Alkynylhalocarbenes

3.* Synthesis of 2-(alk-1-ynyl)oxiranes from 1,1-dichloroalk-2-ynes and 3-substituted 3-bromo-1,1,1-trichloropropanes under the action of potassium *tert*-butoxide in the presence of alkali metal alkoxides

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(Alk-1-ynyl)chlorocarbenes (**3**), generated from 1,1-dihaloalk-2-ynes and 3-substituted 3-bromo-1,1,1-trichloropropanes under the action of Bu^{t}OK in THF at 20 °C, react with excess alkali metal alkoxide **4** to give 3-substituted 2-(alk-1-ynyl)oxiranes (**6**) in 26—78% yields, most likely as a result of insertion of carbene **3** into the α-C—H bond of alkoxides **4** and subsequent cyclization of the resulting 1-substituted 2-chloro-2-(alk-1-ynyl)etoxides. The yields of oxiranes **6** depend on the nature of the alkali metal used to prepare alkoxides **4** and on the method employed for the preparation of the latter.

Key words: (alk-1-ynyl)chlorocarbenes, 1,1-dihaloalk-2-ynes, 3-substituted 3-bromo-1,1,1-trichloropropanes, 3-substituted 2-(alk-1-ynyl)oxiranes, alkali metal alkoxides, Bu^{t}OK, insertion reactions.

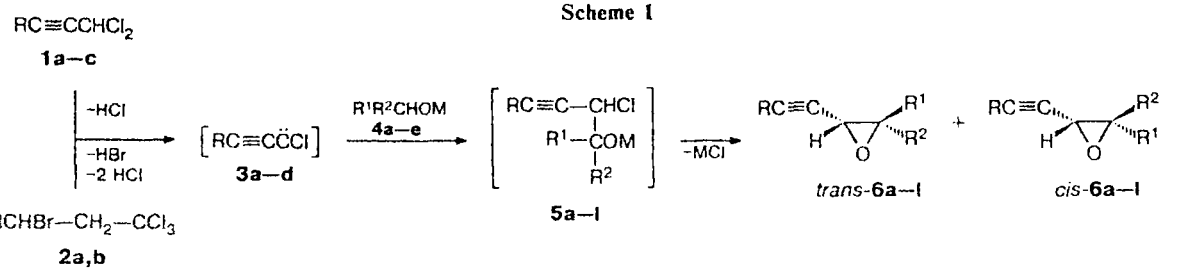
It is known that alkaline solvolysis of 1,1-dihaloalk-2-ynes[1—3] or 3-substituted 1,1,1,3-tetrahalopropanes[4] and photolysis of 5-(bromoethynyl)-3,3-dimethyl-3*H*-pyrazole[5] afford (alk-1-ynyl)halocarbenes, which readily add to double bonds of olefins to give 1-(alk-1-ynyl)-1-halocyclopropanes. However, until recently, no data on the insertion of these carbenes into single bonds have been reported, although these reactions are known for other halocarbenes.[6] For example, chloro(phenyl)carbene generated from dichloro(phenyl)methane under the action of Bu^{t}OK reacts with potassium alkoxides yielding the corresponding 3-substituted 2-phenyloxiranes; these products were suggested[7] to arise *via* insertion of the carbenes into the α-C—H bonds of alkoxides followed by cyclization of the resulting 1-substituted 2-chloro-2-phenylethoxides.

We have found that (alk-1-ynyl)chlorocarbenes are also capable of reacting with alkali metal alkoxides to give the corresponding 3-substituted 2-(alk-1-ynyl)oxiranes (for preliminary communication, see Ref. 8). In the present study, we report on the reactions of a number of carbene species of this type with alkali metal alkoxides.

(Alk-1-ynyl)chlorocarbenes (**3**) were generated by treatment of 1,1-dichloroalk-2-ynes (**1**) or 3-substituted 3-bromo-1,1,1-trichloropropanes (**2**) with a 2.5- or 7.5-fold molar excess of Bu^{t}OK, respectively (Scheme 1). The reaction was carried out in THF at 20 °C for 0.5—2 h in the presence of a threefold molar excess of alkali metal alkoxide (**4**). The yields of 3-substituted 2-(alk-1-ynyl)oxiranes (**6**) were 26—78%. In the case of alkoxides **4a—d** in which $R^1 \neq R^2$ (Table 1), oxiranes **6** were formed as mixtures of *cis*- and *trans*-isomers.

Oxiranes **6** result apparently from the insertion of carbenes **3** into the α-C—H bond of alkoxides **4** followed by cyclization of 1-substituted 2-(alk-1-ynyl)-2-chloroethoxides (**5**). The intermediate participation of

Scheme 1



* For Part 2, see Ref. 1.

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Table 1. Reactions of carbenes **3**, generated from halides **1** and **2** under the action of Bu^{t}OK in THF at 20 °C, with a threefold excess of alkoxide **4**

