

UNEXPECTED PRODUCTS FROM THE REDUCTIVE TRIMETHYLSILYLATION OF BIS(TRIMETHYLSILYL)ACETYLENE*

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SUMMARY

The reductive trimethylsilylation of bis(trimethylsilyl)acetylene leads to two unexpected products: 2,2,4,4,7,7-hexamethyl-6,6-bis(trimethylsilyl)-2,4,7-trisilaoctane (III) and 2,2,4,4,7,7-hexamethyl-3,6,6-tris(trimethylsilyl)-2,4,7-trisilaoctane (IV). Compound III was also obtained by the reductive trimethylsilylation of tris(trimethylsilyl)ethylene. The temperature dependent proton magnetic resonance spectra and other evidence for the structures of (III) and (IV) are discussed. A mechanism for the formation of (III) and (IV) involving an intramolecular metalation competing with metalation of trimethylchlorosilane is proposed.

INTRODUCTION

The chemical reduction with alkali metals of multiple carbon-carbon bonds has been the subject of several reviews¹⁻³. The accepted mechanism for reduction is the trapping, by protonation, of the reactive anion radical or dianion intermediate formed by electron transfer from the alkali metal to the multiple carbon-carbon bond².

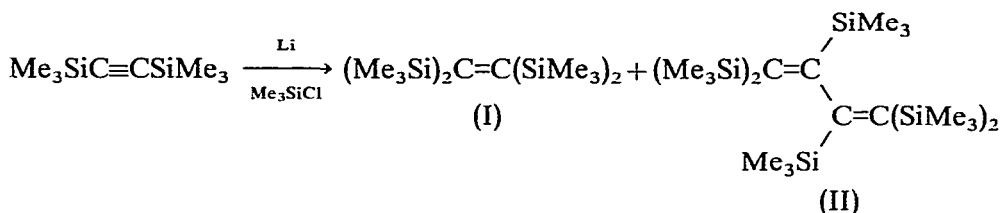
The reductive silylation reaction recently developed⁴⁻⁷ demonstrates the effectiveness of chlorosilanes as derivatizing agents for anionic species. Even though very low equilibrium concentrations of the anion intermediates may be present, the rapid reaction of the anions with chlorosilanes serves to trap them, driving the reaction to completion. Reactive anionic intermediates in the reductive silylation of benzene⁴, substituted benzenes^{4,8}, naphthalene⁵, styrene⁶, and conjugated dienes⁷ have been trapped when these compounds were treated with an alkali metal in the presence of a chlorosilane.

Eisch and Beuhler⁹ have found that when triphenylvinylsilane in tetrahydrofuran (THF) is treated with lithium metal at -78° it undergoes reductive coupling to yield after hydrolysis 1,4-bis(triphenylsilyl)butane. However, the alkylvinylsilanes apparently undergo a styrene-like polymerization⁹. The similarity of the reactions of vinylsilanes, arylethylenes², and diphenylacetylene² when treated with alkali metals

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in inert media prompted the investigation of the applicability of the reductive silylation reaction to bis(trialkylsilyl)acetylenes.

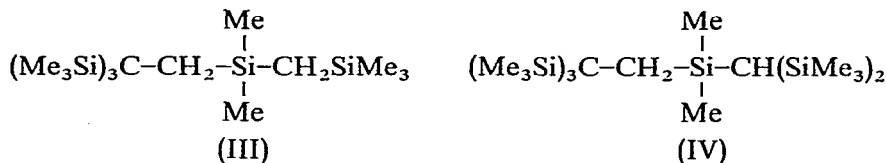
The reaction of bis(trimethylsilyl)acetylene with lithium and trimethylchlorosilane in THF was examined. A monomolecular disilylation of this compound would give tetrakis(trimethylsilyl)ethylene (I) and a bimolecular disilylation would lead to hexakis(trimethylsilyl)butadiene (II). However, the work of Bock and Seidl suggests that silyl substituted ethylenes¹⁰ and butadienes¹¹ should be reduced even more



readily than silylacetylenes¹², so the possibility that (I) and (II) might undergo further reductive silylation to give hexakis(trimethylsilyl)ethane [monomolecular disilylation of (I)] or octakis(trimethylsilyl)-2-butene [monomolecular disilylation of (II)] was also considered.

