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Regioselective Amination of Polyunsaturated Ethers[1]

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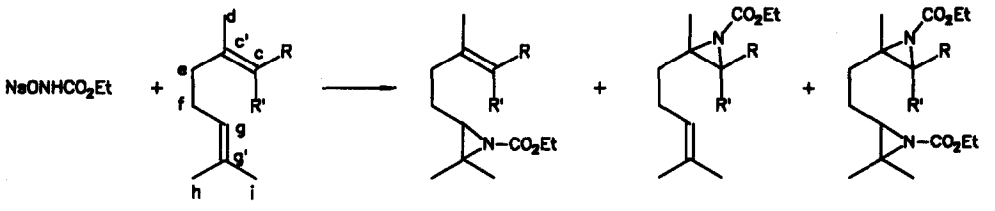
Abstract: *(Ethoxycarbonyl)nitrene (NCO_2Et) adds selectively to methyl neryl ether, geranyl methyl ether, and allyl neryl ether. For all the substrates the main product (up to 50 %) is the aziridine deriving from addition to the double bond remote from the oxygen atom. Competition experiments point to a different reactivity of the two kind of double bonds and these results are compared with those reported for similar substrates in other addition reactions.*

There is a large body of experimental evidence of selective attack of reagents to multifunctional molecules, this being a goal of general interest in synthesis. For instance interesting regioselective reactions have been reported for molecules containing two unconjugated double bonds such as those of derivatives of geraniol and nerol. In these compounds specific interactions between reagents such as hydrogen bonding or oxygen coordination are supposed to be responsible in controlling the regioselectivity of epoxidation,[2] cyclopropanation,[3] and aziridination.[4] The amination of simple allylic ethers has been reported by us[5] and other authors.[6]

As a part of a program of reaction of (ethoxycarbonyl)nitrene (NCO_2Et) with unsaturated compounds,[7] here we report on the investigation of the intermolecular competition reaction between the two types of double bonds in derivatives of geraniol and nerol (Scheme I). Among the possible routes for the generation of NCO_2Et, we used the α-elimination from ethyl *N*-{[(4-nitrophenyl)sulphonyl]oxy}carbamate (**1**, $NsONHCO_2Et$)[8] that we found to give aziridines as the main product when reacted with allylic ethers.[5] With methyl neryl ether (**2a**) using an equimolar amount of **1** and dichloromethane as solvent about 50 % of the substrate remained unreacted and only traces of a product identified as **6** were obtained. We tested higher ratios of **1** to substrate and a higher dilution. The best isolated yields (41 %) of the main product have been obtained using a 4-fold excess of **1**. The spectral data were in agreement with the structure of *N*-(ethoxycarbonyl)aziridine **3a** due to the preferential nitrene addition to the double bond far from the oxygen atom. The same regiochemical addition has been observed with geranyl methyl ether (**2b**) and aziridine **3b** has been isolated in 50 % yield. Allyl neryl ether (**2c**) containing three double bonds under the same conditions gave once again the same regiochemistry and aziridine **3c** was the main

Scheme I

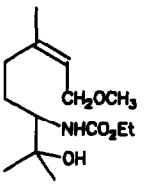


1 2 3 4 5

a, R = H R' = $^{b}CH_2-O-^{a}CH_3$

b, R = $^{b}CH_2-O-^{a}CH_3$ R' = H

c, R = H R' = $^{b}CH_2-O-^{a}CH_2-^{i}CH=^{k}CH_2$



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functionalization product (30 %). In all cases the crude reaction mixtures were analyzed by GC and NMR and we were not able to isolate any C-H insertion product and only in the case of **2b** we were able to collect, after silica gel chromatography, a small quantity (< 1 %) of the nitrene addition product to the allylic double bond, namely aziridine **4b**. However for all substrates a mixture of the double functionalization products **5** have been isolated in lower (12-16 %) yields.