Source of the carbene		Carbene	Alkoxide					Resulting oxirane						
Compound	R		4	R^1	R^2	M	Method[a] of synthesis	6	R	R^1	R^2	Yield (%)	B.p. /°C (Torr)	Ratio of *trans*/*cis* isomers[f]
1a	Bu^t	**3a**	**4a**	Ph	H	Li	*A*	**6a**	Bu^t	Ph	H	61[b]		—
1a	Bu^t	**3a**	**4a**	Ph	H	Na	*A*	**6a**	Bu^t	Ph	H	71[b]		—
1a	Bu^t	**3a**	**4a**	Ph	H	Li	*B*	**6a**	Bu^t	Ph	H	60[b]		—
1a	Bu^t	**3a**	**4a**	Ph	H	Na	*C*	**6a**	Bu^t	Ph	H	51[b]		—
1a	Bu^t	**3a**	**4a**	Ph	H	K	*D*	**6a**	Bu^t	Ph	H	41[b]		—
1a	Bu^t	**3a**	**4a**	Ph	H	Na/Li	*E*	**6a**	Bu^t	Ph	H	60[b]		—
1a	Bu^t	**3a**	**4a**	Ph	H	K/Li	*E*	**6a**	Bu^t	Ph	H	67[b]		—
1a	Bu^t	**3a**	**4a**	Ph	H	Li	*B*	**6a**	Bu^t	Ph	H	48[c]	93—96 (1)	1.4
1b	*cyclo*-Pr	**3b**	**4a**	Ph	H	Li	*B*	**6b**	*cyclo*-Pr	Ph	H	78[d]		1.7
1c	Ph	**3c**	**4a**	Ph	H	Li	*B*	**6c**	Ph	Ph	H	40[c]	180 (1)	1.4
1a	Bu^t	**3a**	**4b**	CH_2=CH	H	Li	*B*	**6d**	Bu^t	CH_2=CH	H	40[c]	71—73 (12)	1.7
1b	*cyclo*-Pr	**3b**	**4b**	CH_2=CH	H	Li	*B*	**6e**	*cyclo*-Pr	CH_2=CH	H	48[c]	88—90 (170)	1.1
1b	*cyclo*-Pr	**3b**	**4b**	CH_2=CH	H	K/Li	*E*	**6e**	*cyclo*-Pr	CH_2=CH	H	50[d]		1.1
1c	Ph	**3c**	**4b**	CH_2=CH	H	Li	*B*	**6f**	Ph	CH_2=CH	H	30[c]	106—107 (1)	1.2
1c	Ph	**3c**	**4b**	CH_2=CH	H	K/Li	*E*	**6f**	Ph	CH_2=CH	H	33[d]		1.2
1c	Ph	**3c**	**4c**	Me	H	Li	*B*	**6g**	Ph	Me	H	56[d]		1.3
1a	Bu^t	**3a**	**4c**	Me	H	Li	*B*	**6h**	Bu^t	Me	H	57[c]	51—53 (10)	1.2
1a	Bu^t	**3a**	**4c**	Me	H	K/Li	*E*	**6h**	Bu^t	Me	H	55[c]	51—53 (10)	1.2
1a	Bu^t	**3a**	**4d**	$MeOCH_2$	H	Li	*B*	**6i**	Bu^t	$MeOCH_2$	H	52[d]		1.1
1a	Bu^t	**3a**	**4d**	$MeOCH_2$	H	K/Li	*E*	**6i**	Bu^t	$MeOCH_2$	H	54[d]		1.1
1c	Ph	**3c**	**4e**	Me	Me	Li	*B*	**6j**	Ph	Me	Me	26[d]		—
1c	Ph	**3c**	**4d**	$MeOCH_2$	H	Li	*B*	**6k**	Ph	$MeOCH_2$	H	39[d]		1.1
2a	Ph	**3c**	**4b**	CH_2=CH	H	Li	*B*	**6f**	Ph	CH_2=CH	H	27[c]	109—111 (1.5)	1.0
2a	Ph	**3c**	**4c**	Me	H	Li	*B*	**6g**	Ph	Me	H	54[c]	84—86 (2)	1.5
2b	Bu^n	**3d**	**4a**	Ph	H	Li	*B*	**6l**	Bu^n	Ph	H	45[d]		2.1

[a] Methods for the synthesis of alkoxides: (*A*) the addition of an equimolar amount of a THF solution of naphthalene-lithium or naphthalene-sodium to a THF solution of an alcohol at 20 °C; (*B*) addition of an equimolar amount of a hexane solution of BuLi to a THF solution of an alcohol at 20 °C; (*C*) stirring of an alcohol with an equimolar amount of NaH in THF for 2—4 h at 20 °C; (*D*) refluxing of an alcohol with an equimolar amount of K in THF for 2—4 h followed by removal of unreacted K; (*E*) addition of BuLi to alkoxides, prepared by method *C* or *D*, in the presence of chlorotriphenylmethane until a red color appears.

[b] The yield was determined by GLC.

[c] The product was isolated by vacuum distillation.

[d] The product was isolated by column chromatography (a 10 : 1 hexane—ethyl acetate mixture as the eluent).

[e] The bath temperature during vacuum microdistillation is given.

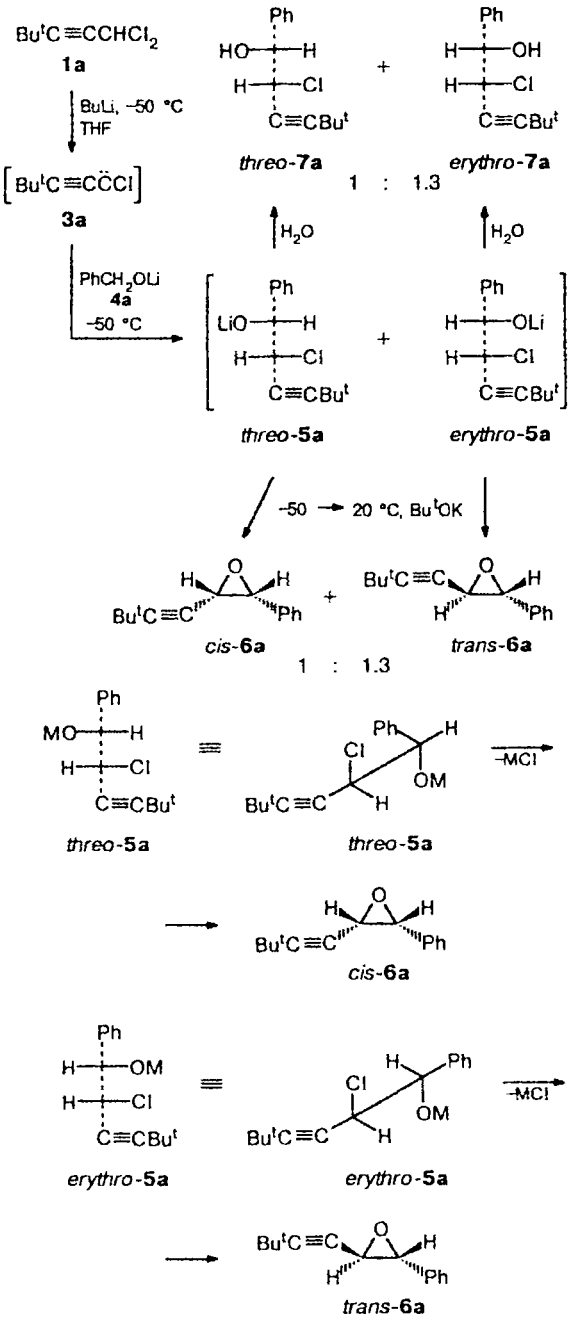
[f] The ratio was determined by the ^{1}H NMR spectra of the isolated products.