RESULTS AND DISCUSSION

Treatment of bis(trimethylsilyl)acetylene with lithium and trimethylchlorosilane in THF gives two major unexpected products for which we propose structures (III) and (IV). The yields of (III) and (IV) account for 60–75% of the unrecovered



bis(trimethylsilyl)acetylene. Two volatile minor products were hexamethyldisilane, an expected product¹³, and 2-chloro-2,4,4-trimethyl-2,4-disilapentane (V), probably arising from metalation of trimethylchlorosilane by an organolithium intermediate¹⁴. No higher molecular weight products were isolated from the reaction.



The ratio of (III) to (IV) obtained in the reaction varied only slightly with the conditions under which the reaction was run (in contrast, a dramatic effect was noted⁶ in the reductive silylation of styrene). As shown in Table 1 a 1/1 ratio of trimethylchlorosilane to bis(trimethylsilyl)acetylene favored (IV), whereas higher ratios of trimethylchlorosilane to bis(trimethylsilyl)acetylene favored (III). The ratio of lithium to bis(trimethylsilyl)acetylene had little or no effect on the ratio of (III) to (IV).

The structures for (III) and (IV) were assigned on the basis of their analyses, molecular weights, and vibrational, mass, and NMR spectra. Of all the structures

TABLE 1

REDUCTIVE TRIMETHYLSILYLATION OF BIS(TRIMETHYLSILYL)ACETYLENE

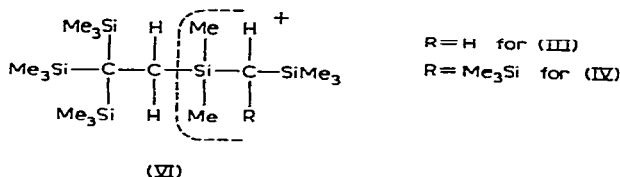
Reagent ratio			Product ratio ^a	
Me ₃ SiC≡CSiMe ₃	Me ₃ SiCl	Li	(III)	(IV)
1	1	3	1	4
1	2	3	1	3.3
1	4	3	1	1.5
1	3	1	1	2.0
1	3	5	1	2.2
1	8	5	1 ^b	1.3 ^b
1	6	10	1	1.1

^a Determined from gas chromatographic area ratios. ^b Isolation of products by distillation gave 35% (III) and 39% (IV).

considered which fit the analytical and molecular weight data obtained, only structures (III) and (IV) are consistent with the infrared, Raman, NMR and mass spectra observed.

The infrared spectra observed for (III) and (IV) are given in the experimental section. The absence of the C=C stretching band in both the infrared and Raman spectra indicated saturated structures. The relatively simple infrared spectra are characterized by absorptions in the 995–1055 cm⁻¹ region. A rather narrow sharp band in this region (distinguishing it from a siloxane absorption) has been attributed to the CH₂ twisting or wagging frequency¹⁵. Thus, the absorption in (III) at 1055 cm⁻¹ is assigned to the disilyl-methylene linkage ($\text{>Si}_2\text{CH}_2$) and we believe one or all three of the 995–1035 cm⁻¹ absorptions for (IV) are due to the trisilylmethine linkage ($\text{>Si}_3\text{CH}$)*. Better evidence, however, for the existence of the disilyl-methylene linkage in (III) and the trisilyl-methine linkage in (IV) are the NMR absorptions at 10.15 (center of doublet) and 10.48 τ , respectively.

