_5^- or $-(\text{CH}_2\text{CN})$ via a reversible interaction of cyanide ion with silane I or II, respectively. Subsequent dehydrogenation of the enolizable ketone with the carbanion to form the ambident-anion V which then reacts with Me_3SiX (where $\text{X} = \text{C}_6\text{F}_5$, CH_2CN or CN) to give the silyl enol ether VI, e.g.:



VIa $\text{R} = \text{tert-Bu}$, $\text{R}' = \text{H}$

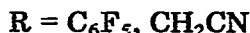
VIb $\text{R} = \text{Ph}$, $\text{R}' = \text{H}$

VIc $\text{R}, \text{R}' = -(\text{CH}_2)_4-$

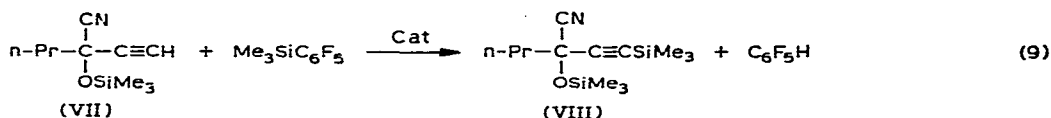
VI d $\text{R} = \text{CH}\equiv\text{C}$, $\text{R}' = \text{Et}$

Recently a similar mechanism has been proposed for the reaction of ketones with $\text{Me}_3\text{SiCH}_2\text{COOEt}$ catalyzed by tetrabutylammonium fluoride [12]. Apparently the catalytic function of the fluoride ion in this reaction is essentially the

same as the function of the cyanide ion in reaction 6. In accord with this view-point, we have found that potassium cyanide-18-crown-6 complex catalyses the silylation reaction of phenylacetylene with silane I and II:



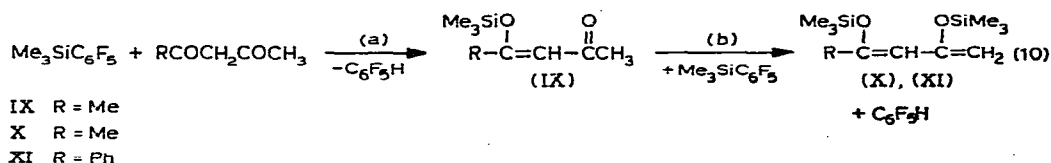
Accordingly, disilylated product (VIII) can be prepared by reaction of 3-trimethylsiloxy-3-cyano-1-hexyne (VII) with silane I.



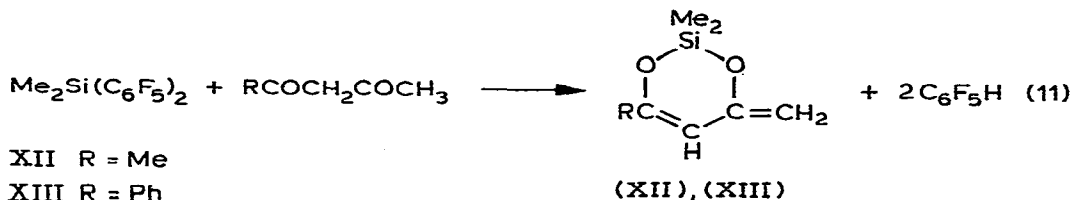
It is well known that $\text{Me}_3\text{SiCH}_2\text{COOEt}$ also undergoes similar reactions (e.g. with phenylacetylene) in the presence of $\text{n-Bu}_4\text{NF}$ as the catalyst [12].

In the absence of the catalyst we were unable to silylate acetophenone and phenylacetylene using silane I even at 80–90°C (49 h).

In order to test the synthetic potential of silane I and related compounds, we have examined their catalytic reactions with 1,3-diketones. Treatment of acetylacetone with two molar equivalents of I in the presence of KCN, 18-crown-6 catalyst gives a mixture of the known compound 2-trimethylsiloxy-2-penten-4-one (IX) [25] and 2,4-bis(trimethylsiloxy)-1,3-pentadiene (X) in yields of 34% and 50%, respectively. Treatment of benzoylacetone with silane I under the same conditions gives similar results. In the case of acetylacetone (benzoylacetone was not examined in this respect) use of one molar proportion of the reagents leads only to the product IX. This indicates that the rate of reaction 10a is greater than that of reaction 10b.

