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Preliminary communication

A NOVEL SYNTHESIS OF SILICON-CONTAINING AZIRIDINES

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Summary

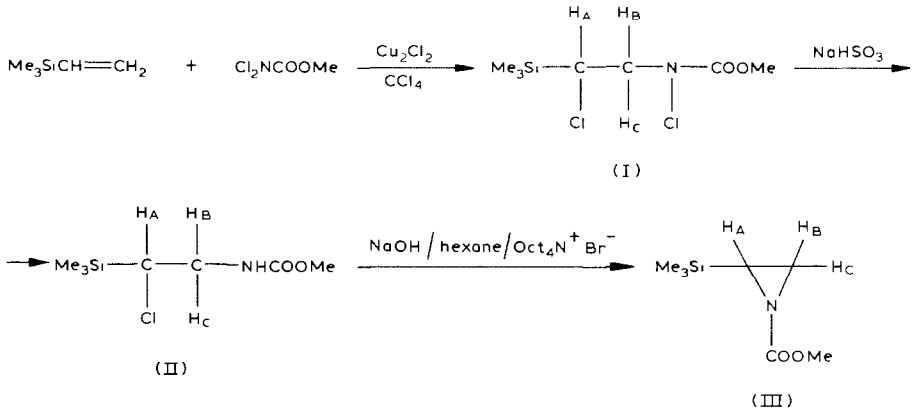
Addition of methyl *N,N*-dichlorocarbamate to trimethylvinylsilane with subsequent reduction with sodium hydrosulphite afforded methyl *N*-(2-chloro-2-trimethylsilyl)ethylcarbamate. Intramolecular alkylation of the latter in a hexane/solid NaOH two-phase system in the presence of a phase transfer catalyst or under ultrasonic irradiation resulted in 1-carbmethoxy-2-trimethylsilylaziridine. Similarly, starting from trimethylallylsilane the 1-carbethoxy-2-(trimethylsilylmethyl)aziridine was prepared.

Silicon-containing aziridines with a Si—C bond were first obtained at low or moderate yield in the reaction of vinylsilanes with arylazides [1,2]. An alternative procedure for the preparation of trialkylsilylaziridines involving the interaction of alkenes (vinylsilanes included therein) with trimethylsilylazide has been put forward by Ettenhuber and Rühlmann [3]. Re-investigation of these two methods described in [4] supported the data of Andrianov et al. [1,2] and refuted that of Ettenhuber and Rühlmann [3]. A procedure is also known for the preparation of silicon-containing 1*H*-aziridines involving reduction of adducts of bromoazide and vinylsilanes with $LiAlH_4$ [5]. Finally, a 30% yield of 2-triethylsilyl-1*H*-aziridine was attained by treating methyl *N*-(2-iodo-2-triethylsilyl)ethylcarbamate, obtained by methanolysis of iodoisocyanate and triethylvinylsilane adduct, with alkaline alcohol [6].

Aziridines with an organosilicon group isolated from the heterocycle are not known. An attempt to obtain such compounds by treating allylsilane with phenylazide has been unsuccessful [1].

Bearing in mind the data described in [6], as well as the results of intramolecular alkylation of 3-arylamino-2-chloropropionitriles to 1-aryl-2-cyanoaziridines [7] and of ethyl 4-chlorobutyrate derivatives to the corresponding esters of cyclopropanecarboxylic acid [8] under conditions of phase transfer catalysis (PTC), we thought it of interest to examine the applicability of a similar cyclization to the synthesis of silicon-containing aziridines.

The reaction of trimethylvinylsilane with methyl *N,N*-dichlorocarbamate (the latter product was prepared using a convenient preparative procedure by treating chlorine with methyl carbamate in acetate buffer solution, as described in [9] for *N,N*-dichlorourethan) in the presence of Cu_2Cl_2 (70°C, 2 h) led to methyl *N*-chloro-*N*-(2-chloro-2-trimethylsilyl)ethylcarbamate (I) (Scheme 1). Yield: 85%; ^{1}H NMR (90 MHz, $CDCl_3$), δ, ppm: 0.17 (s, 9H, $SiMe_3$), 3.65 (m, 1H, H_B), 3.68 (dd, 1H, H_A), 3.82 (s, 3H, OMe), 4.17 (m, 1H, H_C), J_{AB} 3.3 Hz; J_{AC} 12.1 Hz; J_{BC} 15.3 Hz.