the latter was confirmed by the isolation of 5,5-dimethyl-1-phenylhex-3-yn-1-ol (**7a**) as a mixture of *erythro*- and *threo*-isomers (in 1.3 : 1 ratio) upon the generation of carbene **3a** by treatment of dichloride **1a** with an equimolar amount of a hexane solution of BuLi in the presence of a threefold molar excess of lithium phenylmethoxide at −50 °C in THF followed by treatment of the reaction mixture with water at the same temperature. When the reaction mixture was warmed up to room temperature and treated with water, the yield of the minor diastereomer of compound **7a** remained the same, whereas the yield of the major diastereomer decreased by 50%, and the *trans*-isomer of oxirane **6a** appeared. In the case where the reaction mixture was heated to room temperature and then treated with potassium *tert*-butoxide, chloroalkoxide **5a** was completely converted into oxirane **6a** (the ratio *trans*-**6a** : *cis*-**6a** = 1.3 : 1).

Since oxiranes are formed by the mechanism of a bimolecular substitution reaction accompanied by inversion of the configuration at the carbon atom[9] from which halogen is eliminated, it should be assumed that *cis*-epoxide **6a** is produced from the *threo*-isomer of **5a**, while *trans*-epoxide **6a** is formed from *erythro*-**5a**.

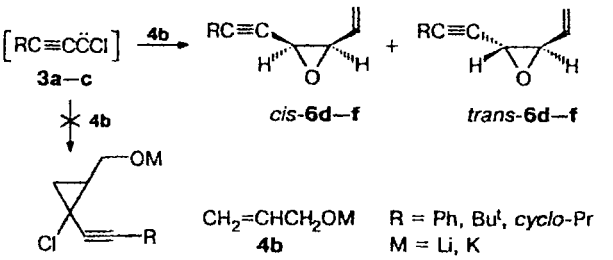
Thus, the *erythro*-isomer of compound **7a** is the predominant one, whereas the *threo*-isomer is the minor product. Based on this conclusion, we assigned the signals in the NMR spectra of compound **7a** to the *erythro*- and *threo*-isomers.

The structure of alcohol **7a** was proved by the ^{1}H and ^{13}C NMR spectra and also by the GC/MS method. The ^{1}H NMR spectrum exhibits two pairs of doublets in the



δ 4.6—4.9 range with J = 4.3 and 7.9 Hz corresponding to the CH groups in the *erythro*- and *threo*-isomers and also signals for the *tert*-butyl and phenyl groups. The ^{13}C NMR spectrum contains signals at δ 73—98 typical of a triple bond for two diastereomers, and the mass spectrum contains a peak corresponding to the $[M-HCl]^+$ ion. The NMR signals were assigned to *erythro*- and *threo*-isomers by comparing their integral intensities.

Carbenes **3a—d** were made to react with alkoxides **4a—e** derived from allyl and benzyl alcohol and also from primary and secondary aliphatic alcohols. When carbenes **3a—c** were trapped by alkoxide **4b**, the reaction gave oxiranes **6c—f** and absolutely no products of addition of these carbenes to the terminal double bond, indicating that the reactivity of this bond with respect to the carbenes generated in this reaction is lower than that of the α-C—H bond.



The structures of oxiranes **6a—l** synthesized were confirmed by the GC/MS data, NMR spectra, and elemental analysis (Tables 2, 3). The mass spectra of these compounds, except for **6d**, contain molecular ion peaks. The IR spectra exhibit absorption bands for the C≡C bond at 2235—2250 cm^{-1}. The ^{13}C NMR spectra contain signals at δ 73—95 and δ 46—60 characteristic of the triple bond and the oxirane ring, respectively; the ^{1}H NMR spectra display signals for the protons of the oxirane ring in the region of δ 3.3—4.3. The *cis*- and *trans*-isomers of oxiranes **6** were identified by comparison of the spin-spin coupling constants of the protons of the oxirane ring ($J_{trans} > J_{cis}$);[10] the assignment of the other signals in the NMR spectra to the corresponding isomers was based on a comparison of integral intensities of these signals. In those cases where the *trans*/*cis*-ratio did not differ much from 1, the mixture was enriched in one of the isomers by column chromatography or distillation.

When 1,1-dichloro-4,4-dimethylpent-2-yne (**1a**) reacted with Li and Na phenylmethoxides, prepared by addition of solutions of lithium or sodium naphthalide (method *A*) to a THF solution of benzyl alcohol, the yields of oxirane **6a**, according to GLC, were 61 and 71%, respectively; thus, the yield depends on the nature of the alkali metal used to prepare the alkoxide. The increase in the yield of **6a** on going from Li to Na is apparently due to the enhanced oxyanionic effect[11] in the corresponding alkoxides. Note that the isolation of oxiranes **6** from the mixtures produced in these reactions is a fairly complicated and labor-consuming task, because these mixtures contain large amounts of naphthalene and dihydronaphthalene.