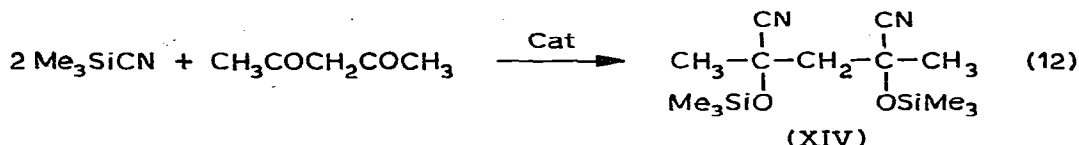


Accordingly, treatment of dimethylbis(pentafluorophenyl)silane with one molar equivalent of acetylacetone or benzoylacetone proceeded with formation of the 1,3-exocyclic-endocyclic dienes XII or XIII, respectively



The reactions 10 and 11 were carried out in evacuated sealed ampoules in diethyl ether in the presence of a catalytic amount of potassium cyanide-18-

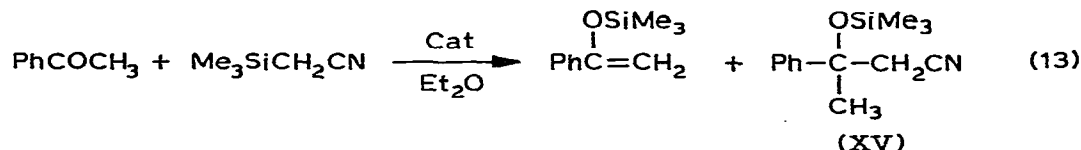
crown-6 complex. We found that the reaction of acetylacetone with Me_3SiCN under comparable experimental conditions takes a completely different pathway than $\text{Me}_3\text{SiC}_6\text{F}_5$ or $\text{Me}_2\text{Si}(\text{C}_6\text{F}_5)_2$. When trimethylcyanosilane is treated with acetylacetone, 2,4-dicyano-2,4-bis(trimethylsiloxy)pentane is formed in 86% yield, but the product is a mixture of *meso*- and *d,l*-isomers



If only one equivalent of trimethylcyanosilane is employed, the 2/1 adduct XIV is also formed and approximately half of the starting β -diketone is recovered.

As reported by Ryu and coworkers [26], acetylacetone reacts with one equivalent of Me_3SiCN to give the silyl enol ether IX in a high yield. The reaction conditions used by Ryu et al. were not reported. Moreover, these authors reported that a reaction of $\text{Me}_2\text{Si}(\text{CN})_2$ with β -diketones affords 5-cyano-2,6-dioxa-1-sila-cyclohex-3-enes. The reaction proceeded immediately without any catalysts. In the course of this reaction the enol portion of the β -diketone converts to a silyl enol ether fragment while the other carbonyl group is undergoing cyanosilylation [26]. These observations are in contrast to the observed mode of the sealed tube reaction with trimethylcyanosilane (eqn. 12). The effects of experimental conditions on these reactions were of great interest, but the mechanisms of these effects are not clear as yet. Moreover, our results (eqn. 12) as well as those reported by Ryu et al. [26] suggest that cyanosilanes, Me_3SiCN and $\text{Me}_2\text{Si}(\text{CN})_2$, are less effective reagents for the dehydrogenative silylation of acetylacetone than $\text{Me}_3\text{SiC}_6\text{F}_5$ and $\text{Me}_2\text{Si}(\text{C}_6\text{F}_5)_2$.

As mentioned above, treatment of acetophenone with silane I resulted in formation of the expected silyl enol ether VIb as the only product (eqn. 7). It is noteworthy that the similar reaction with silane II yielded the same product VIb along with 3-phenyl-3-trimethylsiloxybutyronitrile (XV)



The adduct XV results from a competitive reaction depicted in eqn. 13.

Thus, in the reactions studied the dehydrogenative silylating ability of the silanes increases in the order $\text{Me}_3\text{SiCN} \approx \text{Me}_2\text{Si}(\text{CN})_2 < \text{Me}_3\text{SiCH}_2\text{CN} < \text{Me}_3\text{SiC}_6\text{F}_5 \approx \text{Me}_2\text{Si}(\text{C}_6\text{F}_5)_2$.

Experimental

All reactions were carried out in evacuated sealed ampoules following the technique described in ref. 27. The IR spectra were recorded on a UR-20 spectrophotometer. NMR spectra were obtained on a Tesla BS 487 C (80 MHz) instrument with cyclohexane as internal standard.

