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REACTIONS OF VINYLSILANES WITH ETHOXYCARBONYLNITRENE UNDER PHASE-TRANSFER CONDITIONS: A NOVEL ROUTE TO SILICON-CONTAINING AZIRIDINES

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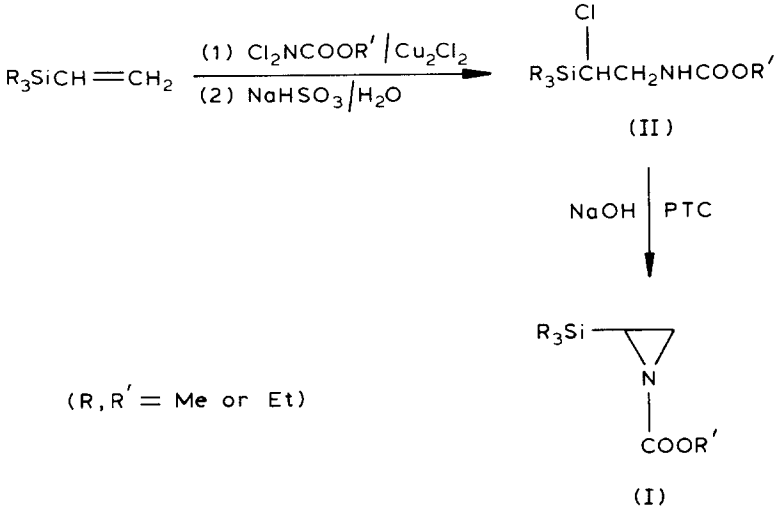
Summary

The addition of ethoxycarbonylnitrene, generated from ethyl *N*-(*p*-nitrobenzenesulphonyloxy)carbamate under liquid–liquid phase-transfer conditions to vinyl-, α-bromovinyl- and (β-methoxycarbonylvinyl)(trialkyl)silanes affords the corresponding 1-ethoxycarbonyl-2-trialkylsilylaziridines.

Introduction

We have recently reported on the phase-transfer catalysed intramolecular alkylation of alkyl *N*-(2-trialkylsilyl-2-chloro)ethylcarbamates (II), which are formed as a result of vinylsilane and *N*,*N*-dichlorocarbamate adduct reduction, this is a con-



SCHEME 1

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venient method for the preparation of 1-ethoxycarbonyl-2-trialkylsilylaziridines (I) (Scheme 1) [1,2].

The above method is somewhat limited in its application because of the presence of more than one electron-accepting substituent at the α-carbon atom in silicon-containing carbamates II. The latter is therefore desilylated in the presence of bases [2] and hence this route fails to give functionally substituted silylaziridines. The reaction of alkenes with ethoxycarbonylnitrene, =NCOOEt, is a common and convenient method for the synthesis of 1-ethoxycarbonylaziridines [3] suggesting that the reaction between vinylsilanes and =NCOOEt resulting in aziridines of the type I can serve as an alternative pathway to that shown in Scheme 1. These reactions were performed for vinyl-, α-bromovinyl- and (β-methoxycarbonyl)-vinyl(trialkyl)silanes, in this work.

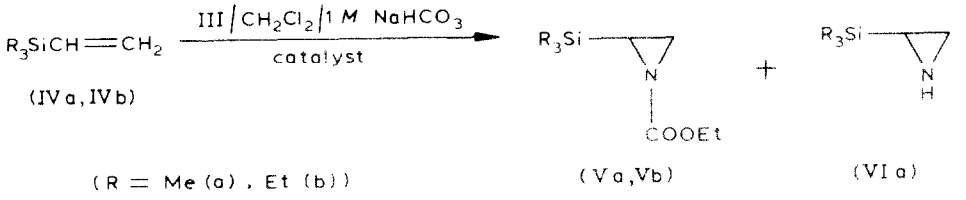
Results and discussion

Among the methods available for =NCOOEt generation [3], we chose base-induced α-elimination of the *p*-nitrobenzenesulphonate anion from ethyl *N*-(*p*-nitrobenzenesulphonyloxy)carbamate (III), which can be carried out under liquid–liquid phase-transfer conditions (PTC) [4,5].

1-Ethoxycarbonyl-2-trimethylsilylaziridine (Va) was obtained as the main product by stirring a two-phase mixture consisting of vinyltrimethylsilane (IVa), a nitrene precursor (III) and triethylbenzylammonium chloride (TEBA) dissolved in dichloromethane and 1 *M* aqueous sodium bicarbonate under conditions similar to those described in [4] (Scheme 2, Table 1). 2-Trimethylsilyl-1*H*-aziridine (VIa), apparently resulting from hydrolysis and decarboxylation of Va [2], was also found in the reaction mixture.