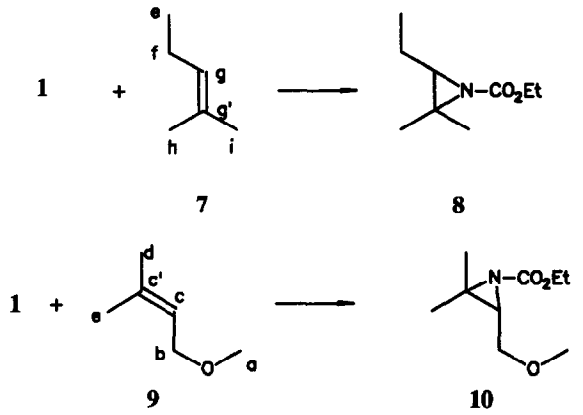
These results indicate a highly regioselective attack of the NCO_2Et to the "remote" double bond. In order to check whether the stereochemistry of the allylic double bond plays a role in the reactivity of the remote double bond, we tested the intermolecular competition reaction between the two substrates **2a** and **2b** toward NCO_2Et. We found that the reactivity ratio is 1.0. With the aim of gaining more insight into the intramolecular competition data we performed experiments of intermolecular competition of **2a** *versus* 2-methyl-2-pentene (**7**) and methyl prenyl ether (**9**) as simple models. In our hands **7** gave **8**[9] in 44 % yield and **9** gave **10** in 29 % yield (Scheme II). We found **7** to be 1.5 times more reactive than **2a** and **2a** 3.3 times more reactive than **9**. These quantitative data might be a basis to understand either the formation of negligible amounts of aziridine **4** or the not negligible amounts of double functionalization products **5** found in all the reaction mixtures. The competitive experiments suggest that there is an intrinsic difference of reactivity between a double bond with an oxygen in β position and a remote double bond, the first being less reactive than the second one.

Actually it is likely that the first aziridine function introduced by a slow addition of NCO_2Et to the allylic double bond does not deactivate the other double bond and a further fast addition of NCO_2Et takes place. On the other hand, we can not exclude, *a priori*, that a coordination of NCO_2Et by the carbonyl oxygen of the carbamate function of **3**, as recently observed for the epoxidation of substituted olefins[10] and previously by some of us in the Simmons-Smith reaction[11] might affect the product distribution.

The regioselectivity observed seems to be in agreement with an inductive effect due to the heteroatom, as we observed in the NCO_2Et insertion into alkyl halides,[12] while it is conflicting with data of selectivity observed in the same reaction with saturated ethers.[13]

An analogous regioselectivity has been also observed in the aziridination of geranyl chloride with 3-acetoxyamino-2-ethylquinazolone,[4] in the addition of dichlorocarbene to citral diethyl acetal[14] or to geraniol and its acetate,[15] and in the microbial oxidation of geranyl *N*-phenylcarbamate.[16]

Scheme II



EXPERIMENTAL SECTION

GC analyses were performed on a Carlo Erba GI gas chromatograph with a SPB-20 glass capillary column (30 m x 0.75 mm). MS were determined on a HP 5970 Chemstation Mass Selective Detector connected with a HP 5890 gas chromatograph using a 15 m capillary column coated with fluid methyl silicone. MS(FAB) and HRMS(EI) were obtained on a Kratos MS80 spectrometer. IR spectra were recorded in carbon tetrachloride on a Perkin Elmer 298 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded in deuteriochloroform usually on a VARIAN XL-300 spectrometer or on a Bruker WP-80 SY spectrometer and are referenced to internal chloroform (δ 7.27) or deuteriochloroform (δ 77.00), respectively. The structure of compounds **2a** and **3a** were assigned on the basis of homo- and heteronuclear 2D spectroscopy and of APT experiments. The presence of an aziridine ring in **3a** was confirmed carrying out a ^{13}C NMR gated decoupled spectrum to measure the $^1J_{CH}$ (162.1 Hz) that is in good agreement with the reported value for three-membered rings.[17] For all the other compounds the signals were attributed on the basis of monodimensional spectra by comparison with those of **2a** and **3a**. CH_2Cl_2 was distilled over $CaCl_2$. Et_3N was dried by standing over KOH and then distilled. Ethyl *N*-[(nosyl)oxy]carbamate (**1**) was prepared by a reported procedure.[8]

Synthesis of Unsaturated Ethers.