The mass spectra for (III) and (IV) are given in the experimental section. Although the molecular-ion was not obtained for either compound, the more intense peak due to loss of CH₃^{16,17} was observed. The isotope contributions to the "M - 15" ions (M - 15 + 1) agree with the calculated isotope contributions. These two pieces of evidence confirm the analytical and membrane osmometer molecular weight data obtained for the two compounds. The greater part of the observed masses, as in the permethylcarbosilanes¹⁷, result from cleavage of a Si-C bond. The mass spectral base peak (most intense peak in the range given) for (III) of 145 and for (IV) of 217 further support the proposed structures (III) and (IV). The observed base peaks result from fragmentation of the parent molecules as shown in (VI). Other structures



* Tris(trimethylsilyl)methane has a single strong absorption at 1010 cm⁻¹; R. West, unpublished data.

for (III) and (IV) cannot be readily visualized which would yield these base peaks.

The temperature dependence of the NMR spectra for (III) and (IV), shown in Figs. 1 and 2 respectively, is of unusual interest*. The spectrum of (III) at 35° is remarkably complex, apparently because of steric hindrance to free rotation as a result of the large interference radii of the bulky trimethylsilyl groups. At 163° the

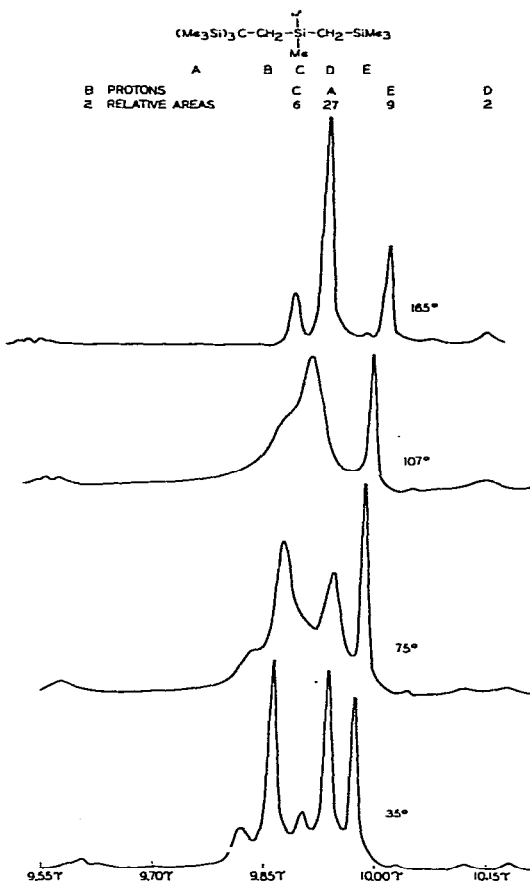


Fig. 1. Temperature dependence of the proton NMR spectrum of (III).

spectrum of (III) is greatly simplified (Fig. 1), allowing the given assignments to be made on the basis of relative intensities and chemical shifts. However, even at 163° complete collapse of the "B" protons of relative area two does not occur, and the "B" protons appear as a complex multiplet.

The temperature dependent NMR spectrum of (IV) (Fig. 2) shows the same general features as that of (III). The additional trimethylsilyl group in (IV) leads to still greater steric hindrance, resulting in lack of free rotation even at 181°. The assignments given in Fig. 2 have been made on the basis of relative intensities, chemical

* These are the only examples known to the authors in which hindered rotation of triorganosilyl groups result in temperature dependent NMR spectra. However, other cases may be known, and we invite correspondence from workers who have observed similar phenomena.