The yields of Va decreased when saturated aqueous solutions of Na_2CO_3 and K_2CO_3, were used as the base. Only negligible amounts of Va were formed without a phase-transfer catalyst (Table 1). Other well-known phase-transfer catalysts showed similar activity in the reaction of IVa with =NCOOEt. Polymer-bound phosphonium salts were found to be somewhat less effective than their soluble analogues, the catalyst in which the onium cation was separated from the polymer matrix by a longer methylene chain was more effective. To our knowledge, this is the first case where the reactions involving nitrenes have been performed under "triphase catalysis" [6] conditions.

With these results in mind we studied =NCOOEt addition to other vinylsilanes in the CH_2Cl_2/1 *M* $NaHCO_3$ two-phase system with TEBA as the catalyst. Under these conditions, vinyltriethylsilane (IVb) is converted to 1-ethoxycarbonyl-2-trieth-



SCHEME 2

TABLE 1

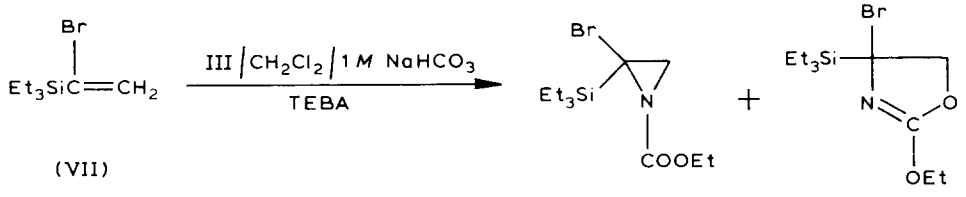
REACTIONS OF VINYLTRIALKYLSILANES WITH ETHOXYCARBONYLNITRENE UNDER PTC CONDITIONS [a]

Vinylsilane [b]	Base	Catalyst	Products (yield, %) [c]
$Me_3SiCH{=}CH_2$ (IVa)	1 *M* $NaHCO_3$	TEBA	Va (30), Va (3)
IVa	1 *M* $NaHCO_3$	–	Va (1.5)
IVa	2 *M* Na_2CO_3	TEBA	Va (18), VIa (2)
IVa	8 *M* K_2CO_3	TEBA	Va (15), VIa (2)
IVa	1 *M* $NaHCO_3$	$Bu_4N^+ H SO_4^-$	Va (32), VIa (3)
IVa	1 *M* $NaHCO_3$	$Bu_3N^+ CH_2Ph Cl^-$	Va (31), VIa (3)
IVa	1 *M* $NaHCO_3$	Aliquat®336 [d]	Va (33), VIa (2)
IVa	1 *M* $NaHCO_3$	$Bu_4P^+ Cl^-$	Va (30), VIa (1)
IVa	1 *M* $NaHCO_3$	$Bu_3P^+ C_{16}H_{33} Br^-$	Va (35), VIa (2)
IVa	1 *M* $NaHCO_3$	[*p*]-$CH_2P^+ Bu_3 Cl^-$ [e]	Va (18), VIa (0.5)
IVa	1 *M* $NaHCO_3$	[*p*]-$(CH_2)_6P^+ Bu_3 Br^-$ [f]	Va (24), VIa (0.5)
$Et_3SiCH{=}CH_2$ (IVb)	1 *M* $NaHCO_3$	TEBA	Vb (38)

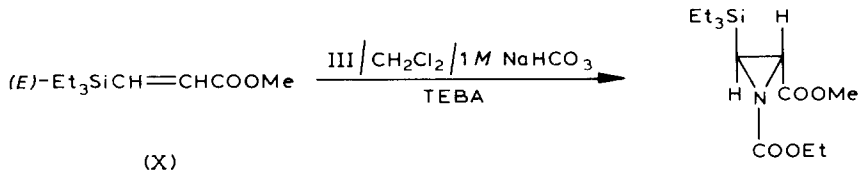
[a] Molar ratio vinylsilane: *p*-$O_2NC_6H_4SO_3NHCOOEt/NaHCO_3$/catalyst 1/0.5/1.5/0.1. [b] 0.4 *M* solution in dichloromethane. [c] GLC data. [d] Tricaprylmethylammonium chloride. [e] Polymer-bound tributylmethylphosphonium chloride (0.78 mmol Cl/g). [f] Polymer-bound hexyltributylphosphonium bromide (0.83 mmol Br/g).

ylsilylaziridine (Vb), the yield being 38%. The corresponding 1*H*-aziridine is not formed in this case. Similarly, α- and β-substituted vinylsilanes react with ethoxycarbonylnitrene to give the corresponding substituted aziridines as main products (Scheme 3).

