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Synthesis of silatranyl- and 3,7,10-trimethylsilatranyl-cyclopropanes

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Abstract

Treatment of silatranyl- and 3,7,10-trimethylsilatranyl-ethylenes with diazomethane/$Pd(OAc)_2$ gives the corresponding silatranylcyclopropanes in high yields.

Introduction

The reactions of silatranylalkenes with a variety of reagents have been much studied, *e.g.* hydrometallations [1–3] and radical-initiated additions of species containing S–H, P–H, C–H, C–Br or C–I bonds [1,4] which occur with retention of the Si–C bond and reactions with electrophiles, *e.g.* sulphenyl chlorides, which give 1-chlorosilatranes with cleavage of a silicon carbon bond [5–7]. More interesting are certain reactions involving participation the carbon–carbon double bond that occur with retention of the silatranyl fragment; as and we previously reported the peroxide- and metal complex-catalyzed addition of methyltrichloroacetate to silatranylalkenes [8], and the reaction with Br_2/H_2O to give silatranylethylenebromohydrines in high yields, which are useful reagents for the synthesis of silatranylacetaldehydes [9,10].

We report below on the cyclopropanation of silatranylalkenes by the $CH_2N_2/Pd(OAc)_2$ system, which has not previously been used in silatrane chemistry.

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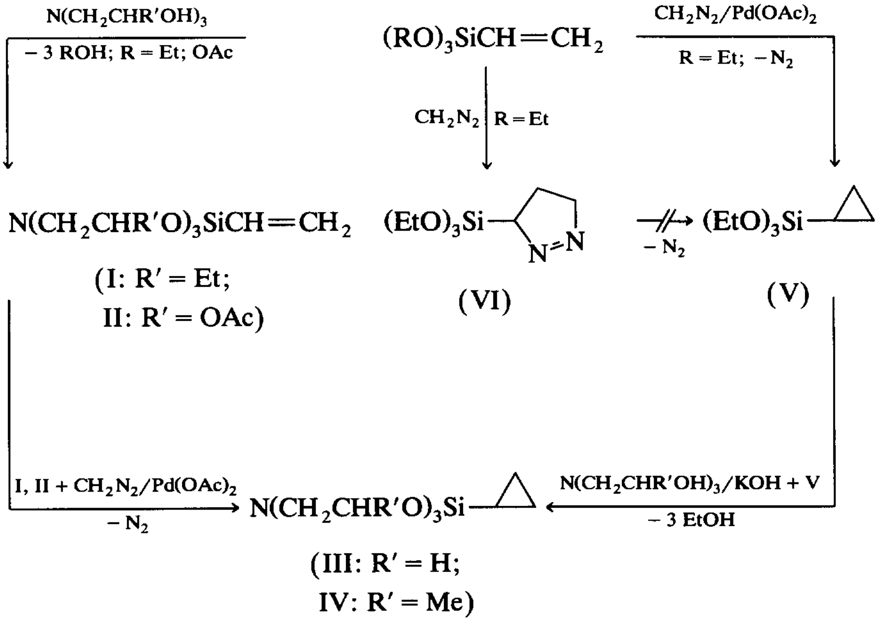
Results and discussion

The starting materials, silatranylethylenes I and II are best prepared from $(EtO)_3SiCH=CH_2$ or $(AcO)_3SiCH=CH_2$ by treatment with trialkanolamines; the triacetoxysilylethylenes are preferred because they react under mild conditions without the need for a catalyst. Both silatranylethylenes react readily with $CH_2N_2/Pd(OAc)_2$ to give dinitrogen and the corresponding silatranylcyclopropanes III and IV. The silatranyl-substituted cyclopropanes were identified by ^1H and ^{13}C NMR spectra; in the case of compound IV there is clear evidence for the presence of two diastereomeric species.

An alternative synthesis of silatranylcyclopropanes was developed, starting with the cyclopropanation of the readily available $(EtO)_3SiCH=CH_2$ with $CH_2N_2/Pd(OAc)_2$, which give V in good yields; transesterification of V gave an almost quantitative yield of silatranylcyclopropane III [11]. This approach was employed previously for the synthesis of 1-silatranyl-2-chlorocyclopropane [12], the only other example of this type of compound.



