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Preliminary communication

CHEMISTRY OF ORGANOSILICON COMPOUNDS

CXIX. PREPARATION AND SOME REACTIONS OF 1,2-DISILACYCLOBUTENES

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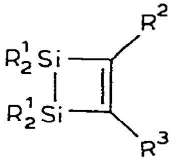
Summary

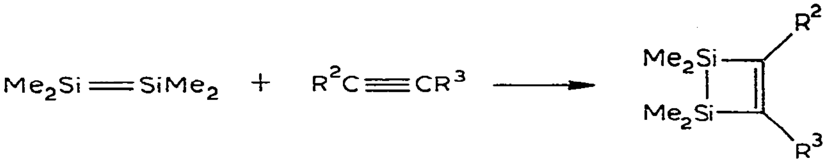
Two new 1,2-disilacyclobutenes have been prepared by the reaction of tetramethyldisilene with acetylenes. Several reactions of these new 1,2-disilacyclobutenes including oxidation, silylene insertion, iron carbonyl insertion, and addition to acetylenes and dienes are reported.

1,2-Disilacyclobutenes represent an interesting ring system. Atwell and Uhlmann prepared 1,1,2,2,3,4-hexamethyl-1,2-disilacyclobut-3-ene (Ia) by the reaction of dimethylsilylene and 2-butyne [1]. Similarly, the reaction between difluorosilylene and t-butylacetylene gave a disilacyclobutene (Ib) [2,3]. Recently, Barton and Kilgour attempted to prepared Ia by the reaction of tetramethyldisilene with 2-butyne, but Ia was not isolated although there was a good indication of its formation [4]. More recently, Seyferth has prepared 1,1,2,2-tetramethyl-3,4-bis(trimethylsilyl)-1,2-disilacyclobut-3-ene (Ic) by the reaction between 1,1-dimethyl-2,3-bis(trimethylsilyl)-1-silacycloprop-ene and dimethylsilylene [5].



(Ia) $R^1 = R^2 = R^3 = Me$
(Ib) $R^1 = F$, $R^2 = H$, $R^3 = t\text{-}Bu$
(Ic) $R^1 = Me$, $R^2 = R^3 = Me_3Si$

During the course of our study on disilene intermediates [6], we have found that tetramethyldisilene reacts with some acetylenes to give the corresponding 1,2-disilacyclobutenes in good yield. This is the first clear demonstration of the cycloaddition reaction of disilenes and acetylenes. In this paper, we also report several interesting reactions of these compounds.



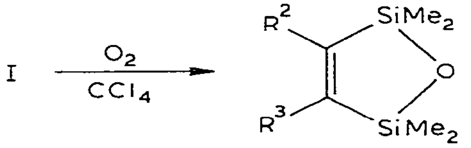
(Id) $R^2 = R^3 = Ph$

(Ie) $R^2 = Ph, R^3 = Me_3Si$

Tetramethyldisilene was generated by using Peddle's system [7]. 1-Phenyl-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octadiene (II) was more convenient than 7,7,8,8-tetramethyl-7,8-disila-2,3-benzobicyclo[2.2.2]octadiene (III), since thermolysis of II can be effected at lower temperature (250—270°C) than III (350°C).

A sealed tube containing II (10.9 g, 40 mmol) and diphenylacetylene (7.5 g, 42 mmol) was heated at 250°C for 12 h. A viscous oil was obtained and distillation of the mixture gave Id (7.5 g, 26 mmol, 64% yield), b.p. 110—114°C (0.3 mmHg); M^+ *m/e* 294 (41.6%), 116 (100%); ^{1}H NMR δ(CCl_4): 0.43 (12H, s, $SiMe_2$), 6.8—7.3 (10H, m, arom) ppm. Anal. Found: C, 73.50; H, 7.80. $C_{18}H_{22}Si_2$ calcd.: C, 73.40; H, 7.53%. Similarly, a mixture of II (10.9 g, 40 mmol) and phenyltrimethylsilylacetylene (7.7 g, 44 mmol) was heated at 260°C for 18 h to give Ie (5 g, 17 mmol, 43%), b.p. 75°C (0.3 mmHg), ^{1}H NMR δ(CCl_4): —0.10 (9H, s, $SiMe_3$), 0.30 (6H, s, $SiMe_2$), 0.37 (6H, s, $SiMe_2$), 6.8—7.4 (5H, m, arom) ppm. Since Ie was contaminated with a small amount of the corresponding siloxane IVe, analytically pure Ie has not been obtained. The reaction of bis(trimethylsilyl)acetylene and II also was attempted. The expected Ic was not isolated but the corresponding siloxane was obtained after oxidation (35% yield).