The use of Li alkoxides prepared by adding an equimolar amount of a hexane solution of BuLi to alcohols (method *B*) markedly facilitates the isolation of oxiranes **6**, and in this case, products with purities of more than 95% can be isolated in 26—78% yields (see Table 1). The reaction of BuLi with alcohols occurs almost instantaneously. This can be easily checked by adding traces of chlorotriphenylmethane to the reaction mixture; the mixture turns red as a result of formation of

Table 2. Spectral data of 3-substituted 2-(alk-1-ynyl)oxiranes **6**

Compound	^{1}H NMR ($CDCl_3$, 200 MHz, δ, *J*/Hz)				NMR ($CDCl_3$, 50 MHz, δ)			
	H^1	R^2	R	R^1	C≡C	*cyclo*-C_2O_3	R	R^1, R^2
cis-**6a**	3.36 (d, *J* = 2)	3.98 (d, *J* = 2)	1.29 (s, 9 H)	7.3—7.5 (m, 5 H)	74.9, 93.0	49.7, 60.0	27.4 ($\underline{C}Me_3$); 30.7 ($C(\underline{C}H_3)_3$)	136.1 (C_{ipso}) 125.5, 127.1,
trans-**6a**	3.72 (d, *J* = 4)	4.09 (d, *J* = 4)	1.1 (s, 9 H)		73.2, 95.0	48.3, 58.7	27.3 ($\underline{C}Me_3$); 30.3 ($C(\underline{C}H_3)_3$)	134.5 (C_{ipso}) 127.5, 128.1, 128.4
cis-**6b**	3.32 (dd, *J* = 1.9, *J* = 1.5)	3.98 (d, *J* = 1.9)	0.45—1.0 (m, 4 H, 2 CH_2);	7.3—7.5 (m, 5 H)	71.7, 88.2	49.7, 59.9	−0.6 ($\underline{C}H$); 8.0 (2 CH_2)	135.9 (C_{ipso}) 125.4, 126.8,
trans-**6b**	3.72 (dd, *J* = 4, *J* = 1.5)	4.07 (d, *J* = 4)	1.08—1.21 (m, 1 H, CH)		69.5, 90.6	48.4, 58.7	−0.6 ($\underline{C}H$); 8.2 (2 CH_2)	134.4 (C_{ipso}) 127.5, 128.1, 128.4
cis-**6c**	3.60 (d, *J* = 2)	4.17 (d, *J* = 2)	7.3—7.5 (m, 10 H)		83.7, 85.3	49.6, 60.3	121.9 (C_{ipso})	134.2 (C_{ipso}) 121.8, 121.9, 125.6, 126.9, 127.8, 128.2,
trans-**6c**	3.99 (d, *J* = 4)	4.24 (d, 1 H, *J* = 4)			83.9, 86.0	48.7, 59.2	121.8 (C_{ipso})	135.7 (C_{ipso}) 128.4, 128.6, 128.7, 128.9, 131.6, 131.8
cis-**6d**	3.11 (d, *J* = 2.2)	3.5—3.56 (m)	1.17 (s, 9 H)	5.21—5.27 (m, 1 H, —CH=); 5.44—5.49(m, 2 H, $=CH_2$)	74.7, 92.9	47.2, 59.9	27.3 ($\underline{C}Me_3$); 30.7 ($C(\underline{C}H_3)_3$)	120.0 (CH_2); 134.3 (—CH=)
trans-**6d**	3.47 (d, *J* = 3.8)	3.5—3.56 (m)	1.18 (s, 9 H)	5.37 (dd, 1 H, *E*-H in $=CH_2$, *J* = 10.1, 1.6); 5.49 (dd, 1 H, *Z*-H in $=CH_2$, *J* = 16.9, 1.6); 5.68 (ddd, 1 H, —CH=, *J* = 16.9, 10.1, 7.6)	73.3, 94.6	46.3, 57.8	27.4 ($\underline{C}Me_3$); 30.7 ($C(\underline{C}H_3)_3$)	121.5 (CH_2); 133.1 (—CH=)
cis-**6e**	3.18 (dd, *J* = 1.8, *J* = 1.3)	3.38—3.45 (m)	0.45—1.0 (m, 4 H, 2 CH_2);	5.28—5.33 (m, 1 H,—CH=); 5.50—5.53 (m, 2 H, $=CH_2$)	71.4, 90.1	47.5, 60.2	−0.5 ($\underline{C}H$); 8.3 (2 CH_2)	120.4 ($=CH_2$); 134.2 (=CH—)
trans-**6e**	3.54 (dd, *J* = 3.7, *J* = 1.3)	3.38—3.45 (m)	1.08—1.21 (m, 1 H, CH)	5.44 (dd, 1 H, *E*-H in $=CH_2$, *J* = 10.2, 1.4); 5.57 (dd, 1 H, *Z*-H in $=CH_2$, *J* = 17.5, 1.3); 5.74 (ddd, 1 H, —CH=, *J* = 17.5, 10.2, 7.6)	69.8, 88.4	46.7, 58.2	−0.5 ($\underline{C}H$); 8.4 (2 CH_2)	121.9 ($=CH_2$); 133.1 (=CH—)
cis-**6f**	3.49 (d, *J* = 2)	3.61—3.68 (m)	7.3—7.5 (m, 5 H)	5.35—5.42 (m, 1 H, —CH=); 5.58—5.62 (m, 2 H, $=CH_2$)	83.9, 85.5	47.4, 60.3	121.8, 121.9, 128.2, 128.5, 128.7, 131.8	120.6 (CH_2); 133.8 (—CH=)
trans-**6f**	3.84 (d, *J* = 4)	3.61 (dd, *J* = 4, *J* = 8)		5.52 (dd, 1 H, *E*-H in $=CH_2$, *J* = 10, 1.6); 5.67 (dd, 1 H, *Z*-H in $=CH_2$, *J* = 17.1, 1.6); 5.90 (ddd, 1 H, —CH=, *J* = 17.1, 10, 8)	83.7, 85.0	46.7, 58.4		122.1 (CH_2); 132.7 (—CH=)