Geranyl methyl ether (**2b**) was prepared by a standard procedure:[18] ^{13}C NMR δ 16.16 (d), 17.41 (h), 25.43 (i), 26.23 (f), 39.41 (e), 57.41 (a), 68.74 (b), 120.63 (c), 123.83 (g), 131.30 (g'), 140.00 (c'). According to the same method it was possible to prepare methyl neryl ether (**2a**),[19] and allyl methyl ether (**2c**), but not methyl prenyl ether (**9**),[20] which was synthesized (30 % after distillation) by a procedure reported for benzyl methyl ether.[21] Methyl neryl ether (**2a**) was obtained in 72 % yield, upon column chromatography [silica gel, 94:6 petroleum ether (bp 40-70 °C) / ethyl acetate]: ^{13}C NMR δ 17.54 (h), 23.38 (d), 25.61 (i), 26.66 (f), 32.18 (e), 57.70 (a), 68.64 (b), 121.72 (c), 123.81 (g), 131.81 (g'), 140.38 (c'). Allyl neryl ether (**2c**) was obtained in 61 % yield, upon column chromatography [silica gel, 95:5 petroleum ether (bp 40-70 °C) / ethyl acetate]: IR 3090, 1670, 1650, 1610, 1210 cm^{-1}; ^1H NMR δ 1.61 (br s, 3 H, h), 1.68 (br s, 3 H, i), 1.75 (d, J = 1.5 Hz, 3 H, d),

2.04-2.23 (m, 4 H, e and f), 3.94-4.10 (m, 4 H, a and b), 5.07-5.15 (m, 1 H, g), 5.15-5.31 (m, 2 H, k), 5.37 (dt, 1 H, c), 5.86-5.99 (m, 1 H, j); ^{13}C NMR δ 17.60 (h), 23.45 (d), 25.66 (i), 26.69 (f), 32.25 (e), 66.31 (a), 70.99 (b), 116.81 (k), 121.80 (c) 123.86 (g), 131.89 (g'), 135.05 (j), 140.39 (c'); MS *m/z* (relative intensity) 194 (M^+, 1), 153 (2), 121 (8), 93 (28), 81 (16), 80 (14), 69 (58), 68 (15), 67 (17), 55 (12), 53 (12), 43 (10), 41 (100); HRMS calcd for $C_{13}H_{22}O$ 194.1670, found 194.1671.

Ethyl (Z)-N-*[1-(1-Hydroxy-1-methylethyl)-6-methoxy-4-methyl-4-hexenyl]carbamate* (**6**). To a stirred solution of methyl neryl ether (**2a**, 0.84 g, 5 mmol) and **1** (1.45 g, 5 mmol) in 6.7 ml of CH_2Cl_2 was added a solution of Et_3N (0.707 g, 7 mmol) in 1.25 ml of CH_2Cl_2 from a syringe at room temperature over a period of 1 h. After stirring for an additional 3 h, petroleum ether (bp 30- 50 °C) was added to promote precipitation of Et_3NH^+ NsO^-, which was filtered off. The filtrate was concentrated *in vacuo* and the residue was chromatographed (silica gel, 8:2 hexane / ethyl acetate) to give the starting material (50 %) and 68 mg (5 %) of an oil, identified as **6**: IR 3600, 3450, 3100, 1728 cm^{-1}; ^{1}H NMR δ 1.19 (s, 3 H, h or i), 1.23 (s, 3 H, h or i), 1.26 (t, 3 H, C*H*$_3$CH$_2$), 1.34-1.54 (m, 2 H, f), 1.74 (br s, 3 H, d), 1.76 (s, 1 H, OH), 2.05-2.27 (m, 2 H, e), 3.32 (s, 3 H, a), 3.87 (dd, 2 H, b), 4.12 (q, 2 H, C*H*$_2$CH$_3$), 4.24 (q, 1 H, g), 5.06 (br d, 1 H, NH), 5.41 (t, 1 H, c); ^{13}C NMR δ 14.61 (*C*H$_3$CH$_2$), 23.27 (d), 26.20 (h or i), 27.51 (h or i), 27.86 (f), 28.89 (e), 57.90 (a), 59.50 (g), 60.99 (*C*H$_2$CH$_3$), 68.40 (b), 72.95 (g'), 121.98 (c), 140.72 (c'), 157.61 (CO); MS *m/z* (relative intensity) 255 (M^+ - H_2O, 5), 214 (15), 182 (32), 160 (13), 144 (13), 125 (15), 115 (69), 114 (26), 102 (37), 94 (100), 93 (69), 90 (91), 81 (36), 79 (20), 70 (20), 67 (21), 62 (54), 59 (39), 56 (30), 55 (23), 45 (32), 44 (29), 43 (98), 42 (20), 41 (73); HRMS calcd for $C_{14}H_{25}NO_3$ 255.1834, found 255.1838 (M^+ - H_2O).