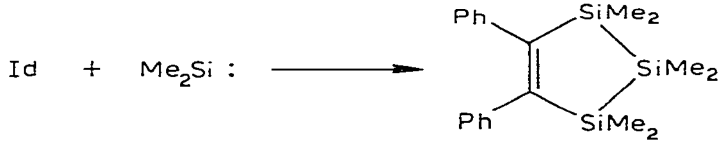
Disilacyclobutenes are extremely air sensitive and give the corresponding disiloxane IV [1,4,5]. Autoxidation of Id took place exothermally in carbon tetrachloride solution to give IVd in 63% yield. Similarly, Id in benzene gave IVe in 54% yield.



(IVd) $R^2 = R^3 = Ph$

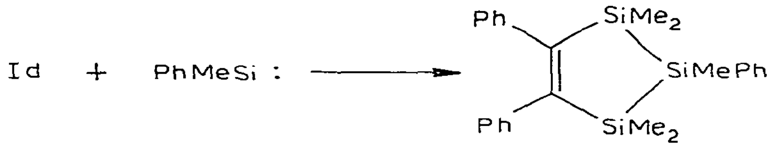
(IVe) $R^2 = Ph, R^3 = Me_3Si$

The silicon—silicon bond of I is susceptible to insertion of divalent species. The reaction of Id with dimethylsilylene generated from 1,2,3,4-tetraphenyl-7,7-dimethyl-5,6-benzo-7-silabicyclo[2.2.1]heptadiene at 350°C for 1 h (in a sealed tube) resulted in the formation of 1,1,2,2,3,3-hexamethyl-4,5-diphenyl-1,2,3-trisilacyclopentene (Vd) in 88% yield.



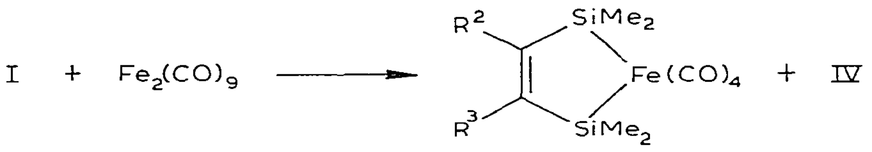
(Vd)

The reaction of Id with the phenylmethylsilylene derived from 1,2,3,4,7-pentaphenyl-7-methyl-5,6-benzo-7-silabicyclo[2.2.1]heptadiene gave a single product (Vd-Ph) in high yield. The structure of Vd-Ph was evidenced by ^{1}H NMR data with three Si-Me signals at 0.13, 0.20, and 0.60 ppm in 2/2/1 ratio. These findings are the first clear demonstration of organosilylene insertion into the silicon—silicon bond.



(Vd-Ph)

The reaction of Id and Ie with diiron nonacarbonyl at room temperature gave VId and VIe in 31 and 45% yield, respectively. In this reaction, the disiloxanes IVd and IVe were obtained in 35 and 28% yield, respectively, as by-products.

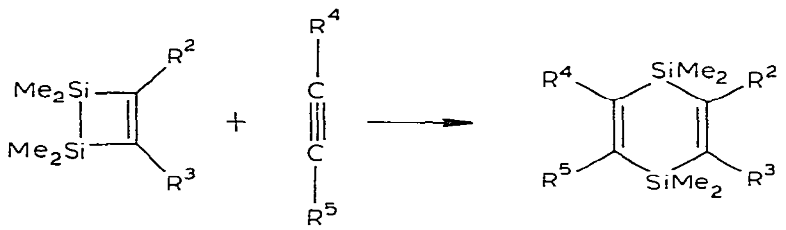


(VId) $R^2 = R^3 = Ph$

(VIe) $R^2 = Ph$, $R^3 = Me_3Si$

A similar nickel carbonyl analog has been reported by Liu and Cheng in the reaction between Ib and nickel tetracarbonyl [3], and platinum and other metal analogues have been prepared by a completely different pathway [8,9].

The reaction of disilacyclobutenes with acetylenes is especially interesting, since I is a key intermediate in the scheme of 1,4-disilacyclohexadiene (VII) formation proposed by Barton and Kilgour [4].