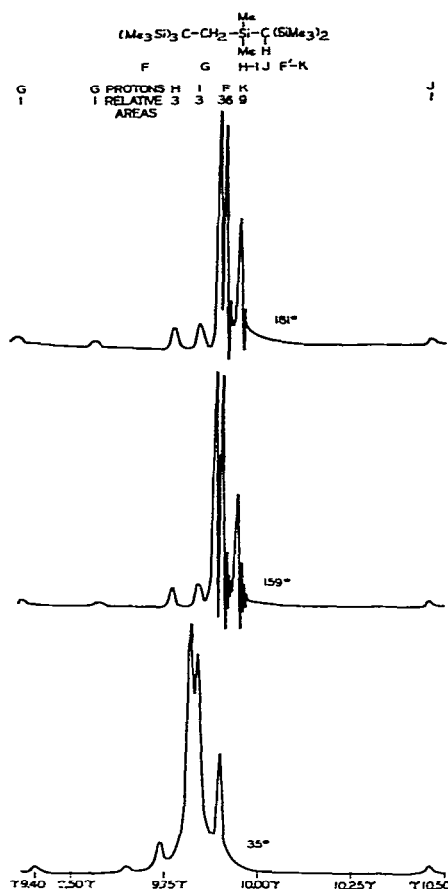
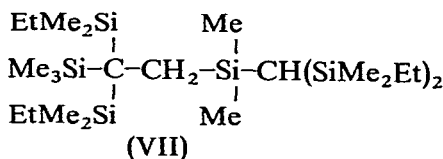


Fig. 2. Temperature dependence of the proton NMR spectrum of (IV).

shifts, and by analogy to the NMR spectrum of (III). From the 159° spectra for (IV) it appears that the "F" and "K" proton absorptions remain complex, overlap still occurring. Therefore, assignment is made primarily on the basis of relative intensities. If higher temperatures could be obtained, the complex doublet for the "G" protons should theoretically continue to collapse, the "H" and "I" absorptions should form a singlet as in (III) and the two "F" absorptions and the "K" absorption should form two absorptions of relative intensity 27/18 like the "A" and "E" pair in (III).

In contrast to the clean reaction observed with trimethylchlorosilane, the reductive silylation of bis(trimethylsilyl)acetylene with lithium and ethyldimethylchlorosilane resulted in a very complex reaction. The increased steric requirement of the ethyldimethylsilyl group apparently accounts for the observed results. The principal product was (VII), the ethyldimethylsilyl analog of (IV), obtained in 48%



yield. The structure proposed for (VII) is based on analytical, infrared, NMR, membrane osmometer molecular weight and mass spectra data.