Thus, (α-bromovinyl)triethylsilane (VII) gives 1-ethoxycarbonyl-2-bromo-2-triethylsilylaziridine (VIII) in 27% GLC yield. According to GLC/MS data, the

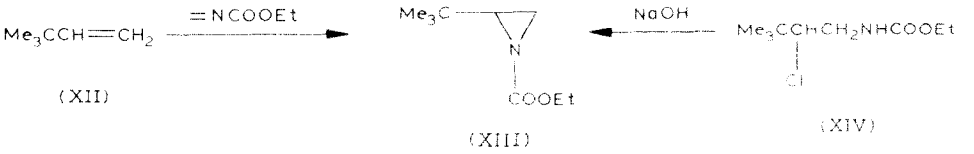


(VII) (VIII) (IX)



(X) (XI)

SCHEME 3



SCHEME 4

reaction mixture also contains a product (~ 6%) isomeric to aziridine VIII. This is apparently 4-bromo-4-triethylsilyl-2-ethoxy-1,3-oxazoline-2 (IX) formed either as a result of the rearrangement of VIII [7] or by 1,3-dipolar addition of ethoxycarbonylnitrene to the silane VII [3]. The addition of =NCOOEt to methyl *trans*-3-triethylsilylacrylate * (X) affords 1-ethoxycarbonyl-*trans*-2-triethylsilyl-3-methoxycarbonylaziridine (XI) with 22% yield. The stereospecificity of addition indicates that the reacting species is the singlet, ethoxycarbonylnitrene [3].

The reaction of 3,3-dimethylbutene-1 (XII) (a carbon-containing analogue of vinylsilane IVa) with =NCOOEt was also studied for comparison. Under similar conditions the alkene XII was converted to 1-ethoxycarbonyl-2-t-butylaziridine (XIII) in 57% GLC yield (Scheme 4).

Compound XIII was also obtained by alternative synthesis using intramolecular alkylation of ethyl *N*-(2-t-butyl-2-chloro)ethylcarbamate (XIV) [8] under solid–liquid PTC conditions [2] (Scheme 4).

The difference in reactivity observed for the vinylsilane IVa and the alkene XII may be due to the π-accepting properties of the silicon atom [9], which reduce the nucleophilicity of the C=C bond.

Thus, the reaction of vinylsilanes with ethoxycarbonylnitrene represents a new route to silicon-containing aziridines. Although the above method is characterized by somewhat lower yields as compared with the procedure described in [1,2] (Scheme 1), the nitrene route being a single-step process, is easy to perform and hence provides an attractive alternative to intramolecular alkylation of silicon-containing carbamates II [1,2] and other known synthetic routes leading to silicon-containing aziridines with a Si–C bond [10–15].

Experimental

The ^{1}H NMR spectra were recorded on a WH-90/DS spectrometer (Bruker) with $CDCl_3$ as solvent and TMS as internal standard. The mass spectra were recorded on a MS-25 apparatus (Kratos), the ionizing energy was 70 eV. The GLC analysis was carried out with a Chrom-5 apparatus fitted with a flame-ionization detector. A glass column (1.2 m × 3 mm) was packed with 5% OV-17/Chromosorb W-HP (80–100 mesh); helium was used as carrier gas (50 cm^3/min). The temperature range was 100 to 170°C depending on the reaction-mixture composition. All catalysts and vinyltrialkylsilanes were purchased from Fluka except for Aliquat^R

* Compound X was prepared by hydrosilylation of methyl propiolate with triethylsilane in tetrahydrofuran in the presence of $H_2PtCl_6 \cdot 6H_2O$, the reaction mixture containing both X and the α-adduct, methyl 2-triethylsilylacrylate (XI). The latter was separated because it alone reacts when the mixture is treated with 1,1-dimethylhydrazine (see Experimental section).

336 obtained from Aldrich. (α-Bromovinyl)triethylsilane was prepared as described in [15]. Ethyl-*N*-(*p*-nitrobenzenesulphonyloxy)carbamate (III) was synthesized by the reaction of *N*-hydroxyurethane [16] with *p*-nitrobenzenesulphochloride according to [17]. Ethyl *N*-[2-t-butyl-2-chloro]ethylcarbamate (XIV) was obtained using the conventional method [8].

Methyl-trans-3-triethylsilylacrylate (X)