Reaction of trimethylpentafluorophenylsilane with benzaldehyde

A mixture of 11.01 g of $\text{Me}_3\text{SiC}_6\text{F}_5$, 4.42 g of benzaldehyde, 0.02 g of KCN, 0.12 g of 18-crown-6 and 30 ml of diethyl ether was stirred magnetically at ambient temperature for 4 h. The solvent was removed under reduced pressure and the residue was distilled in vacuo to give 8.14 g (56.5%) of phenyl(trimethylsiloxy)pentafluorophenylmethane (IIIa), b.p. 82–84°C/1 mmHg, n_D^{20} 1.4793. (Found: C, 55.61; H, 4.38; F, 27.86. $\text{C}_{16}\text{H}_{15}\text{F}_5\text{OSi}$ calcd.: C, 55.48; H, 4.37; F, 27.42%). NMR (CCl_4) (δ , ppm): 7.28 (m, 5H, C_6H_5), 6.18 (s, 1H, OCH), 0.13 (s, 9H, Me_3Si).

1-Pentafluorophenyl-1-trimethylsiloxy-2-methylpropane (IIIb)

The adduct was prepared in 37.3% yield by the general method described above. B.p. 89–90°C/11 mmHg, n_D^{20} 1.4230. (Found: C, 49.88; H, 5.74; F, 32.33. $\text{C}_{13}\text{H}_{17}\text{F}_5\text{OSi}$ calcd.: C, 49.99; H, 5.49; F, 32.01%) NMR (CCl_4) (δ , ppm): 4.88 (d, 1H, OCH, 3J 10 Hz), 2.43 (m, 1H, $\equiv\text{CH}$), 1.07 (q, 6H, Me_2C 3J 6 Hz), 0.27 (s, 9H, SiMe_3).

1-Pentafluorophenyl-1-trimethylsiloxy-2-butene (IIIc)

6.86 g of $\text{Me}_3\text{SiC}_6\text{F}_5$, 2.01 g of crotonaldehyde and 30 ml of ether were stirred at room temperature for 36 h in the presence of 0.02 g of KCN and 0.12 g of 18-crown-6. The reaction mixture was worked up as usual to give 5.01 g (56.4%) of IIIc, b.p. 53–54°C/1 mmHg, n_D^{20} 1.4336. (Found: C, 50.06; H, 4.80; F, 29.61; Si, 8.84. $\text{C}_{13}\text{H}_{15}\text{F}_5\text{OSi}$ calcd.: C, 50.31; H, 4.87; F, 30.61; Si, 9.05%) IR (cm^{-1}): $\nu(\text{Me}_3\text{Si})$ 755, 850, 1255, $\nu(\text{SiOC})$ 1100–1122, $\nu(\text{=CH})$ 950, 3046, $\nu(\text{C}_6\text{F}_5)$ 1506–1524, $\nu(\text{C=C})$ 1652. NMR (CCl_4) (δ , ppm): 5.48–5.77 (m, 3H, CH=CH-CH), 1.72 (d, 3H, CH_3 , 3J 4.4 Hz), 0.10 (s, 9H, SiMe_3).

1-Pentafluorophenyl-1-trimethylsiloxy-3-phenyl-2-propene (IIId)

9.09 g of $\text{Me}_3\text{SiC}_6\text{F}_5$, 5.02 g of PhCH=CHCHO , 0.02 g of KCN, 0.12 g of 18-crown-6 and 30 ml of diethyl ether were stirred at ca. 20°C for 20 h. Fractionation of the reaction mixture gave 5.65 g (40.1%) of IIId, b.p. 110–112°C/1 mmHg, n_D^{17} 1.5081. (Found: C, 57.59; H, 4.49; F, 25.82; Si, 7.27. $\text{C}_{18}\text{H}_{17}\text{F}_5\text{OSi}$ calcd.: C, 58.05; H, 4.60; F, 25.51; Si, 7.54%). IR (cm^{-1}): $\nu(\text{Me}_3\text{Si})$ 745–760, 848, 1255, $\nu(\text{=CH})$ 948, 3040, $\nu(\text{SiOC})$ 1080, $\nu(\text{C}_6\text{F}_5)$ 1502. NMR (CCl_4) (δ , ppm): 5.80 (m, 5H, C_6H_5), 5.11 (m, 2H, CH=CH), 4.24 (d, 1H, $\equiv\text{CH}$, 3J 5.8 Hz) 0.17 (s, 9H, SiMe_3).