(Z)-*1-(Ethoxycarbonyl)-2,2-dimethyl-3-(5-methoxy-3-methyl-3-pentenyl)aziridine* (**3a**). The above procedure was modified using a 4-fold amount of both **1** and Et_3N and a 20-fold amount of CH_2Cl_2. The addition of Et_3N was done in 2 h and petroleum ether was added after this time. The chromatographic separation was carried out using 92:2:2 petroleum ether (bp 40-70 °C) / ethyl acetate / Et_3N. **3a** was isolated in 41 % yield: IR 3100, 1720, 1610 cm^{-1}; ^{1}H NMR δ 1.23 (s, 3 H, h), 1.24 (s, 3 H, i), 1.25 (t, 3 H, C*H*$_3$CH$_2$), 1.40-1.67 (m, 2 H, f), 1.74 (m, 3 H, d), 2.13-2.28 (m, 3 H, e and g), 3.29 (s, 3 H, a), 3.89 (d, 2 H, b), 4.05-4.21 (m, 2 H, C*H*$_2$CH$_3$), 5.36 (t, 1 H, c); ^{13}C NMR δ 14.42 (*C*H$_3$CH$_2$), 19.41 (h), 22.84 (i), 23.33 (d), 27.22 (f), 29.64 (e), 44.21 (g'), 47.84 (g), 57.79 (a), 61.86 (*C*H$_2$CH$_3$), 68.51 (b), 122.09 (c), 139.63 (c'), 162.24 (CO); MS *m/z* (relative intensity) 255 (M^+, 3), 142 (100), 119 (11), 98 (49), 93 (12), 85 (14), 83 (15), 81 (13), 70 (60), 67 (15), 55 (18), 53 (12), 45 (18), 43 (30), 42 (14), 41 (32);HRMS calcd for $C_{14}H_{25}NO_3$ 255.1834, found 255.1839. In addition **5a** was obtained in 15 % yield as a mixture of isomers, one of which was purified (4 %): ^{1}H NMR δ 1.17-1.33 (15 H, CH_3), 1.55-1.80 (m, 4 H, e and f), 2.22 (t, 1 H, g), 2.51 (t, 1 H, c), 3.30-3.55 (s and m, 5 H, a and b), 4.15 (q, 4 H, C*H*$_2$CH$_3$); ^{13}C NMR δ 14.40 and 14.49 (*C*H$_3$CH$_2$), 19.39, 20.14, and 22.87 (d, h, and i), 24.82 (f), 30.98 (e), 44.26 (g'), 46.42 (c'), 46.55 (c), 47.69 (g), 58.89 (a), 61.93 and 62.16 (*C*H$_2$CH$_3$), 70.46 (b), 161.77 and 162.26 (CO); MS *m/z* (relative intensity) 342 (M^+, 1), 297 (2), 196 (19), 180 (11), 168 (76), 154 (10), 142 (13), 140 (11), 124 (28), 122 (12), 108 (27), 107 (12), 98 (25), 96 (74), 94 (29), 83 (30), 82 (47), 70 (34), 68 (73), 67 (21), 58 (29), 56 (24), 55 (37), 45 (100); MS(FAB) *m/z* 343 (M^+ + 1).

(E)-*1-(Ethoxycarbonyl)-2,2-dimethyl-3-(5-methoxy-3-methyl-3-pentenyl)aziridine* (**3b**). The same procedure as for **3a** starting from geranyl methyl ether (**2b**) gave **3b** in 50 % yield: IR 3100, 1720, 1610 cm^{-1}; ^{1}H NMR δ 1.15 (s, 3 H, h or i), 1.17 (s, 3 H, h or i), 1.18 (t, 3 H, C*H*$_3$CH$_2$), 1.48-1.57 (m, 2 H, f), 1.60 (br s, 3 H, d), 2.06-2.15 (m, 3 H, e and f), 3.22 (s, 3 H, a), 3.84 (dd, 2 H, b), 4.04 (m, 2 H, C*H*$_2$CH$_3$), 5.30 (br t, 1 H, c); ^{13}C NMR δ 14.32 (*C*H$_3$CH$_2$), 16.32 (d), 19.34 (h), 22.77 (i), 26.64 (f), 36.82 (e), 44.08 (g'), 47.74 (g), 57.65 (a), 61.71 (*C*H$_2$CH$_3$), 68.74 (b), 121.09 (c), 139.22 (c'), 162.17 (CO); MS *m/z* (relative intensity) 255 (M^+, 2), 142 (100), 119 (10), 98 (32), 93 (10), 85 (15), 83 (12), 81 (13), 79 (10), 70 (62), 67 (17), 55 (19), 53 (13), 45 (23), 43 (32), 42 (16), 41 (35); HRMS calcd for $C_{14}H_{25}NO_3$ 255.1834, found 255.1844.

