(Alk-1-ynyl)oxiranes in the Reaction of (Alk-1-ynyl)chlorocarbenes with Alkali Metal Alkoxides

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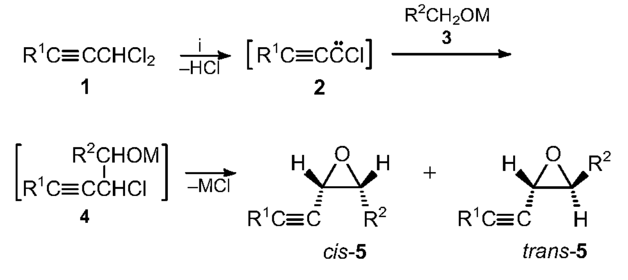
The reaction of (alk-1-ynyl)chlorocarbenes **2a–c**, generated from dichlorides **1a–c**, with alkali metal alkoxides **3** gives 2-(alk-1-ynyl)oxiranes **5a–f** in 30–70% yield.

It has been found that (alk-1-ynyl)halocarbenes, generated by base solvolysis of the corresponding 1,1-dihaloalk-2-ynes[1] or photolysis of 3,3-dimethyl-5-(bromoethynyl)-3*H*-pyrazole,[2] readily add to the double bond of olefins with formation of 1-halo-1-(alk-1-ynyl)cyclopropanes. However, no experimental evidence for the ability of these species to undergo insertion reactions into σ bonds has so far been available. However, for other halocarbenes such reactions are well known,[3] and in particular chlorophenylcarbene, generated from phenyldichloromethane by the action of Bu^{t}OK, reacts with potassium alkoxides to give the corresponding 3-substituted 2-phenyloxiranes as a result of carbene insertion into the α-C–H bond of alkoxides with subsequent cyclization of the intermediate 1-substituted 2-chloro-2-phenylethoxides.[4]

We have found that, on the generation of (alk-1-ynyl)chlorocarbenes **2** from 1,1-dichloroalk-2-ynes **1** under the action of Bu^{t}OK in THF at 20 °C in the presence of a three-fold molar excess of alkali metal alkoxides **3**, 3-substituted 2-(alk-1-ynyl)oxiranes **5**† were formed in 30–70% yield as a mixture of *cis*- and *trans*-isomers. The yield of oxiranes **5** depends on the alkali metal used for the preparation of alkoxides **3** and increases in the order: Li < Na < K (for **5a**, 50%, 65% and 70%, respectively), which may be associated with a build up of oxyanionic effect in the corresponding alkoxides which greatly facilitates the carbene insertion into the α-C–H bond of the latter.[5]

These results point to the fact that carbene **2** obtained in the reaction inserts into the α-C–H bond of alkoxides **3** to give 1-substituted 2-chloro-2-(alk-1-ynyl)ethoxides **4** which eliminate alkali metal chloride forming oxiranes **5** (Scheme 1).



1,2a	R^1 = Bu^t	**3a**	R^2 = Ph	**4,5a**	R^1 = Bu^t	R^2 = Ph
1,2b	R^1 = Ph	**3b**	R^2 = CH=CH$_2$	**4,5b**	R^1 = Ph	R^2 = Ph
1,2c	R^1 = Pr^c	**3c**	R^2 = Me	**4,5c**	R^1 = Bu^t	R^2 = CH=CH$_2$
				4,5d	R^1 = Ph	R^2 = CH=CH$_2$
				4,5e	R^1 = Pr^c	R^2 = Ph
				4,5f	R^1 = Ph	R^2 = Me

Scheme 1 *Reagents and conditions*: i, Bu^{t}OK, THF, room temperature, 30–45 min (30–70%). Pr^c = cyclopropyl.