In Fig. 3 a proposed reaction scheme is presented for a possible pathway by

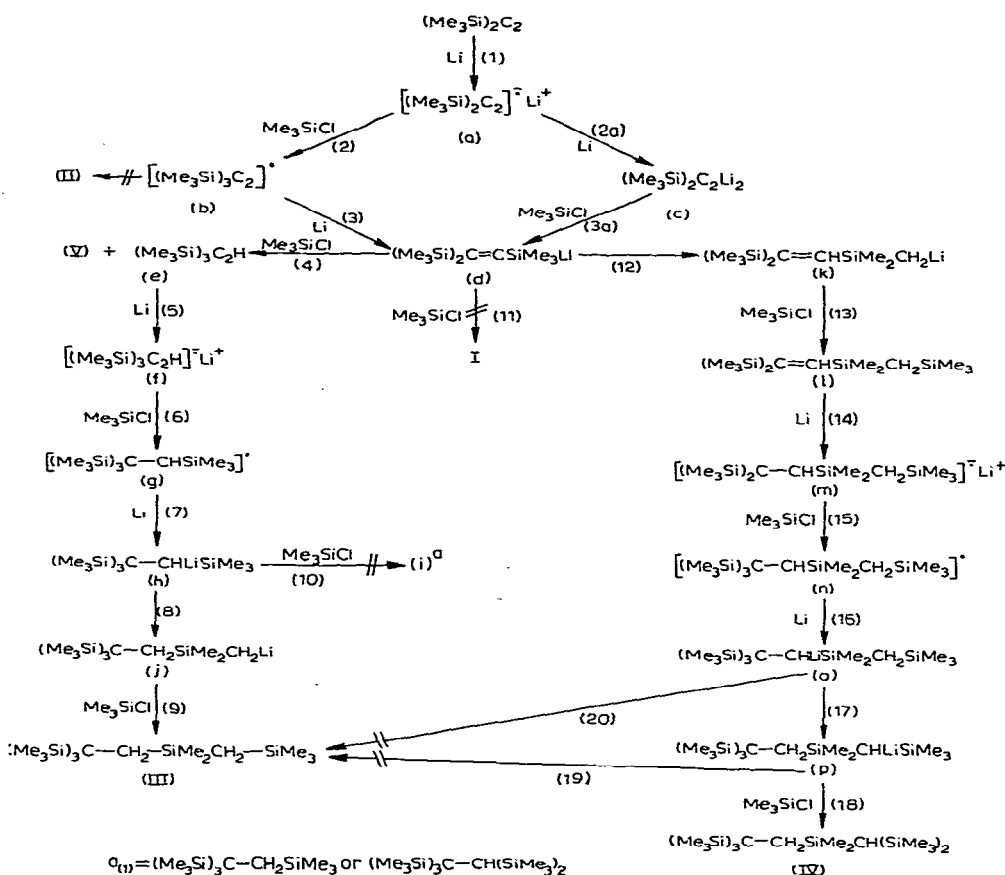


Fig. 3. Proposed reaction scheme for the reductive trimethylsilylation of bis(trimethylsilyl)acetylene.

which the observed products (III) and (IV) may be formed. The reaction schemes for other reductive silylation reactions⁵ have been shown to be similar to that for chemical reduction of carbon-carbon unsaturated compounds³. If the reductive silylation of bis(trimethylsilyl)acetylene proceeds similarly, it could go via either steps (2) and (3) or (2a) and (3a) with steps (2a) and (3a) probably being the preferred pathway under the conditions employed⁷.

Three of the possible pathways by which the organolithium intermediate (d) could react are shown in Fig. 3. Coupling with trimethylchlorosilane to yield (I) (step 11) is not observed due to nonbonding interactions. This leaves open pathways (4) and (12) which are believed to be competitive, with larger ratios of trimethylchlorosilane to bis(trimethylsilyl)acetylene favoring step (4) (see Table 1). In step (4) the intermediate (d) metalates trimethylchlorosilane¹⁴ to give (e) and (V). Isolation of compound (V) from the reaction provides evidence for the metalation of trimethyl-

chlorosilane by an alkyllithium intermediate. Although (V) could arise from either step 4 or step 20, metalation occurring at step (4) seems more likely for steric reasons. Consistent with step (4) is our finding that tris(trimethylsilyl)ethylene, (c), gives (III) in 70% yield when subjected to reductive silylation (see Experimental). The apparent ease with which tris(trimethylsilyl)ethylene is reduced compared to bis(trimethylsilyl)acetylene accounts for the fact that it cannot be detected in the reaction. The third pathway shown by which (d) can react is by an intramolecular metalation (step 12) to give the intermediate (k).

The formation of (III) and (IV) by further reductive silylation of the intermediates (e) and (k), respectively, is depicted in Fig. 3. The radicals (g) and (n) are the preferred isomers since (as can be shown from models) 1,2-trimethylsilyl interactions are larger than 1,1-trimethylsilyl interactions. The organolithium intermediates (h) and (o) undergo intramolecular metalation, steps (8) and (17) respectively, for steric reasons or to give the more stable organolithium compounds (j) and (p). The intermediates (j) and (p) react with trimethylchlorosilane to give the observed products (III) and (IV), respectively.

EXPERIMENTAL

All reactions with lithium were carried out in an atmosphere of prepurified argon. The lithium wire was cleaned and cut in an argon stream directly into apparatus which had been flame-dried while being flushed with argon. Dry THF was obtained immediately before use by distillation from lithium aluminum hydride. Bis(trimethylsilyl)acetylene was prepared by the *in situ* method from tetrachloroethylene, trimethylchlorosilane, and lithium metal¹⁹. Ethyldimethylchlorosilane was prepared from dimethyldichlorosilane by a standard procedure²⁰.