Triethylsilane (11.6 g, 0.1 mol) and 5 drops of $H_2PtCl_6 \cdot 6H_2O$ solution in 2-propanol (0.01 *M*) were added to a solution of methyl propiolate (8.4 g, 0.1 mol) in anhydrous tetrahydrofuran (100 ml). The mixture was heated to 50°C to initiate a vigorous exothermic reaction and was gradually cooled to room temperature (~ 2 h). The solvent was removed by distillation and the residue fractionated in vacuo to give a colourless liquid (14 g) (b.p. 50°C/0.7 mmHg), consisting of methyl-*trans*-3-triethylsilylactylate (X) and methyl-2-triethylsilylacrylate (XI) (70 : 30, ^{1}H NMR data). 1,1-Dimethylhydrazine (2.2 g, 1.5 mol-equiv. with respect to XI) was added to a mixture of X and XI (10 g, 0.05 mol) which was allowed to stand for 4 h at 70°C. The reaction mixture was diluted with diethyl ether (50 ml) and washed with 10% hydrochloric acid (3 × 30 ml) to remove the adducts of 1,1-dimethylhydrazine and XI. The organic layer was washed with 2% aqueous sodium hydrocarbonate (2 × 50 ml), water (2 × 50 ml), and dried over anhydrous sodium sulphate. The ether was removed by distillation and the residue was fractionated in vacuo to obtain X (5 g, yield 71%), b.p. 60°C/1 mmHg; ^{1}H NMR spectrum, δ (ppm): 0.71–0.96 (m, 15H, $SiEt_3$), 3.76 (s, 3H, OMe), 6.27 (d, 1H, *J* 19.1 Hz, SiCH), 7.24 (d, 1H, *J* 19.1 Hz, C*H*COOMe); MS (*m/e*, rel. intensity, %): 172 (18, $M^+ - 28$), 171 (100, $M^+ - 29$), 144 (15), 143 (100), 115 (38), 87 (12), 61 (15), 59 (48), 55 (19), 53 (15).

Reactions of vinylsilanes, IVa, IVb, VIII, X and XII with ethyl-N-(p-nitrobenzenesulphonyloxy)carbamate (III) (general procedure)

1 *M* aqueous sodium bicarbonate (15 ml) was added to a solution of vinylsilane (10 mmol) and III (5 mmol) in dichloromethane (25 ml) containing the catalyst (1 mmol) and stirred for 2 h at room temperature. The course of the reaction was monitored by GLC. The organic layer was separated, washed with water (2 × 50 ml), and dried over $MgSO_4$. The solvent was removed by distillation in vacuo. The aziridines Va, Vb and XIII were isolated by distillation of the residue in vacuo; their physical data, ^{1}H NMR and mass spectra coincided with those described for Va, Vb in [2] and for XIII in [18]. Aziridines VIII and XI were isolated by preparative GLC * and characterized by means of ^{1}H NMR and mass spectroscopy.

^{1}H NMR spectrum of VIII, δ, ppm: 0.56–1.06 (m, 15H, $SiEt_3$), 1.29 (t, 3H, *J* 7 Hz, OCH_2CH_3), 2.47 (s, 1H), 2.62 (c, 1H), 4.24 (q, 2H, *J* 7 Hz, OCH_2CH_3); MS of VIII (*m/e*, rel. intensity, %): 280/278 (6/6, $M^+ - 29$, $^{81}Br/^{79}Br$), 228 (12, $M^+ -$ Br), 167/165 (24/24), 149/147 (31/32), 115 (40), 103 (27), 87 (85), 75 (17), 70 (24), 56 (65), 43 (22), 29 (100). MS of X: 309/307 (8/8, M^+), 280/278 (12/12, $M^+ - 29$), 252/250 (19/18), 154 (11), 144/142 (17/18), 126 (91), 109 (11), 98 (22), 87 (11), 70 (21), 59 (14), 43 (11), 29 (100). ^{1}H NMR spectrum of XI: 0.51–0.98 (m,

* Pye Unicam 105 chromatograph, the glass column (1 m × 7 mm) was packed with 20% SE-30 on Chromosorb W (60–80 mesh), helium as carrier gas (120 cm^3/min), at 200°C.

15H, $SiEt_3$), 1.24 (t, 3H, *J* 7 Hz, OCH_2CH_3), 2.10 (d, 1H, *J* 4 Hz, SiC*H*), 2.93 (d, 1H, *J* 4 Hz, C*H*COOMe), 3.77 (s, 3H, OMe), 4.17 (q, 2H, *J* 7 Hz, OCH_2CH_3); MS of XI: 287 (2, M^+), 258 (45, $M^+ - 29$), 189 (29), 143 (16), 131 (40), 129 (12), 128 (17), 127 (15), 117 (51), 115 (25), 103 (42), 101 (15), 100 (27), 96 (63), 89 (45), 88 (20), 87 (95), 75 (51), 61 (28), 59 (100), 44 (21).

1-Ethoxycarbonyl-2-t-butylaziridine (III) from ethyl N-(2-t-butyl-2-chloro)ethylcarbamate (XIV)

Finely-ground sodium hydroxide (4 g, 0.1 mol) was added to a solution of XIV (10.3 g; 0.05 mol) and tetraoctylammonium bromide (1.36 g; 2.5 mmol) in anhydrous acetonitrile (50 ml). The suspension obtained was stirred for 4 h at room temperature, filtered and evaporated. The residue was distilled in vacuo to afford XIII (5.2 g) (yield 60%) identical with that obtained in the reaction of XII and =NCOOEt (see above), and that described in [18].

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