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†All new compounds **5a**–**f** gave satisfactory analytical and spectral data. For **5a**: (*trans*/*cis* = 1.2) b.p. 93–96 °C/1 mmHg; IR ν_{max}/cm^{-1} 2250 (C≡C), 1605 and 1497 (Ph); ^{1}H NMR (90 MHz, $CDCl_3$) δ *cis*-**5a**: 1.15 (s, 9H, CMe_3); 3.23 (d, 1H, ≡CCH, *J* = 2.2 Hz); 3.86 (d, 1H, PhCH, *J* = 2.2 Hz); 7.1–7.4 (m, 5H, Ph); *trans*-**5a**: 0.98 (s, 9H, CMe_3); 3.61 (d, 1H, ≡CCH, *J* = 3.5 Hz); 3.97 (d, 1H, PhCH, *J* = 3.5 Hz); 7.1–7.4 (m, 5H, Ph); ^{13}C NMR (50 MHz, $CDCl_3$) δ *cis*-**5a**: 27.38 (1C, *C*Me$_3$); 30.69 (3Me, CMe_3); 49.68 and 60.01 (2CH in cyclo-C_2H_2O); 74.92 and 93.05 (2C, C≡C); 136.06 (C-1 in Ph); *trans*-**5a**: 27.27 (1C, *C*Me$_3$); 30.38 (3Me, CMe_3); 48.28 and 58.70 (2CH in cyclo-C_2H_2O); 73.19 and 95.03 (2C, C≡C); 134.53 (C-1 in Ph); 125.48, 127.07, 127.49, 128.07, 128.44 (CH in Ph, *cis*- and *trans*-**5a**); *m*/*z*: 200 [M]$^+$.

For **5b:** (*trans*/*cis* = 1.3), b.p. 171–175 °C/1 mmHg; IR ν_{max}/cm^{-1} 2240 (C≡C), 1600 and 1492 (Ph); ^{1}H NMR (90 MHz, $CDCl_3$) δ *cis*-**5b**: 3.60 (d, 1H, ≡CCH, *J* = 2.0 Hz); 4.17 (d, 1H, PhCH, *J* = 2.0 Hz); 7.1–7.7 (m, 10H, 2Ph); *trans*-**5b**: 3.99 (d, 1H, ≡CCH, *J* = 4.0 Hz); 4.24 (d, 1H, PhCH, *J* = 4.0 Hz); 7.1–7.7 (m, 10H, 2Ph); ^{13}C NMR (50 MHz, $CDCl_3$) δ *cis*-**5b**: 49.64 and 60.37 (2CH in cyclo-C_2H_2O); 83.93 and 86.00 (2C, C≡C); 121.92 (*C*C≡ in Ph); 134.24 (C-1 in Ph); *trans*-**5b**: 48.68 and 59.20 (2CH in cyclo-C_2H_2O); 83.72 and 85.33 (2C, C≡C); 121.84 (*C*C≡ in Ph); 135.69 (C-1 in Ph); 125.58, 126.98, 127.81, 128.22, 128.36, 128.41, 128.59, 128.72, 128.87, 131.65, 131.81, 131.89 (CH in Ph, *cis*- and *trans*-**5b**); *m*/*z*: 220 [M]$^+$.