Scheme 1.

In the absence of a catalyst, the silatranylethylene I and CH_2N_2 do not react to form the corresponding silatranylsubstituted cyclopropane, even under UV irridation. In contrast, $(EtO)_3SiCH=CH_2$ and CH_2N_2 readily undergo a 1,3-cycloaddition to give the silyl-substituted heterocycle 3-triethoxysilyl-1-pyrazoline (VI) (Scheme 1). An analogous product way obtained previously from the reaction of $Me_3SiCH=CH_2$ with diazomethane in the absence of a catalyst [13].

We have shown that silatranylethylenes can be converted into the corresponding cyclopropanes by reaction with CH_2N_2 in the presence of $Pd(OAc)_2$; the silatranylcyclopropane III can also be obtained by the transesterification of triethoxysilylcyclopropane V with triethanolamine.

Experimental

The ^1H and ^{13}C NMR spectra were recorded on a Varian XR-400 spectrometer with TMS as an internal standard. Diazomethane was prepared in the usual way from *N*-methylnitrosourea in ethereal solution at a concentration of *ca.* 2 g of CH_2N_2 in 100 ml of dry ether.

Silatranylcyclopropane (III)

Method A. $Pd(OAc)_2$ (10 mg) was added to a vigorously stirred solution of 0.4 g (2 mmol) of silatranylethylene (I) in 15 ml of the CH_2N_2/ether solution containing *ca.* 0.3 g (7.1 mmol) of diazomethane. The stirred mixture was kept at −5°C for *ca.* 30 min, then for 1 h at room temperature. The solid (catalyst) was filtered off and some ether evaporated from the filtrate and n-pentane added to give white crystals. These were filtered off and recrystallized from $CHCl_3$/n-pentane. Yield: 0.4 g (93%), m.p. 145–146°C. Lit. [1] 143–144°C; Lit. [11] 150°C. ^1H NMR (δ in ppm, $CDCl_3$): −0.55 to −0.46 (m, 1H, SiCH); 0.3–0.34 (m, 2H, cyclopr.); 0.4–0.45 (m, 2H, cyclopr.); 2,79 (t, 6H, NCH_2); 3.77 (t, 6H, OCH_2). ^{13}C NMR: −4.38 (SiCH); 1.18 (CH_2); 51.46 (NCH_2); 57.91 (OCH_2).

Method B. A mixture of 0.5 g (2.4 mmol) of triethoxysilylcyclopropane (V), 0.35 g (2.4 mmol) of triethanolamine, 20 ml of benzene and 1 pellet of KOH was heated and the ethanol formed in the transesterification reaction was removed together with benzene. The residue was dissolved in $CHCl_3$ and n-pentane added, the white precipitate filtered off and washed with n-pentane. After drying *in vacuo* 0.49 g (95%) of III was obtained, m.p. 144–145°C.

3,7,10-trimethylsilatranylcyclopropane (IV)

The preparation was analogous to that used for III from 0.5 g (2.1 mmol) of 3,7,10-trimethylsilatranylethylene, 15 ml of diazomethane/ether solution, and 10 mg $Pd(OAc)_2$. Yield: 0.53 g (100%) m.p. 75–76°C. ^1H NMR: −0.54 to −0.46 (m, 1H, SiCH); 0.3–0.34 (m, 2H, cyclopr.); 0.4–0.44 (m, 2H, cyclopr.); ^{13}C NMR: −4.31 (SiCH); 1.48, 1.62 (CH_2 cyclopr.); 20.31, 20.38, 20.75, 23.07 (Me); 58.97, 61.79, 61.91, 63.43, 65.02, 65.20, 66.87 (NCH_2, OCH_2); 2 diastereomers.