SCHEME 1

Reduction of I with 20% aqueous sodium hydrosulphite (15°C, 3 h) afforded methyl *N*-(2-chloro-2-trimethylsilyl)ethylcarbamate (II). Yield: 80%; ^{1}H NMR, δ, ppm: 0.14 (s, 9H, $SiMe_3$), 3.17 (m, 1H, H_B), 3.46 (m, 1H, H_C), 3.67 (s, 3H, OMe), 3.76 (dd, 1H, H_A), 5.16 (s, 1H, NH); J_{AB} 4.0 Hz; J_{BC} 12.3 Hz; J_{AC} 10.1 Hz.

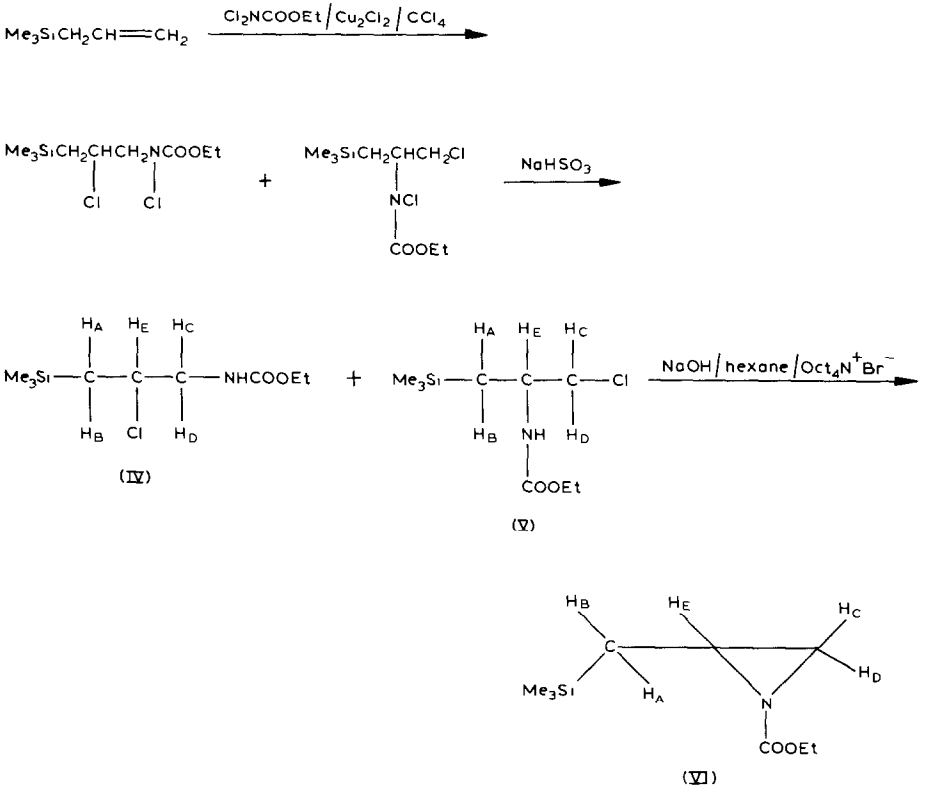
Carbamate II under liquid-solid PTC conditions (hexane solution of II/solid NaOH/catalyst Oct_4/N^+Br^-) underwent intramolecular alkylation and was converted (25°C, 4 h) to 1-carbmethoxy-2-trimethylsilylaziridine (III). Yield: 75%; ^{1}H NMR, δ, ppm; 0.09 (s, 9H, $SiMe_3$), 1.73 (dd, 1H, H_B), 2.05 (dd, 1H, H_C), 2.42 (dd, 1H, H_A), 3.73 (s, 3H, OMe); J_{AB} 7.0 Hz; J_{AC} 4.8 Hz; J_{BC} 1.0 Hz; mass spectrum (70 eV), *m/e* (relative intensity %))*: 172 (M^+ − 1,2), 158 (M^+ − Me, 6), 114 (57), 100 (28), 89 (95), 86 (38), 73 (78), 59 (98), 45 (33), 43 (32).

Under the same conditions but in the absence of catalyst, cyclization of carbamate II to aziridine III also occurred, but at a much slower rate (ca. by one order of magnitude). This prompted us to test the feasibility of heterogeneous reaction II→III without catalyst under ultrasonic irradiation, since we were aware of many cases where organic and organometallic heterogeneous reactions had been induced or accelerated by ultrasound (see, for example, [10] and ref. cited therein). Experiments have shown that ultrasonic irradiation (100 W, 55 kHz) significantly accelerates cyclization of II to III in the presence of alkali, as compared to the reaction without catalyst. There-

*Here and below are given the peaks of characteristic ions and peaks with > 10% intensity.

by, compound III is formed at about the same rate and yield as under PTC conditions. To our knowledge, the intramolecular alkylation of II leading to III is the first example of ultrasound-facilitated reactions of this type.