Analyses and membrane osmometer molecular weights were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. Infrared, NMR, and mass spectra were determined using Perkin-Elmer Model 457, Varian A-60A, and Consolidated Electronics Corporation 21-103C spectrometers, respectively. Raman spectra were obtained on a Cary Model 81 spectrometer at the University of Maryland (we thank Dr. Linda Whatley for determining the Raman data). The high temperature NMR spectra were obtained using a Varian V-6040 variable temperature controller with ethylene glycol to calibrate the temperature. Gas chromatographic separations were made on a Varian/Aerograph Model 705 chromatograph using a column packed with SE 30 (20%) on 40-60 Chromosorb W. Melting points and boiling points are uncorrected.

Reductive trimethylsilylation of bis(trimethylsilyl)acetylene

Trimethylchlorosilane (86.9 g, 0.80 mole) was added to finely-cut lithium wire (3.47 g, 0.50 g-atom) in THF (200 ml). Bis(trimethylsilyl)acetylene (17.04 g, 0.10 mole) was added and the reaction mixture was stirred rapidly at room temperature for 5 days. During this time several color changes occurred. The reaction mixture was filtered to remove unreacted lithium and the filtrate was hydrolyzed. The hydrolyzed reaction mixture was extracted with ether; the ether extract was washed several times with water, dried over anhydrous magnesium sulfate, and distilled to give unreacted bis(trimethylsilyl)acetylene (4.79 g), (III) (9.80 g, 37%), and (IV) (12.95 g, 39%).

2,2,4,4,7,7-Hexamethyl-6,6-bis(trimethylsilyl)-2,4,7-trisilaoctane (III), b.p. 125–130°/0.15 mm, n_D^{20} 1.4850, membrane osmometer molecular weight 380 (391.0 calcd.), was identified by its analysis and spectroscopic properties. (Found: C, 52.22; H, 12.07; Si, 35.97. $C_{17}H_{46}Si_5$ calcd.: C, 52.22; H, 11.86; Si, 35.92%.) The infrared spectrum (neat film) showed the following absorptions: 2950s, 2900m, 2800w, 1415w, 1250s, 1055m, 1025w, 840s, 760m, 710w, and 680m, cm^{-1} . The 70-eV mass spectrum showed the following peaks*: 375(0.04), 317(0.02), 303(0.1), 287(3.3), 230(36.2), 217(2.0), 215(2.6), 213(4.8), 203(6.6), 199(2.0), 157(29.0), 155(2.7), 145(100.0), 141(12.7), 131(9.8), 129(9.8), 127(2.3), 115(5.0), and 113(2.0).

2,2,4,4,7,7-Hexamethyl-1,6,6-tris(trimethylsilyl)-2,4,7-trisilaoctane (IV), b.p. 160–165°/0.15 mm, m.p. 87–88° (from ethanol), membrane osmometer molecular weight 467 (463.2 calcd.), showed the following infrared absorptions (CS_2 soln.): 2950s, 2900s, 2820m, 2800m, 1415w, 1250s, 1035w, 1010m, 995m, 850s, 800m, 760m, 715w, and 675m, cm^{-1} . The 70-eV mass spectrum showed the following peaks*: 447(0.06), 359(0.5), 303(0.1), 275(2.0), 230(2.9), 217(100.0), 213(4.2), 203(4.4), 201(4.6), 157(5.0), 141(2.4), 131(6.3), 129(27.0), 115(2.5), and 113(2.1). (Found: C, 52.11; H, 11.40; Si, 36.33. $C_{20}H_{54}Si_6$ calcd.: C, 51.86; H, 11.75; Si, 36.39%.)

Both compounds (III) and (IV) showed, in the Raman spectrum, no significant lines between 1500–2000 cm^{-1} . The proton NMR spectra for the two compounds are given in Figs. 1 and 2, respectively.

When the reaction mixture from the above procedure was worked up without hydrolysis, 2-chloro-2,4,4-trimethyl-2,4-disilapentane (V) (1.5 g, separated by gas chromatography), n_D^{22} 1.4340 (lit.²¹ n_D^{20} 1.4322) was obtained and identified by comparison of its infrared, NMR, and gas chromatography retention time with those of an authentic sample.