Hydrolysis of the adduct IIIb. Preparation of 1-Pentafluorophenyl-2-methylpropanol-1

Dilute HCl (1.5 N, 6 ml) was added to a solution of IIIb (3.23 g) in 20 ml of THF. The mixture was stirred at room temperature for 8 h. The organic layer was washed with water, dried over Na_2SO_4 and evaporated. The residue was distilled [b.p. 79–85°C (bath temperature)/1 mmHg] as a white solid (m.p. 51–52°C) in 56.5% yield. (Found: C, 49.08; H, 3.87; F, 39.05; $\text{C}_{10}\text{H}_9\text{F}_5\text{O}$ calcd.: C, 50.01; H, 3.78; F, 39.55%). IR (cm^{-1}): $\nu(\text{C}_6\text{H}_5)$ 1100, 1500, 1655, $\nu(\text{OH})$ 3300. NMR (CCl_4) (δ , ppm): 4.43 (t, 1H, OCH), 2.11 (m, 2H, $\text{C}^>\text{CH}$ and OH), 0.82 (q, 6H, Me_2C , 3J 6 Hz).

1-Pentafluorophenyl-2-buten-1-ol

Using the method described above for IIIb, hydrolysis of IIIc gave the desired product (62.8% yield). M.p. 37–39°C. (Found: C, 50.56; H, 3.35; F, 39.78. $C_{10}H_7F_5O$ calcd.: C, 50.44; H, 2.96; F, 39.89%). NMR (CCl_4) (δ , ppm): 5.76 (m, 2H, CH=CH), 5.39 (s, 1H, OH), 4.37 (d, 1H, $\equiv CH$, 3J 5 Hz), 1.72 (d, 3H, CH_3 , 3J 4.6 Hz).

1-Pentafluorophenyl-3-phenyl-2-propen-1-ol

Using the method described above for IIIb, hydrolysis of IIId gave the desired alcohol (81.3% yield). M.p. 124–125°C. (Found: C, 60.28; H, 3.27; F, 31.82. $C_{15}H_9F_5O$ calcd.: C, 60.01; H, 3.02; F, 31.64%). NMR (CCl_4) (δ , ppm): 7.26 (m, 5H, C_6H_5), 6.55 (m, 2H, CH=CH), 5.64 (s, 1H, OH), 2.11 (m, 1H, $\equiv CH$).

3-Phenyl-3-trimethylsiloxypropionitrile (IIIe)

A mixture of 2.13 g of Me_3SiCH_2CN , 2.01 g of benzaldehyde, 0.02 g of KCN, 0.13 g of 18-crown-6 and 20 ml of THF was stirred at room temperature for 1 h. The reaction mixture was worked up as usual to give 2.91 g (70.2%) of IIIe, b.p. 95–96°C/1 mmHg, n_D^{20} 1.4920. (Found: C, 66.84; H, 7.65; N, 6.54; Si, 12.44. $C_{12}H_{17}NOSi$ calcd.: C, 66.70; H, 7.81; N, 6.39; Si, 12.81%). IR (cm^{-1}): $\nu(SiOC)$ 1128, $\nu(C\equiv N)$ 2220, 2250. NMR (CCl_4) (δ , ppm): 7.29 (m, 5H, C_6H_5), 4.94 (t, 1H, OCH, 3J 7 Hz), 2.55 (d, 2H, CH_2 , 3J 7 Hz), 0.11 (s, 9H, $SiMe_3$).

Hydrolysis of the adduct IIIe

A mixture of the adduct IIIe (5.01 g), methanol (10 ml) and water (5 ml) was refluxed for 6 h, then poured into water (75 ml) and extracted with ether (4 $\times$ 50 ml). The combined extracts were washed with water, dried and evaporated. The residue was distilled in vacuo to give 2.90 g (86.3%) of β -hydroxy- β -phenylpropionitrile, b.p. 146–149°C/4 mmHg, n_D^{20} 1.5379 (lit. [30] b.p. 147–151°C/4–5 mmHg, n_D^{20} 1.5388).