(E)-*1-(Ethoxycarbonyl)-2-methoxymethyl-3-methyl-3-(4-methyl-3-pentenyl)aziridine* (**4b**). The title compound was obtained in < 1 % yield during the preparation of **3b**: IR 3100, 1720, 1610 cm^{-1}; ^1H NMR δ 1.28 (t, 3 H, CH_3CH_2), 1.29 (s, 3 H, d), 1.61 (s, 3 H, h or i), 1.68 (s, 3 H, h or i), 1.83-2.14 (m, 4 H, e and f), 2.51 (t, 1 H, c), 3.42 (s, 3 H, a), 3.43-3.58 (2dd[22], J = 6.1, 11.0 Hz, 2 H, b), 4.11-4.21 (m, 2H, CH_2CH_3), 5.05 (t, 1 H, g); ^{13}C NMR δ 14.43 (CH_3CH_2), 17.04 (d), 17.64 (h), 24.74 (i), 25.64 (f), 37.42 (e), 45.31 (c), 46.60 (c'), 58.79 (a), 62.14 (CH_2CH_3), 70.66 (b), 123.00 (g), 132.33 (g'), 161.67 (CO); MS *m/z* (relative intensity) 255 (M^+, < 1), 210 (15), 146 (18), 142 (13), 123 (19), 122 (14), 121 (100), 119 (20), 102 (22), 93 (25), 82 (18), 79 (21), 70 (13), 69 (38), 67 (16), 62 (15), 58 (16), 55 (19), 53 (13), 45 (55), 44 (17), 43 (33), 42 (21), 41 (73). In addition **5b** was obtained in 16 % yield as a mixture of isomers: ^1H NMR δ 1.18- 1.34 (15 H, CH_3), 1.55-2.11 (m, 4 H, e and f), 2.20 (t, 1 H, g), 2.50 and 2.57 (2t, 1 H, c), 3.29-3.63 (s and m, 5 H, a and b), 4.06-4.21 (m, 4 H, CH_2CH_3); ^{13}C NMR δ 14.39 and 14.44 (CH_3CH_2), 16.86, 19.44, 19.48, and 22.79 (d, h, and i), 25.16 and 25.22 (f), 34.94 and 35.07 (e), 44.20 (g'), 44.89 and 45.11 (c), 46.05 and 46.17 (c'), 47.42 and 47.45 (g), 58.79 and 58.83 (a), 61.93 and 62.14 (CH_2CH_3), 70.43 and 70.51 (b), 161.36, 161.49, 162.06, and 162.10 (CO); MS *m/z* (relative intensity) 342 (M^+, < 1), 297 (4), 196 (100), 124 (25), 82 (13), 55 (14), 45 (22), 44 (14), 42 (23).