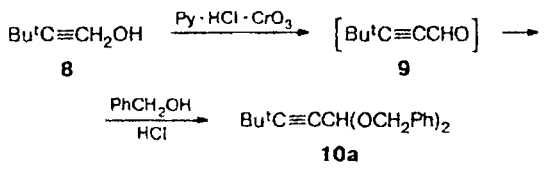
(to be continued)

Table 2 (*continued*)

Compound	^{1}H NMR ($CDCl_3$, 200 MHz, δ, *J*/Hz)				NMR ($CDCl_3$, 50 MHz, δ)			
	H^1	R^2	R	R^1	C≡C	*cyclo*-C_2O_3	R	R^1, R^2
cis-**6g**	3.1—3.3 (m, 2 H)		7.3—7.5	1.32 (d, 3 H, *J* = 5)	83.4, 84.2	46.6, 56.8	122.1, 128.3,	17.3
trans-**6g**	3.61 (d, *J* = 4)	3.1—3.3 (m)	(m, 5 H)	1.47 (d, 3 H, *J* = 5.2)	85.2, 85.8	45.8, 54.3	128.7, 131.9	14.7
cis-**6h**	2.9—3.12 (m, 2 H)		1.09 (s, 9 H)	1.19 (d, 3 H, *J* = 5)	73.4, 92.3	45.4, 56.3	27.3 ($\underline{C}Me_3$); 30.5 ($C(\underline{C}H_3)_3$)	17.2
trans-**6h**	3.26 (d, *J* = 4.1)	2.9—3.12 (m)	1.11 (s, 9 H)	1.28 (d, 3 H, *J* = 5.1)	75.2, 94.1	46.3, 53.5	27.2 ($\underline{C}Me_3$); 30.6 ($C(\underline{C}H_3)_3$)	14.3
cis-**6i**	3.25 (d, *J* = 2.1)	3.14—3.23 (m)	1.21 (s, 9 H)	3.38 (s, 3 H, OCH_3); 3.41 (dd, 1 H, 1 H in CH_2, *J* = 11.6, 4.5); 3.62 (dd, 1 H, 1 H in CH_2, *J* = 11.6, 3.1)	74.7, 92.8	43.2, 58.7	27.6 ($\underline{C}Me_3$); 30.7 ($C(\underline{C}H_3)_3$)	59.2 (OCH_3); 71.5 (CH_2)
trans-**6i**	3.45 (d)	3.14—3.23 (m)	1.22 (s, 9 H)	3.43 (s, 3 H, OMe); 3.55 (dd, 1 H, 1 H in CH_2, *J* = 11.6, 5.8); 3.70 (dd, 1 H, 1 H in CH_2, *J* = 11.6, 4.5)	72.9, 94.7	43.8, 55.6	27.4 ($\underline{C}Me_3$); 30.7 ($C(\underline{C}H_3)_3$)	59.1 (OCH_3); 71.3 (CH_2)
6j	3.43 (s, 3 H)	1.4 (s, 3 H)	7.28—7.5 (m)	1.52 (s, 3 H)	85.0, 85.3	52.4 (CH); 61.0 ($\underline{C}Me_2$)	122.3 (C_{ipso}); 128.4, 128.7, 131.9	20.4 (Me); 23.5 (Me)
cis-**6k**	3.53 (d, *J* = 2.0)	3.4—3.7 (m)		3.39 (s, 3 H, OMe); 3.4—3.7 (m, 2 H, CH_2)	83.8, 85.5	43.8, 56.1	121.8 (C_{ipso});	59.2 (OCH_3); 71.1 (CH_2)
trans-**6k**	3.71 (d, *J* = 4.2)	3.34 (ddd, *J* = 4.2, *J* = 4.2, *J* = 6.0)	7.25—7.5 (m)	3.46 (s, 3 H, OCH_3); 3.64 (dd, 1 H, 1 H in CH_2, *J* = 11.5, 6.0); 3.62 (dd, 1 H, 1 H in CH_2, *J* = 11.6, 4.2)	83.2, 85.1	43.1, 59.1	128.3, 128.7, 128.8, 131.8 (C_{ipso}) 121.8	58.8 (OCH_3); 71.4 (CH_2)
cis-**6l**	4.00 (d, *J* = 1.9)	3.35 (dt, *J* = 1.9, *J* = 1.6)	0.96 (t, 3 H, CH_3, *J* = 7.1); 1.1—1.7 (m, 4 H, 2 CH_2); 2.28 (td, 2 H, ≡CCH_2, *J* = 7.0, *J* = 1.6)		76.3, 85.1	49.8, 60.0	13.5 (CH_3); 18.4, 21.9, 30.3 (3 CH_2)	136.0 (C_{ipso})
trans-**6l**	4.08 (d, *J* = 4.0)	3.35 (dt, *J* = 4.0, *J* = 1.6)	0.84 (t, 3 H, CH_3, *J* = 7.1); 1.1—1.7 (m, 4 H, 2 CH_2); 2.11 (td, 2 H, ≡CCH_2, *J* = 7.0, *J* = 1.6)	7.25—7.5 (m)	74.3, 87.4	48.5, 58.7	13.4 (CH_3); 18.2, 21.5, 30.1 (3 CH_2)	134.5 (C_{ipso}) 125.5, 126.8, 126.9, 127.5, 128.1, 128.4

the triphenylmethyl anion immediately after the addition of excess BuLi.