For **5c**: (*trans*/*cis* = 1.2), b.p. 71–73 °C/14 mmHg; IR ν_{max}/cm^{-1} 2250 (C≡C), 1642 (C=C); ^{1}H NMR (250 MHz, $CDCl_3$) δ *cis*-**5c**: 1.17 (s, 9H, CMe_3); 3.17 (d, 1H, ≡CCH, *J* = 2.2 Hz); 3.30–3.35 (m, 1H, =CCH); 5.20–5.27 (m, 1H, CH=); 5.44–5.49 (m, 2H, CH_2=); *trans*-**5c**: 1.18 (s, 9H, CMe_3); 3.33 (dd, 1H, =CCH, *J* = 3.7 Hz, *J* = 7.7 Hz); 3.49 (d, 1H, ≡CCH, *J* = 3.7 Hz); 5.36 (dd, 1H, *E*-H, CH_2=, *J* = 9.7 Hz, *J* = 1.6 Hz); 5.49 (dd, 1H, *Z*-H, CH_2= , *J* = 16.9 Hz, *J* = 1.6 Hz); 5.66 (ddd, 1H, CH=, *J* = 16.9 Hz, *J* = 9.7 Hz, *J* = 1.6 Hz); ^{13}C NMR (50 MHz, $CDCl_3$,) δ *cis*-**5c**: 27.37 (1C, *C*Me$_3$); 30.79 (3Me, CMe_3); 47.26 and 59.98 (2CH in cyclo-C_2H_2O); 74.72 and 92.94 (2C, C≡C); 120.07 (CH_2=); 134.32 (CH=); *trans*-**5c**: 27.44 (1C, *C*Me$_3$); 30.79 (3Me, CMe_3); 46.31 and 57.83 (2CH in cyclo-C_2H_2O); 73.32 and 94.60 (2C, C≡C); 121.55 (CH_2=); 133.14 (CH=); *m*/*z*: 149 [M–H]$^+$.

For **5d**: (*trans*/*cis* = 1.2) , b.p. 106–107 °C/1 mmHg; IR ν_{max}/cm^{-1} 2240 (C≡C), 1600, 1490 (Ph), 1640 (C=C); ^{1}H NMR (250 MHz, $CDCl_3$) δ *cis*-**5d**: 3.49 (d, 1H, ≡CCH, *J* = 1.9 Hz); 3.59–3.64 (m, 1H, =CCH); 5.31–5.39 (m, 1H, CH=); 5.55–5.59 (m, 2H, CH_2=); 7.2–7.5 (m, 5H, Ph); *trans*-**5d**: 3.56 (dd, 1H, =CCH, *J* = 3.88 Hz, *J* = 7.7 Hz); 3.81 (dd, 1H, ≡CCH, *J* = 3.88 Hz, *J* = 1.3 Hz); 5.49 (dd, 1H, *E*-H, CH_2=, *J* = 10.5 Hz, *J* = 1.1 Hz); 5.64 (dd, 1H, *Z*-H, CH_2=, *J* = 17.1 Hz, *J* = 1.1 Hz); 5.91 (ddd, 1H, CH=, *J* = 17.1 Hz, *J* = 7.7 Hz, *J* = 10.5 Hz); 7.2–7.5 (m, 5H, Ph); ^{13}C NMR (50 MHz, $CDCl_3$), δ *cis*-**5d**: 47.44 and 60.30 (2CH in cyclo-C_2H_2O); 83.95 and 85.56 (2C, C≡C); 120.6 (CH_2=); 133.79 (CH=); *trans*-**5d**: 46.70 and 58.39 (2CH in cyclo-C_2H_2O); 83.77 and 85.07 (2C, C≡C); 122.08 (CH_2=); 132.77 (CH=); 121.82 and 121.88 (C-1 in Ph, *cis*- and *trans*-**5d**); 128.24, 128.52, 128.73, 131.44 (CH in Ph, *cis*- and *trans*-**5d**); *m*/*z*: 170 [M]$^+$.

For **5e**: (*trans*/*cis* = 1.2); ^{1}H NMR (200 MHz, $CDCl_3$) δ *cis*-**5e**: 0.44–1.05 (m, 5H, cyclo-C_3H_5); 3.32 (dd, 1H, ≡CCH, *J* = 1.95 Hz, *J* = 1.7 Hz); 3.98 (d, 1H, PhCH, *J* = 1.95 Hz); 7.2–7.5 (m, 5H, Ph); *trans*-**5e**: 0.44–1.05 (m, 5H, cyclo-C_3H_5); 3.72 (dd, 1H, ≡CCH, *J* = 4.0 Hz, *J* = 1.5 Hz); 4.06 (d, 1H, PhCH, *J* = 4.0 Hz); 7.2–7.5 (m, 5H, Ph); ^{13}C NMR (50 MHz, $CDCl_3$,) δ *cis*-**5e:** –0.64 (CH in cyclo-C_3H_5); 8.01 (2CH_2 in cyclo-C_3H_5); 49.70 and 59.93 (2CH in cyclo-C_2H_2O); 71.8 and 88.1 (2C, C≡C); 135.89 (C-1 in Ph); *trans*-**5e:** –0.64 (CH in cyclo-C_3H_5); 8.20 (2CH_2 in cyclo-C_3H_5); 48.45 and 58.69 (2CH in cyclo-C_2H_2O); 69.5 and 90.3 (2C, C≡C); 134.42 (C-1 in Ph); 125.40, 126.85, 127.54, 128.09, 128.41 (CH in Ph, *cis*- and *trans*-**5e**); *m*/*z*: 184 [M]$^+$.