(Z)-*1-(Ethoxycarbonyl)-2,2-dimethyl-3-[5-(2-propenyl)oxy]-3-methyl-3-pentenyl)aziridine*(**3c**). The same procedure as for **3a** starting from allyl neryl ether (**2c**) gave **3c** in 30 % yield: IR 3100, 1720, 1610 cm^{-1}; ^1H NMR δ 1.21 (s, 3 H, h or i), 1.22 (s and t, 6 H, h or i and CH_3CH_2), 1.43-1.68 (m, 2 H, f), 1.72 (s, 3 H, d), 2.10-2.30 (m, 3 H, e and g), 3.83-3.96 (m, 4 H, a and b), 4.05-4.16 (m, 2 H, CH_2CH_3), 5.09-5.25 (m, 2 H, k), 5.36 (t, 1 H, c), 5.81-5.95 (m, 1 H, j); ^{13}C NMR δ 14.36 (CH_3CH_2), 19.35 (h), 22.78 (i), 23.31 (d), 27.16 (f), 29.61 (e), 44.12 (g'), 47.76 (g), 61.78 CH_2CH_3), 66.06 (a), 70.96 (b), 116.80 (k), 122.08 (c), 134.79 (j), 139.50 (c'), 162.15 (CO); MS *m/z* (relative intensity) 266 (M^+ - 15, 1), 240 (2), 142 (100), 124 (13), 107 (14), 95 (12), 93 (19), 81 (31), 79 (16), 70 (61), 69 (18), 67 (23), 55 (24), 53 (14), 43 (36), 42 (21), 41 (83); HRMS calcd for $C_{15}H_{24}NO_3$ 266.1756, found 266.1750 (M^+ - 15). In addition **5c** was obtained in 12 % yield as an approximately equimolar mixture of two stereoisomers: ^1H NMR δ 1.18-1.80 (m, 19 H, CH_3, e, and f), 2.18 and 2.24 (2t, 1 H, g), 2.48 and 2.49 (2t, 1 H, c), 3.35-3.75 (2m, 2 H, b), 3.85-4.25 (m, 6 H, a and CH_2CH_3), 5.08-5.29 (m, 2 H, k), 5.78-5.95 (m, 1 H, j); ^{13}C NMR δ 14.29 and 14.33 (CH_3CH_2), 19.23, 19.34, 19.91, and 19.99 (d and h), 22.72 (i), 24.65 and 24.69 (f), 30.79 and 30.94 (e), 44.06 and 44.14 (g'), 44.89 and 45.11 (c'), 46.50 and 46.70 (g), 47.53 and 47.81 (c), 61.73 and 61.95 (CH_2CH_3), 67.73 and 67.82 (a), 71.67 and 71.78 (b), 116.93 and 117.21 (k), 134.26 and 134.30 (j), 161.58 and 162.06 (CO); MS *m/z* (relative intensity) 368 (M^+, 1), 323 (5), 297 (13), 251 (7), 209 (12), 208 (28), 198 (26), 197 (18), 196 (80), 182 (29), 180 (19), 168 (100), 167 (15), 166 (47), 156 (25), 155 (25), 154 (40), 152 (25), 142 (38), 140 (16), 136 (22), 130 (16), 126 (21), 124 (60), 122 (26), 108 (46), 107 (27), 96 (99), 94 (43), 84 (47), 83 (49), 82 (87), 81 (38), 70 (73), 69 (35), 68 (89), 67 (35), 58 (52), 56 (55), 55 (68).

1-(Ethoxycarbonyl)-2-ethyl-3,3-dimethylaziridine (**8**). The same procedure as for **3a** starting from 2-methyl-2-pentene (**7**) gave **8**[9] in 44 % yield.

1-(Ethoxycarbonyl)-2-methoxymethyl-3,3-dimethylaziridine (**10**). The same procedure as for **3a** starting from methyl prenyl ether (**9**) gave **10** in 29 % yield: ^1H NMR δ 1.22 (t, 3 H, CH_3CH_2), 1.24 and 1.25 (2s, 6 H, d and e), 2.46 (dd,[22] J = 5.9, 6.6 Hz, 1 H, c), 3.34 (s, 3 H, a), 3.30-3.60 (2dd,[22] J = 5.9, 6.6, 10.5 Hz, 2 H, b), 4.10 (q, 2 H, CH_2CH_3); ^{13}C NMR δ 14.22 (CH_3CH_2), 19.35 (e), 22.48 (d), 43.63 (c'), 45.86 (c), 58.74 (a), 62.06 (CH_2CH_3), 70.71 (b), 162.07 (CO); MS *m/z* (relative intensity) 187 (M^+, 0.2), 172 (1), 156 (6), 114 (100), 84 (22), 83 (20), 82 (26), 73 (33), 70 (16), 68 (28), 58 (14), 56 (15), 55 (28), 45 (89), 44 (21), 43 (21), 42 (67), 41 (47).

Competition Reactions.

The same procedure as for **3a**, starting from 0.8 mmol of **1**,[23] 1.0 mmol of **2a**, and 1.0 mmol of **2b** or **7** or **9** gave a mixture of aziridines **3a** and **3b** or **8** or **10**. The reactivity ratios were determined as the molar ratio of

the two aziridines measured by GC, after correction by the response factors (RF). Experimental RF were in agreement with those calculated by a method recently reported.[24]

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