3-Trimethylsiloxy-4-hexenenitrile (IIIff)

Starting from crotonaldehyde and Me_3SiCH_2CN this adduct was prepared in 69.5% yield by the general method described above. B.p. 84–85°C/10 mmHg, n_D^{20} 1.4353. (Found: C, 58.75; H, 9.02; N, 7.63; Si, 15.43. $C_9H_{17}NOSi$ calcd.: C, 58.98; H, 9.35; N, 7.64; Si, 15.33%). IR (cm^{-1}): $\nu(Me_3Si)$ 755, 850, 1255, $\nu(SiOC)$ 1075–1100, $\nu(=CH)$ 945, 3000, 3040, $\nu(C=C)$ 1645, 1670, $\nu(C\equiv N)$ 2220, 2255. NMR (CCl_4) (δ , ppm): 5.53 (m, 2H, CH=CH), 4.30 (q, 1H, $\equiv CH$, 3J 5 Hz), 2.30 (d, 2H, CH_2 , 3J 6 Hz), 1.69 (d, 3H, CH_3 , 3J 5 Hz), 0.09 (s, 9H, $SiMe_3$).

3-Trimethylsiloxy-5-phenyl-4-pentenitrile (IIIg)

Starting from cinnamaldehyde and Me_3SiCH_2CN this adduct was prepared in 73.2% yield by the general method described above. B.p. 132–134°C/1 mmHg, n_D^{20} 1.5199. (Found: C, 63.66; H, 7.56; N, 5.81; Si, 10.18. $C_{13}H_{19}NOSi$ calcd.: C, 63.65; H, 7.81; N, 5.71; Si, 11.45%). IR (cm^{-1}): $\nu(SiOC)$ 1080–1120, $\nu(C=C)$ 1620, 1652, $\nu(C\equiv N)$ 2217, 2255.

1-Pentafluorophenyl-1-trimethylsiloxy-2-triethylgermyl-1-propene (IV)

The procedure described for adduct III_d was followed, using methyl(triethylgermyl)ketene in place of cinnamaldehyde, and yielded 89.1% of the desired adduct IV, b.p. 90–91°C/1 mmHg, n_D^{20} 1.4684. (Found: C, 48.05; H, 6.31; F, 19.93; Ge, 15.14; Si, 5.92. $C_{18}H_{27}F_5GeOSi$ calcd.: C, 47.51; H, 5.98; F, 20.87; Ge, 15.95; Si, 6.17%). NMR (CCl_4) (δ , ppm): 1.48 (s, 3H, CH_3), 1.03 (m, 15H, Et_3Ge), 0.02 (s, 9H, $SiMe_3$).

Reaction of $Me_3SiC_6F_5$ with cyclohexanone

A mixture of 9.81 g of $Me_3SiC_6F_5$, 4.03 g of cyclohexanone, 0.03 g of KCN, 0.21 g of 18-crown-6 and 30 ml of THF was stirred magnetically at ambient temperature for 24 h. The solid was filtered off and the filtrate was distilled to give 2.52 g (36.5%) 1-trimethylsiloxy-1-cyclohexene (VI_c), b.p. 71–73°C/20 mmHg, n_D^{20} 1.4451 (lit. [28] b.p. 63–64°C/12 mmHg, n_D^{20} 1.4466). GLC analysis of the volatile products showed 2.13 g (31.1%) of pentafluorobenzene. The crystalline solid was washed with ether and was filtered off to give 2.51 g (41.5%) of polymeric tetrafluorophenylene, dec. >360°C (cf. [24]).

Reaction of $Me_3SiC_6F_5$ with acetophenone

The reaction was carried out as described above to give α -trimethylsiloxy-styrene (VI_b) (68.1% yield), b.p. 53–54°C/1 mmHg, n_D^{20} 1.5030 (lit. [29] b.p. 53–54°C/1 mmHg, n_D^{20} 1.5040).