Reductive ethyldimethylsilylation of bis(trimethylsilyl)acetylene

Bis(trimethylsilyl)acetylene (8.52 g, 0.05 mole) was added to a suspension of finely-cut lithium wire (1.74 g, 0.25 g-atom) and ethyldimethylchlorosilane (24.54 g, 0.20 mole) in THF (100 ml). The reaction mixture was stirred at room temperature for 5 days, filtered to remove excess lithium, and hydrolyzed. The hydrolyzed mixture was extracted with ether and the ether extract dried over anhydrous magnesium sulfate. Distillation resulted in recovery of bis(trimethylsilyl)acetylene (2.8 g), a large number of minor products and (VII) (8.5 g, 48%), b.p. 180–185°/0.25 mm, n_D^{20} 1.5169. (Found: C, 55.42; H, 12.06; Si, 32.43. $C_{24}H_{62}Si_6$ calcd.: C, 55.51; H, 12.04; Si, 32.46%.) The infrared spectrum shows absorptions at 1035, 1010, and 995 cm^{-1} as in (IV). A molecular weight of 506 found by membrane osmometer agrees favorably with the 519.3 calculated value. The mass spectra shows peaks at 503 (parent- CH_3), 489 (parent- CH_3CH_2), and a base peak of 245, $^+SiMe_2CH(SiMe_2Et)_2$, analogous to the base peaks observed for (III) and (IV). The complex NMR gives an integrated proton ratio of 22/39/1 vs. the calculated proton ratio for $(SiEt + CH_2)/SiMe/CH = 22/39/1$. A trisilylmethine proton is observed falling at 10.47 τ .

Preparation of tris(trimethylsilyl)ethylene

Bis(trimethylsilyl)acetylene (36.2 g, 0.21 mole) and 0.4 ml of a 2% solution of

* Peaks below m/e 300 and less than 2.0 in relative intensity are not reported.

chloroplatinic acid in isopropanol were heated to 110° in a flask equipped with a dry-ice condenser. Trichlorosilane (43.1 g, 0.32 mole) was added slowly maintaining the reaction temperature above 100°. The reaction temperature was maintained above 100° until the solution stopped refluxing, showing the absence of unreacted trichlorosilane. Ether (200 ml) was added to the cooled reaction mixture and methylmagnesium bromide (233 ml of a 3.0 M solution, 0.70 mole) was added slowly maintaining a gentle reflux. The reaction mixture was stirred for 24 h at room temperature, hydrolyzed with a saturated solution of ammonium chloride, and filtered to remove salts. The ether layer was washed twice with water and dried over anhydrous magnesium sulfate. Distillation gave tris(trimethylsilyl)ethylene (26.4 g, 51%), b.p. 96–97°/10 mm (lit.¹⁰ 43–45°/0.5 mm), n_D^{20} 1.4647 (lit.¹⁰ 1.4649), infrared absorption 1499 cm^{-1} (lit.¹⁰ 1499 cm^{-1}), and an NMR absorption 2.67 τ (lit.¹⁰ 2.67).

Reductive trimethylsilylation of tris(trimethylsilyl)ethylene

Tris(trimethylsilyl)ethylene (13.58 g, 0.055 mole) was added to a suspension of finely-cut lithium wire (0.77 g, 0.11 g-atom) and trimethylchlorosilane (18.15 g, 0.17 mole) in THF (75 ml). Upon addition of the tris(trimethylsilyl)ethylene, the reaction mixture turned deep red and a mild exothermic reaction resulted. After 90 min the reaction mixture turned light yellow and after 5 h became colorless. After 72 h the colorless reaction mixture was filtered, hydrolyzed, and extracted with ether. The ether extract was dried over anhydrous magnesium sulfate. Fractional distillation gave 14.8 g (69%) of (III).

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