Our findings allowed us to expect that, by using the above method, so far unknown silicon-containing aziridines with a silicon atom isolated from the heterocycle by a methylene group might be obtained from trimethylallylsilane as a starting compound. In fact, allylsilane reacted with ethyl *N*,*N*-dichlorocarbamate to form a mixture of β- and γ-adducts, whose reduction with sodium hydrosulphite gave a mixture of ethyl *N*-(2-chloro-3-trimethylsilyl)-propylcarbamate (IV) and ethyl *N*-(1-chloromethyl-2-trimethylsilyl)ethylcarbamate (V) (Scheme 2) at a 1/1 ratio (according to ^{1}H NMR data). Total yield: 40%. The structures of IV and V were supported by ^{1}H NMR spectral data, as well as by mass spectra recorded during GLC-MS analysis of the mixture of these carbamates. ^{1}H NMR of IV (360 MHz, $CDCl_3$), δ, ppm: 0.10 (s, 9H, $SiMe_3$), 1.13 (dd, 1H, H_A, J_1 6.3 Hz; J_2 14.2 Hz), 1.21 (dd, 1H, H_B, J_1 8.6 Hz, J_2 14.2 Hz), 1.25 (t, 3H, OCH_2CH_3, J 6.7 Hz), 3.14 (m, 1H, H_C, J_1 8.5 Hz, J_2 13.9 Hz, J_3 4.9 Hz), 3.64 (m, 1H, H_D, J_1 3.0 Hz; J_2 13.9 Hz; J_3 5.0 Hz), 4.11 (q, 2H, OCH_2CH_3), 4.15 (m, 1H, H_E), 5.18 (bs, 1H, NH); mass spectrum of IV (*m/e*, relative intensity, %): 222 (M^+ — Me, 5), 202 (M^+ — Cl, 14), 128 (12), 102 (24), 100 (12), 95 (12), 93 (30), 75 (19), 74 (11), 73 (100), 56 (14), 45 (11), 41 (22); ^{1}H NMR of V (360 MHz, $CDCl_3$),



SCHEME 2

δ, ppm: 0.10 (s, 9H, $SiMe_3$), 1.10 (dd, 1H, H_A, J_1 6.1 Hz, J_2 14.6 Hz), 1.17 (dd, 1H, H_B, J_1 8.0 Hz, J_2 14.6 Hz), 1.36 (t, 3H, OCH_2CH_3, J 6.7 Hz), 3.69 (m, 1H, H_C, J_1 4.2 Hz, J_2 11.3 Hz), 3.73 (m, 1H, H_D, J_1 6.1 Hz; J_2 11.3 Hz), 4.30 (q, 2H, OCH_2CH_3, J 6.7 Hz), 4.98 (m, 1H, H_E); mass spectrum of V (*m/e*, relative intensity, %): 222 (M^+ — Me, 9), 188 (M^+ — CH_2Cl, 57), 119 (13), 103 (10), 100 (16), 93 (11), 75 (45), 74 (12), 73 (100), 45 (13), 43 (11), 41 (21).

Cyclization of the mixture of IV and V under PTC conditions as described above for the reaction II→III led to 1-carbethoxy-2-(trimethylsilyl)methylaziridine (VI). Yield: 20%; ^{1}H NMR, δ, ppm: 0.09 (s, 9H, $SiMe_3$), 0.56 (dd, 1H, H_A, J_1 14.2, J_2 7.0 Hz), 1.04 (dd, 1H, H_B, J_1 14.2 Hz; J_2 5.6 Hz), 1.27 (t, 3H, CH_2CH_3, J 6.8 Hz), 1.91 (d, 1H, H_C, J 3.6 Hz), 2.33 (d, 1H, H_D, J 5.0 Hz), 2.45 (m, 1H, H_E), 4.16 (q, 2H, CH_2CH_3, J 6.8 Hz); mass spectrum (*m/e*, relative intensity, %): 201 (M^+, 1), 186 (M^+ — Me, 5), 172 (M^+ — Et, 3), 158 (8), 140 (11), 128 (20), 112 (10), 103 (18), 100 (20), 97 (19), 86 (15), 75 (28), 74 (10), 73 (100), 61 (10), 59 (18), 45 (15), 43 (10), 41 (18).

Thus, addition of dichlorocarbamates to vinyl- and allylsilanes with subsequent reduction and cyclization may serve as a method for the preparation of silicon-containing aziridines.

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