When carbene **3a** was generated in the presence of sodium phenylmethoxide, prepared by the interaction of equimolar amounts of benzyl alcohol and NaH in THF during 2—4 h (method *C*), or potassium phenylmethoxide, prepared by mixing the corresponding alcohol with an equimolar amount of K in THF (method *D*), in addition to oxirane **6a** (yields 51 and 41%, respectively), the reaction gave 1,1-di(phenylmethoxy)-4,4-dimethylpent-2-yne (**10a**) (yield 3% (*C*) and 5% (*D*)) and a number of nonidentified products in small amounts. The structure of acetal **10a** was proved by comparing the mass spectrum and the retention time with the corresponding data for the same acetal prepared by oxidation of 4,4-dimethylbut-2-yn-1-ol (**8**) by the complex $Py \cdot HCl \cdot CrO_3$ followed by acetalization of the resulting aldehyde **9** with an excess of benzyl alcohol in the presence of HCl.



The addition of chlorotriphenylmethane and 0.05—0.1 equiv. of BuLi to Na and K phenylmethoxides thus obtained did not cause a red coloration, indicating that $PhCH_2OH$ had not been entirely converted into the alkoxide. The reaction mixture turned red only after the addition of a solution containing 0.3—0.5 equiv. of BuLi (method *E*). When this alkoxide mixture was used subsequently for the preparation of oxirane **6a**, the yield of the oxirane increased by 10—15% (see Table 1) and only traces of acetal **10a** (<1%) were present in the reaction mixture. Conversely, when $PhCH_2OH$ was added to lithium phenylmethoxide prepared using BuLi (by procedure *B*), the yield of oxirane **6a** decreased, whereas the yield of acetal **10a** increased (Table 4).

We also showed that stirring of dichloride **1a** for 0.5—24 h with alkali metal phenylmethoxides prepared by methods *B* and *E* but without Bu^tOK gives neither oxirane **6a** nor acetal **10a**.

These results indicate that acetal **10a** is produced most likely upon the reaction of carbene **3a**, generated from **1a** under the action of Bu^tOK, with the $PhCH_2OH$

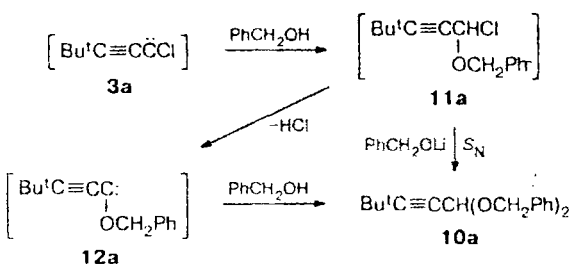


Table 3. Data of the IR and mass spectra and elemental analysis of 3-substituted 2-(alk-1-ynyl)oxiranes

Compound	Mass spectrum, *m/z* (EI, 70 eV)	Found / Calculated (%) C	Found / Calculated (%) H	IR spectrum, νC≡C /cm⁻¹
6a	200 $[M]^+$	84.05 / 83.96	7.96 / 8.05	2250
6b	184 $[M]^+$	84.61 / 84.75	6.65 / 6.58	2245
6c	220 $[M]^+$	87.32 / 87.25	5.38 / 5.49	2240
6d*	149$[M-H]^+$	79.51 / 79.36	9.42 / 9.39	2250
6e	134 $[M]^+$, 133 $[M-H]^+$	80.33 / 80.56	7.68 / 7.51	2243
6f	170 $[M]^+$	84.82 / 84.68	6.01 / 5.92	2240
6g	158 $[M]^+$	83.59 / 83.52	6.21 / 6.37	2250
6h	138 $[M]^+$	77.97 / 78.21	10.39 / 10.21	2250
6i	168 $[M]^+$	71.43 / 71.39	9.71 / 9.59	2250
6j	172 $[M]^+$	83.52 / 85.69	7.13 / 7.02	2250
6k	188 $[M]^+$	86.71 / 86.57	6.32 / 6.43	2252
6l	200 $[M]^+$	84.04 / 83.96	7.91 / 8.05	2242

*The molecular ion could not be detected.

present in the reaction mixture rather than upon nucleophilic substitution of the phenylmethoxy group for the chlorine atoms in the initial dichloride **1a**. Thus, the pathway to acetal **10a** can be described as the insertion of carbene **1a** generated during the reaction into the O—H bond of benzyl alcohol to give chlorinated ether **11a**, which is then converted into acetal **10a** *via* nucleophilic substitution of a phenylmethoxy group for the

Table 4. Composition of the products of interaction of dichloride **1a** with Bu^tOK in THF at 20 °C in the presence of lithium phenylmethoxide prepared by method *B* and benzyl alcohol

The ratio $PhCH_2OH$ / $PhCH_2OLi$	Yield* of oxirane **6a** (%)	Yield* of acetal **10a** (%)	The ratio **6a**/**10a**
0	60	0.9	75 : 1
0.5	55	4	14 : 1
1	47	7.5	6.3 : 1
1.5	44	9	4.9 : 1

* According to GLC.

chlorine atom or *via* (*tert*-butylethynyl)(phenylmethoxy)carbene (**12a**).

The predominant formation of the products of insertion into the α-C—H bond rather than into the polarized O—metal bond in the reaction of (alk-1-ynyl)chlorocarbenes **3** with alkali metal alkoxides **4** is apparently due to the fact that the negative charge on the oxygen atom facilitates elimination of a hydride ion from the α-position and, hence, promotes the insertion of electrophilic carbenes **3**,[2] which occurs presumably[12] according to the hydride ion abstraction—recombination pattern.