For **5f**: (*trans*/*cis* = 1.00) ^{1}H NMR (300 MHz, $CDCl_3$) δ *cis*-**5f**: 1.38 (d, 3H, Me, *J* = 4.3 Hz); 3.2–3.3 (m, 2H, 2CH in cyclo-C_2H_2O); 7.2–7.5 (m, 5H, Ph); *trans*-**5f**: 1.51 (d, 3H, Me, *J* = 5.7 Hz); 3.2–3.3 (m, 1H, MeCH); 3.62 (d, 1H, ≡CCH, *J* = 3.9 Hz); 7.2–7.5 (m, 5H, Ph); ^{13}C NMR (50 MHz, $CDCl_3$,) δ *cis*-**5f**: 17.35 (Me); 46.56 and 56.86 (2CH in cyclo-C_2H_2O); 84.22 and 85.25 (2C, C≡C); *trans*-**5f**: 14.77 (Me); 45.79 and 54.34 (2CH in cyclo-C_2H_2O); 83.45 and 85.88 (2C, C≡C); 122.16 (C-1 in Ph, *cis*- and *trans*-**5f**); 128.32, 128.72, 131.87 (CH in Ph, *cis*- and *trans*-**5f**); *m*/*z*: 158 [M]$^+$.

The formation of intermediates **4** was confirmed by reaction of **1a** with an equimolar amount of BuLi in the presence of a three-fold molar excess of $PhCH_2OLi$ at −45 °C and isolation of 5,5-dimethyl-2-chloro-1-phenylhex-3-yn-1-ol[‡] **4a′** on treating the reaction mixture with water. After warming the reaction mixture up to room temperature and addition of Bu^tOK the oxirane **5a** was obtained.

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[‡] *Spectral data for* **4a′**: ^{1}H NMR (300 MHz, $CDCl_3$) δ *erythro*-**4a′**: 1.13 (s, 9H, CMe_3); 3.0 (bs, 1H, OH); 4.74 (d, 1H, CHCl, *J* = 4.4 Hz); 4.91 (d, PhCH, *J* = 4.4 Hz); 7.2–7.5 (m, 5H, Ph); *threo*-**4a′**: 1.22 (s, 9H, CMe_3); 3.0 (bs, 1H, OH); 4.64 (d, 1H, CHCl, *J* = 7.9 Hz); 4.79 (d, PhCH, *J* = 7.9 Hz); 7.2–7.5 (m, 5H, Ph); ^{13}C NMR (50 MHz, $CDCl_3$,) δ *erythro*-**4a′**: 27.77 (1C, CMe_3); 30.63 (3Me, CMe_3); 56.41 and 78.03 (2CH); 74.20 and 98.04 (2C, C≡C); 138.61 (C-1 in Ph); *threo*-**4a′**: 27.87 (1C, CMe_3); 30.50 (3Me, CMe_3); 54.89 and 76.94 (2CH); 73.29 and 98.41 (2C, C≡C); 138.72 (C-1 in Ph); 127.05, 127.34, 128.13, 128.61 (CH in Ph, *erythro*- and *threo*-**4a′**); *m*/*z*: 200 $[M-HCl]^+$.

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