3-Trimethylsiloxy-3-hexen-1-yne (VI_d)

A mixture of 12.49 g of $Me_3SiC_6F_5$ and 5.01 g of 1-hexyn-3-one and 30 ml of ether was stirred at room temperature. After 1 h, the reaction mixture was distilled to give 6.11 g (69.8%) of VI_d, b.p. 70–72°C/35 mmHg, n_D^{20} 1.4389. (Found: C, 64.12; H, 9.63; $C_9H_{16}OSi$ calcd.: C, 63.80; H, 10.06%). IR (cm^{-1}): $\nu(SiOC)$ 1190, $\nu(C=C)$ 1635, $\nu(C\equiv C)$ 2100, $\nu(=CH)$ 3040, $\nu(\equiv CH)$ 3315. Based on the NMR, this material appears to be a mixture of the *cis* and *trans* isomers: *cis* isomer VI_d had NMR (CCl_4) (δ , ppm): 5.03 (t, 1H, $=CH$, 3J 7.5 Hz), 2.71 (s, 1H, $\equiv CH$), 2.00 (m, 2H, CH_2), 0.91 (m, 3H, CH_3), 0.21 (s, 9H, $SiMe_3$). *trans* isomer VI_d: 5.21 (t, 1H, $=CH$, 3J 7.5 Hz), 2.96 (s, 1H, $\equiv CH$), 2.13 (m, 2H, CH_2), 0.94 (t, 3H, CH_3), 0.36 (s, 9H, $SiMe_3$).

Assignments of *cis* and *trans* are based on the chemical shift of the olefinic proton, which is farther downfield in the *trans* isomer (proton *trans* to acetylenic group) as compared to the *cis*.

Reaction of $Me_3SiC_6F_5$ with phenylacetylene

A mixture of 10.01 g of $Me_3SiC_6F_5$, 4.25 g of $PhC\equiv CH$, 0.02 g of KCN, 0.22 g of 18-crown-6 and 30 ml of THF was stirred overnight at room temperature. Fractionation of the reaction mixture gave 4.93 g (68.0%) of $PhC\equiv CSiMe_3$, b.p. 66–68°C/5 mmHg, n_D^{20} 1.5265. GLC analysis of the volatile products showed 4.41 g (63.1%) of pentafluorobenzene.

3-Trimethylsiloxy-3-cyano-1-hexyne (VII)

5.81 g of Me_3SiCN , 5.62 g of 1-hexyn-3-one, 0.02 g of KCN, 0.11 g of 18-crown-6 and 15 ml of THF were stirred overnight at ambient temperature.

The solvent was removed under reduced pressure and the residue was distilled in vacuo to give 8.77 g (76.8%) of the adduct VII, b.p. 76–79°C/10 mmHg, n_D^{20} 1.4230 (Found: C, 61.31; H, 9.02; N, 7.13; Si, 14.49. $C_{10}H_{17}NOSi$ calcd.: C, 61.49; H, 9.77; N, 7.17; Si, 14.38%).

1-Trimethylsilyl-3-trimethylsiloxy-3-cyano-1-hexyne (VIII)

A mixture of 3.69 g of $Me_3SiC_6F_5$, 3.01 g of the adduct VII, 0.02 of potassium cyanide, 0.11 g of 18-crown-6 and 30 ml of ether was stirred at ca. 20°C for 5 days. The reaction mixture was distilled to give 1.75 g (47.3%) of VIII, b.p. 61–62°C/1 mmHg, n_D^{20} 1.4358. (Found: C, 58.80; H, 9.80; N, 5.35; Si, 19.89. $C_{13}H_{25}NOSi_2$ calcd.: C, 58.36; H, 9.42; N, 5.24; Si, 21.00%). IR (cm^{-1}): $\nu(Me_3Si)$ 770, 860, 1252, $\nu(SiOC)$ 1110, $\nu(C\equiv C)$ 1180, $\nu(C\equiv N)$ 2238, NMR (CCl_4) (δ , ppm): 1.79 (m, 4H, CH_2CH_2), 0.95 (m, 3H, CH_3), 0.25 (s, 9H, $CSiMe_3$), 0.18 (s, 9H, $OSiMe_3$).

2,4-Bis(trimethylsiloxy)-1,3-pentadiene (X)

A mixture of 4.01 g of acetylacetone, 19.22 g of $Me_3SiC_6F_5$, 0.02 g of KCN, 0.12 g of 18-crown-6 and 50 ml of diethyl ether was stirred overnight at room temperature. The reaction mixture was worked up as usual to give 5.31 g (54.4%) of the pentadiene X, b.p. 78–79°C/4 mmHg, n_D^{20} 1.4470. (Found: C, 53.66; H, 9.58; Si, 22.40. $C_{11}H_{24}O_2Si_2$ calcd.: C, 54.04; H, 9.89; Si, 22.9%). IR (cm^{-1}): $\nu(SiOC)$ 1030, $\nu(C\equiv C)$ 1600, 1656, $\nu(=CH-)$ 3060, $\nu(=CH_2)$ 3130. NMR (CCl_4) (δ , ppm): 4.59 (s, 1H, $=CH-$), 4.21, 4.69 (d, d, 2H, $=CH_2$, $^2J(HH)$ 1.93 Hz), 1.79 (s, 3H, CH_3), 0.20 (s, 9H, $SiMe_3$), 0.18 (s, 9H, $SiMe_3$).