Thus, we proposed a novel general method for the synthesis of 3-substituted 2-(alk-1-ynyl)oxiranes **6**, whose yields depend both on the nature of the alkali metal and on the procedure used to prepare alkoxides **4**. Data indicating that (alk-1-ynyl)chlorocarbenes **3** are capable of being inserted into the α-C—H bonds of alkali metal alkoxides and into the O—H bonds of alcohols were obtained.

Experimental

The GLC analyses of initial compounds and reaction products were carried out on a Hewlett-Packard 5890 Series II instrument with a 30 m×0.153 mm capillary column and a Hewlett-Packard 3396A automated integrator. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AC-200p and Bruker AM-300 spectrometers for solutions of the studied compounds in $CDCl_3$. The chemical shifts in the proton spectra were referred to internal tetramethylsilane. In the carbon spectra, the central peak of the $CDCl_3$ signal (δ 77.1) was used as the standard. IR spectra were recorded on a Perkin—Elmer 580 spectrophotometer for solutions in CCl_4, and mass spectra were measured on a Finnigan MAT INCOS-50 GC/MS spectrometer.

The initial 1,1-dichloroalk-2-ynes **1a—e** were synthesized by a procedure reported previously,[1] and tetrahalides **2a,b** were prepared by a known procedure.[13]

Preparation of THF solutions of alkali metal alkoxides

Method *A*. A solution of naphthalene-lithium or naphthalene-sodium in THF was added with stirring in an argon atmosphere to a solution of an alcohol in 5—20 mL of anhydrous THF until the color of the solution changed from white to light green.

Method *B*. Chlorotriphenylmethane (1 mg) was added to a solution of the starting alcohol in 5—20 mL of anhydrous THF. Then a 1—2.5 *M* solution of BuLi in hexane was added with stirring under argon until a pink color appeared.

Method *C*. Powdered NaH (1 equiv.) was added under argon to a solution of the starting alcohol in 5—20 mL of anhydrous THF, and the mixture was stirred for 2—4 h.

Method *D*. Finely cut metallic potassium (1 equiv.) was added under argon to a solution of the starting alcohol in 5—20 mL of anhydrous THF, and the mixture was refluxed with stirring for 2—4 h. The unreacted potassium was removed by forceps.

Method *E*. Chlorotriphenylmethane (1 mg) was added to an alkoxide solution prepared by method *C* or *D*. Then a solution of BuLi in hexane was added under argon until a pink color appeared.

Preparation of oxiranes 6a—k from 1,1-dichloroalk-2-ynes (1a—c) (general procedure). Freshly prepared potassium *tert*-butoxide (1100 mg, 10 mmol) and then a solution of dichloride **1** (4 mmol) in THF (1—2 mL) were added to an alkali metal alkoxide prepared from 12 mmol of an alcohol by methods *A—E*. The solution was stirred for 30 min at ~20 °C. The reaction mixture was treated with water, the organic layer was separated, and the aqueous layer was extracted with ether (3×10 mL). The combined organic solutions were dried with magnesium sulfate, and the solvent was evaporated on a rotary evaporator. Distillation or column chromatography of the residue (a 10 : 1 hexane—ethyl acetate mixture as the eluent) gave the corresponding oxirane **6**. The yields, boiling points, ratios of the *cis*- and *trans*-isomers, data of elemental analysis, and spectral characteristics of the resulting oxiranes **6** are listed in Tables 1—3.

GLC determination of the yields of products 6a and 10a. The experiments were carried out by the above general procedure, except that together with the initial dichloride **1a**, a portion of an internal standard (dodecane or tridecane), weighed with an accuracy of 0.1 mg, was added. When the reaction was completed, the resulting mixture was analyzed by GLC (without separation), and the yield of the product was determined from the ratio of the areas of peaks of the internal standard and the product based on the preliminary calibration of the detector. The results averaged over three identical experiments are presented in Tables 1 and 4.

Preparation of oxiranes 6f,g,l from tetrahalides 2a,b (general procedure). Freshly prepared potassium *tert*-butoxide (3.36 g, 30 mmol) and after that, a solution of the initial tetrahalide **2** (4 mmol) in 5 mL of THF were added to a solution of lithium alkoxide prepared from 12 mmol of an alcohol by method *B*. The reaction mixture was stirred for 2 h at ~20 °C and treated with water, the organic layer was separated, and the aqueous layer was extracted with ether (3×10 mL). The combined organic solutions were dried with magnesium sulfate, and the solvent was evaporated on a rotary evaporator. Distillation or column chromatography of the residue (a 10 : 1 hexane—ethyl acetate mixture as the eluent) gave the target product. The yields, boiling points, ratios of the *cis*- and *trans*-isomers, data of elemental analysis, and spectral characteristics of oxiranes **6f,g,l** are listed in Tables 1—3.