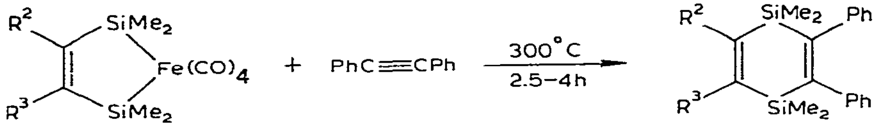


(VII)

The reaction of Id and diphenylacetylene at 350°C for 4 h in a sealed tube gave VIId ($R^2 = R^3 = R^4 = R^5 = Ph$) in only 1.2% yield. Id was recovered in 49% yield as IVd after oxidation. Therefore the present result contrasts quite sharply with that reported by Barton and Kilgour for the case of Ia. We will discuss the mechanism of the formation of VII from acetylene and silylene in a forthcoming paper.

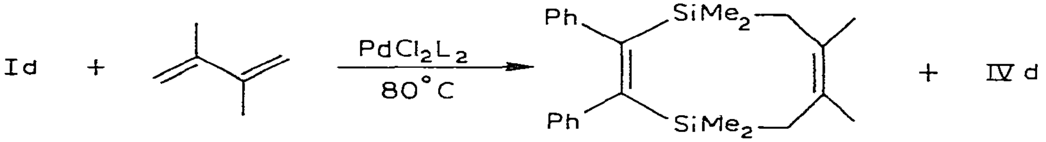
However, the reaction of Id and Ie with acetylenes such as diphenylacetylene and phenyltrimethylsilylacetylene occurred very smoothly in the presence of a palladium complex in 28—71% yield at 25—80° C. $PdCl_2(PPh_3)_2$, $PdCl_2(PEt_3)_2$, $PdCl_2(Ph_2PCH_2CH_2PPh_2)$, $PdCl_2(PhC{\equiv}N)_2$, $Pd(PPh_3)_4$ and Pd on charcoal were effective catalysts.

Interestingly, VI gave VII in the reaction with diphenylacetylene in good yields.



(VII d) $R^2 = R^3 = Ph$ (64 %)
(VII e) $R^2 = Ph, R^3 = Me_3Si$ (46 %)

Finally, the addition reaction of Id with 2,3-dimethylbutadiene also was effected by palladium complexes.



(VIII d)

The ligand (L) on palladium and yields of VIIId and IVd are: PPh_3, 69.9%; PEt_3, 61.12%; Pd/C, 64.18%.

Table 1 links some physical properties of new compounds.

TABLE 1

SOME PHYSICAL PROPERTIES OF NEW COMPOUNDS

IVd: m.p. 86—87° C; *M*$^+$ *m/e* 310 (66.1%), 295 (100%); ^{1}H NMR δ(CCl_4): 0.30 (12H, s, $SiMe_2$), 6.7—7.2 (10H, m, arom) ppm; IR(KBr): 925 (Si—O—Si) cm^{-1}.

IVe: m.p. 63° C; ^{1}H NMR δ(CCl_4): —0.15 (9H, s, $SiMe_3$), 0.15 (6H, s, $SiMe_2$), 6.7—7.3 (5H, m, arom) ppm.

Vd: m.p. 164—165° C; *M*$^+$ *m/e* 352 (100%); ^{1}H NMR δ(CCl_4): 0.13 (12H, s, $SiMe_2$), 0.30 (6H, s, $SiMe_2$), 6.5—7.5 (10H, m, arom) ppm.

VId: m.p. 159—160° C; *M*$^+$ *m/e* 462 (7%), 350 (100%); ^{1}H NMR δ(CCl_4): 0.53 (12H, s, $SiMe_2$) 6.5—7.1 (10H, m, arom) ppm; IR(KBr): 2065, 1995, 1965 (ν(C=O)) cm^{-1}.

VIe: m.p. 103—104° C; *M*$^+$ *m/e* 458 (10%), 346 (100%); ^{1}H NMR δ(CCl_4)—0.17 (9H, s, $SiMe_3$), 0.39 (6H, s, $SiMe_2$), 0.75 (6H, s, $SiMe_2$), 6.7—7.3 (5H, m, Ph) ppm: IR(KBr): 2060, 2000, 1970, 1245 cm^{-1}.

VIIId: an oil, *M*$^+$ *m/e* 376 (81%), 154 (100%); ^{1}H NMR δ(CCl_4): 0.07 (12H, s, $SiMe_2$), 1.84 (10H, s, $SiCH_2$, CH_3) ppm.

Acknowledgment

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