1-Phenyl-1,3-bis(trimethylsiloxy)-1,3-butadiene (XI)

The butadiene XI was prepared in 82.9% yield by the general method described above. B.p. 87–89°C/1 mmHg, n_D^{25} 1.5094. (Found: C, 62.58; H, 8.28; Si, 17.83. $C_{16}H_{26}O_2Si_2$ calcd.: C, 62.69; H, 8.55; Si, 18.33%). IR (cm^{-1}): $\nu(Me_3Si)$ 768, 851, 1252, $\nu(SiOC)$ 1021, 1083, $\nu(C\equiv C)$ 1632, $\nu(=CH_2)$ 3110. NMR (CCl_4) (δ , ppm): 7.00–7.55 (m, 5H, C_6H_5), 4.79 (s, 1H, $=CH-$), 4.37, 5.43 (d, d, 2H, $=CH_2$, $^2J(HH)$ 1.1 Hz), 0.23 (s, 9H, $SiMe_3$), 0.11 (s, 9H, $SiMe_3$).

1,1,3-Trimethyl-5-methylene-2,6-dioxo-1-silacyclohex-3-ene (XII)

The silacyclohexene XII was prepared in 53.4% yield by the general method described above. B.p. 74–76°C/50 mmHg, n_D^{20} 1.4671. (Found: C, 54.01; H, 7.77; Si, 17.73. $C_7H_{12}O_2Si$ calcd.: C, 53.78; H, 7.75; Si, 17.98%). IR (cm^{-1}): $\nu(SiOC)$ 1038, $\nu(C\equiv C)$ 1595, 1660, $\nu(=CH-)$ 3070, $\nu(=CH_2)$ 3127. NMR (CCl_4) (δ , ppm): 4.99 (s, 1H, $=CH-$), 3.79, 3.99 (s, s, $=CH_2$), 1.77 (s, 3H, CH_3), 0.25 (s, 6H, $SiMe_2$).

1,1-Dimethyl-3-phenyl-5-methylene-2,6-dioxo-1-silacyclohex-3-ene (XIII)

The silacyclohexene XIII was obtained in 58.2% yield by the general method described above. B.p. 74–76°C/1 mmHg, n_D^{20} 1.5601. (Found: C, 65.42; H, 6.46; Si, 12.81. $C_{12}H_{14}O_2Si$ calcd.: C, 66.02; H, 6.46; Si, 12.87%). NMR (CCl_4) (δ , ppm): 7.63 (m, 5H, C_6H_5), 5.92 (s, 1H, $=CH-$), 4.32, 4.42 (s, s, $=CH_2$), 0.34 (s, 6H, $SiMe_2$).

2,4-Dicyano-2,4-bis(trimethylsiloxy)pentane (XIV)

Starting from acetylacetone and Me_3SiCN (1 : 2 molar ratio) this adduct was prepared in 86.0% yield by the general method described above. B.p, $84-86^\circ\text{C}/1\text{ mmHg}$, n_D^{20} 1.4361. (Found: C, 53.14; H, 8.63; N, 9.29; Si, 18.55; $\text{C}_{13}\text{H}_{26}\text{N}_2\text{O}_2\text{Si}_2$ calcd.: C, 52.30; H, 8.78; N, 9.38; Si, 18.82%). IR (cm^{-1}): $\nu(\text{Me}_3\text{Si})$ 755, 845, 1257, $\nu(\text{SiOC})$ 1083, 1190, $\nu(\text{C}\equiv\text{N})$ 2235. The product was separated into *d,l*- and *meso*-isomers by preparative GLC. The presence of the isomers is confirmed by two sets of signals in the ^1H NMR spectrum: (δ , ppm): a) 0.28 (s, 9H, SiMe_3), 1.67 (s, 6H, 2 CH_3), 2.12 (s, 2H, CH_2); b) 0.31 (s, 9H, SiMe_3), 1.54 (s, 6H, 2 CH_3), 1.87 (s, 2H, CH_2).

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