2-Chloro-5,5-dimethyl-1-phenylhex-3-yn-1-ol (7a). Chlorotriphenylmethane (5 mg) was added to a solution of benzyl alcohol (324 mg, 3 mmol) in 5 mL of THF. Then a solution of butyllithium in hexane was slowly added under argon until a persistent red color appeared. Then the reaction mixture was cooled to −50 °C, and a 1.4 *M* hexane solution of butyllithium (0.7 mL, 1 mmol) and a solution of the initial dichloride **1a** (165 mg, 1 mmol) in 1 mL of THF were added. The reaction mixture was stirred at the same temperature for 10 min and then treated with 10 mL of water, avoiding warming up. The organic layer was separated, and the aqueous layer was acidified with HCl and extracted with ether (3×10 mL). The combined extracts were dried with magnesium sulfate, and the solvent was evaporated on a rotary evaporator. Column chromatography of the residue (a 10 : 1 hexane—ethyl acetate mixture) gave 57 mg (21%) of product **7a**. ^{1}H NMR, δ for the *erythro*-isomer: 1.15 (s, 9 H, Bu^t); 3.0 (br.s, 1 H, OH); 4.75 (d, 1 H, CHCl, J = 4.3 Hz); 4.91 (d, 1 H, CHOH, J = 4.3 Hz); 7.3—7.5 (m, 5 H, Ph); *threo*-isomer: 1.24 (s, 9 H, Bu^t); 3.0 (br.s, 1 H, OH); 4.64 (d, 1 H, CHCl, J = 7.9 Hz); 4.79 (d, 1 H, CHOH, J = 7.9 Hz); 7.3—7.5 (m, 5 H, Ph). ^{13}C NMR, δ for the *erythro*-isomer: 29.8 ($\underline{C}Me_3$); 30.6 ($C(\underline{C}H_3)_3$); 56.4 and 78.0 (2 CH); 74.2 and 98.0 (C≡C); for the *threo*-isomer: 29.7 ($\underline{C}Me_3$); 30.5 ($C(\underline{C}H_3)_3$); 54.9 and 76.9 (2 CH); 73.3 and 98.4 (C≡C); for both isomers: 127.0, 127.3, 128.1, 128.6, 138.6, 138.7 (Ph). MS, *m/z*: 200 $[M-HCl]^+$.

In a similar experiment in which the reaction mixture was warmed up to ~20 °C and treated with water, separation of the products by column chromatography (using a 10 : 1 hexane—ethyl acetate mixture as the eluent) gave 41 mg (15%) of chloro alcohol **10a** (*erythro* : *threo* = 0.6 : 1) and 14 mg (7%) of the *trans*-isomer of oxirane **6a**.

When the reaction mixture was warmed up to ~20 °C, potassium *tert*-butoxide (224 mg, 2 mmol) was added, and then the mixture was stirred for 10 min, 51 mg (25%) of oxirane **6a** (the isomer ratio *trans* : *cis* = 1.3 : 1) was isolated.

Reaction of dichloride 1a with Bu^{t}OK in the presence of lithium phenylmethoxide and benzyl alcohol. Benzyl alcohol in a quantity calculated using the $PhCH_2OH/PhCH_2OLi$ ratios listed in Table 4 and freshly prepared potassium *tert*-butoxide (110 mg, 1 mmol) were successively added to a solution of lithium phenylmethoxide prepared from benzyl alcohol (108 mg, 1 mmol) by method *B*. Then a solution of dichloride **1b** (55 mg, 0.33 mmol) and dodecane (40 mg) used as the internal standard in 1 mL of THF were added. After 1 h of stirring at ~20 °C, the reaction mixture was treated with water, the organic layer was separated, and the aqueous layer was extracted with ether (3×5 mL). The organic solutions were combined, and the yields of oxirane **6a** and acetal **10a** were determined by GLC (see the section "GLC determination of the yields of products **6a** and **10a**"). The results are listed in Table 4. Retention times and the data of GC/MS analysis of product **10a** coincide with the corresponding parameters of the same acetal prepared by an alternative route.

Synthesis of 1,1-di(phenylmethoxy)-4,4-dimethylpent-2-yne (10a). At 10 °C, 4,4-dimethylbut-2-yn-1-ol (**8**) (280 mg, 2.5 mmol) was added to a stirred suspension of the complex $Py \cdot CrO_3 \cdot HCl$ (0.75 g, 3.75 mmol) in 10 mL of CH_2Cl_2. The reaction mixture was stirred for 2 h, then the temperature was raised to ~20 °C, and an additional portion of $Py \cdot CrO_3 \cdot HCl$ (0.5 g, 2.5 mol) was added. After 1 h, the reaction mixture was cooled to −20 to −30 °C and passed through a thin layer of neutral Al_2O_3, which was then washed with 10 mL of CH_2Cl_2. Benzyl alcohol (1.3 g, 12 mmol) and 1 drop of 35% aqueous HCl were added to the resulting solution of 4,4-dimethylpent-2-ynal **9**. The reaction mixture was stirred for 6 h at ~20 °C and treated with water, the organic layer was separated, and the aqueous layer was extracted with ether (2×5 mL). The combined organic layers were dried with magnesium sulfate, the solvent was evaporated on a rotary evaporator, and excess $PhCH_2OH$ was distilled off in a vacuum of 1—2 Torr. Column chromatography of the residue (a 20 : 1 mixture of hexane—ethyl acetate as the eluent) gave 0.27 g (35%) of acetal **10a**. ^1H NMR, δ: 1.29 (s, 9 H, Bu^t); 4.75 and 4.82 (both d, 2×2 H, 2 CH_2Ph, J = 17 Hz); 5.5 (s, 1 H, ≡CCH); 7.3—7.5 (m, 10 H, 2 Ph). MS (EI, 70 eV), m/z (I_{rel} (%)): 217 $[M-CH_2Ph]^+$ (3), 201 $[M-OCH_2Ph]^+$ (1), 145 (2.5), 107 $[PhCH_2O]^+$ (9.5), 91 $[C_7H_7]^+$ (100), 77 $[Ph]^+$ (11), 65 (13.5).

Reaction of dichloride 1a with alkali metal phenylmethoxides in the absence of potassium *tert*-butoxide. A solution of dichloride **1a** (165 mg, 1 mmol) and dodecane (80 mg) in 1 mL of THF was added to a solution of alkali metal phenylmethoxide prepared by method *A* or *E* from benzyl alcohol (324 mg, 3 mmol). The reaction mixture was stirred at ~20 °C for 0.5 h or 24 h and treated with water, the organic layer was separated, and the aqueous layer was extracted with ether (3×5 mL). The combined organic layers were analyzed by GLC. According to GLC analysis, dichloride **1a** remained practically unchanged, and no oxirane **6a** or acetal **10a** was formed.

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