Triethoxysilylcyclopropane (V)

Diazomethane 1.26 g (30 mmol) in ether was added to a stirred mixture of 2.25 g (11.8 mmol) of triethoxysilylethylene and 24 mg of $Pd(OAc)_2$. The mixture was stirred at −25°C then allowed to rise to room temperature during 40 min with continued stirring. It was then filtered and the filtrate distilled. Yield: 2.2 g (91%), b.p. 41–42°C at 1 torr; n_D^{20} 1.4104. ^1H NMR: −0.49 to −0.41 (m, 1H, SiCH); 0.44–0.48 (m, 2H, cyclopr.); 0.57–0.62 (m, 2H, cyclopr.); 1.23 (t, 9H, $OCCH_3$); 3.84 (t, 6H, OCH_2). ^{13}C NMR: −10.14 (SiCH); 1.00 (CH_2 cyclopr.); 18.32 ($OCCH_3$); 58.54 (OCH_2). Anal. Found: C, 53.50; H, 9.97; Si, 14.08. $C_9H_{20}O_3Si$ calc.: C, 52.90; H, 9.86; Si, 13.74%.

3-Triethoxysilyl-1-pyrazoline (VI)

VI was made in the same way as V but without use of $Pd(OAc)_2$. Yield: 95%, b.p. 105–106°C/4 torr; n_D^{20} 1.4334. ^1H NMR: 1.24 (t, 9H, $OCCH_3$); 3.88 (t, 6H, OCH_2); 1.20–1.26 (m, 2H, $C(4)H_2$); 3.8–3.9 (m, 3H, C(3)H, $C(5)H_2$). ^{13}C NMR: 18.13, 18.23 ($OCCH_3$), C4); 59.17 (OCH_3); 76.39, 79.56 (C3, C5). Anal. Found: C, 46.82; H, 8.97; Si, 11.97. $C_9H_{20}N_2O_3Si$ calc.: C, 46.52; H, 8.68; Si, 12.09%.

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References

1 M.G. Voronkov, V.M. Dyakov and S.V. Kirpichenko, J. Organomet. Chem., 233 (1982) 1.
2 M. Nasim, A.K. Saxena and L.M. Pande, Polyhedron, 7 (1988) 2189.
3 M.G. Voronkov, S.N. Adamovich, N.M. Kudyakov, S. Yu. Khramtsova, V.I. Rakhlin and R.G. Mirskov, Izv. Akad. Nauk SSSR, Ser. Khim., (1986) 488.
4 M.G. Voronkov, L.P. Petuchov, S.N. Adamovich, V.P. Baryshok, V.I. Rakhlin, B.Z. Shterenberg and R.G. Mirskov, Izv. Akad. Nauk SSSR, Ser. Khim., (1987) 204.
5 A. Kutyrev, A.A. Kapura, M.S. Sorokin, R.A. Cherkasov, M.G. Voronkov and A.N. Pudovik, Dokl. Akad. Nauk SSSR, 275 (1984) 1104.
6 G.A. Kutyrev, A.A. Kapura, M.S. Sorokin, R.A. Cherkasov, M.G. Voronkov and A.N. Pudovik, Zh. Obshch. Khim., 55 (1985) 1030.
7 G.M. Svistunov, N.P. Shapkin, V.I. Razov and V.Yu. Glushchenko, Zh. Obshch. Khim., 60 (1990) 1359.
8 A.A. Kamysheva, M. Nasim, G.S. Zaitseva and A.B. Terentjev, Metalloorg. Khim., 4 (1991) 459.
9 M. Nasim, L.I. Livantsova, A.V. Kisin, G.S. Zaitseva and V.S. Petrosyan, Metalloorg. Khim., 3 (1990) 949.
10 M. Nasim, L.I. Livantsova, D.K. Krut'ko, G.S. Zaitseva, J. Lorberth and M. Otto, J. Organomet. Chem., 402 (1991) 313.
11 S.N. Gurkova, A.I. Gusev, N.V. Alekseev and M.I. Ignatenko, Zh. Strukt. Khim., 29 (1988) 203.
12 S.N. Gurkova, A.I. Gusev, N.V. Alekseev and M.A. Ignatenko, Metalloorg. Khim., 1 (1988) 1251.
13 R.T. Conlin and Y.-W. Kwak, J. Organomet. Chem., 293 (1985) 177.