Alkynylhalocarbenes: Generation from 1,1-Dihaloalk-2-ynes by Base Solvolysis and Reaction with Alkenes†

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A series of 1,1-dihaloalk-2-ynes **1–3** has been prepared by halogenation of the formylacetylenes **8** with PCl_5 or an equimolar mixture of PCl_5 and Br_2. A simple, general means of access to the alkynylhalocarbenes **5** has been developed *via* base-initiated α-elimination of 1,1-dihaloalk-2-ynes (**1–3**). The carbenes **5a–i** have been trapped by alkenes, to form 1-alkynyl-1-halocyclopropanes (**11**) in up to 90% yield. Under the same conditions compound **1g** was converted into the butadiene **12**. Experimental evidence for the electrophilicity and the singlet nature of carbenes **5** has been obtained.

Alkynylcarbenes $R(C{\equiv}C)_n\dot{C}H$ (n = 1, 2) with a triplet ground state have been generated[1,2] by photolysis of the appropriate diazoalkynes. Triplet dialkynylcarbenes $R(C{\equiv}C)_2\dot{C}$ have been prepared by pyrolysis of the corresponding lithium salts of diethynyl ketone tosylhydrazones[3] or photolysis of 1-diazo-4-phenylbut-3-yn-2-one,[4] as well as *via* the reaction of 3-bromo-1,5-diphenylpenta-1,3-diyne[5] with Bu'OK. Methoxycarbonyl- and bromo-substituted (4-methylpent-3-en-1-ynyl)carbenes generated by photolysis[6] of the appropriate 3,3-dimethylalk-5-ynyl-3*H*-pyrazoles have also been described. Taking into account the small difference between the electronegativity of the ethynyl group and that of halogen atoms, we supposed, by analogy with haloforms,[7] that the 1,1-dihaloalk-2-ynes **1–3** would α-eliminate hydrogen halide on treatment with base, to yield alkynylhalocarbenes **5** which are a new class of carbene species (Scheme 1). This assumption was later confirmed by quantum-chemical calculations.[8]

In this paper we report the generation of alkynylhalocarbenes **5** from 1,1-dihaloalk-2-ynes[9] **1–3** and their addition to alkenes with the formation of 1-alkynyl-1-halocyclopropanes[10] (**11**).

Results and Discussion

The dihalides **1–3** were obtained by halogenating aldehydes **8**. These labile aldehydes[11] were prepared either by oxidation[12] of the alcohols **6a–d** with the complex CrO_3–Py–HCl (Scheme 2) or by acetolysis[13] of the acetals **7a–c** by formic acid, and were then used directly without isolation.

On the interaction of the aldehydes **8a–g** with PCl_5 in the presence of a catalytic amount of pyridine (Py) at −20 to −10 °C, the dihalides **1a–g** were obtained in 50–75% yields based on the corresponding starting compounds **6a–d** or **7a–c** (Table 1). On treatment of but-2-ynal **8a** with an equimolar mixture of PCl_5–Br_2 in the presence of Py at −50 °C 1,1-dibromobut-2-yne **2a** and the diene **9** (2:1) were obtained in 35% overall yield. Under these conditions the aldehydes **8d, f** gave mixtures of the appropriate 1,1-dibromo- (**2b, c**) and 1-bromo-1-chloroalkynes (**3a, b**), which were separated by distillation.

On treatment with powdered KOH in the presence of benzyltriethylammonium chloride (BTEAC) either at 5–20 °C in CH_2Cl_2 (method A) or at 40–50 °C in hexane (method B), and also with Bu'OK at −10 °C in pentane (method C), compounds

$$R^1C{\equiv}CCHXY \rightleftharpoons R^1C{\equiv}C\bar{C}XY \rightleftharpoons R^1C{\equiv}C\ddot{C}X$$

1 X = Cl, Y = Cl
2 X = Br, Y = Br
3 X = Cl, Y = Br

4 5

Scheme 1

1a–f, 2a–c and **3a, b** α-eliminated hydrogen halides to give the alkynylhalocarbenes **5a–i**, which were trapped using a seven- to ten-fold molar excess of the alkene **10**, resulting in the formation of 1-alkynyl-1-halocyclopropanes **11a–y** in up to 90% yield. The use of 1-bromo-1-chloroalk-2-ynes **3a, b** led exclusively to the 1-alkynyl-1-chlorocyclopropanes **11**. This implies that only the alkynylchlorocarbenes **5a, b** were generated under these conditions. As expected, the *trans*- and *cis*-isomers of the cyclopropanes **11q–y** were formed from the unsymmetrical alkenes **10f–j** (Table 2).

The structures of cyclopropanes **11a–y** were established by IR, ^1H NMR and mass spectrometry (Table 3). In particular, all of the adducts showed characteristic isotope doublets of the molecular ion which contains a bromide or a chloride atom. The IR spectra of these compounds show absorptions due to a triple bond in the region 2225–2255 cm^{-1}. Identification of the *trans*- and *cis*-isomers of **11q–y** was achieved by comparing the chemical shifts of the ^1H NMR signals due to the protons of the substituents R^2, R^3, R^4 and R^5 attached to the cyclopropane ring of one isomer with the corresponding substituent protons in another isomer. In addition, the protons in the R^2 and R^3 groups of *cis*-**11**, being on the same side of the cyclopropane ring as the halogen atom, resonate downfield of those of *trans*-**11** because of greater deshielding. This observation is in accordance with ^1H NMR data for the alkynyl-,[14] alkenyl-[15] and aryl-halocyclopropane[16] isomeric pairs described in the literature.

It should be noted that the behaviour of compounds **1–3** in the presence of bases depends on the nature of the substituents at the triple bond and on the basic solvolysis conditions. Hence, on treatment with KOH under phase-transfer catalysis conditions (method A), methyl- and phenyl-substituted alkynes **1a, b** reacted with the alkenes, to give cyclopropanes **11a, f, l** in less than 5% yield, forming mainly unidentified powdered solids, which dissolved neither in water nor in organic solvents. However, when Bu'OK in pentane was employed as the base (method C), cyclopropanes **11a, f, l** were obtained in 30–50% yield (Table 2). Compound **1g** was converted into butadiene **12** using both methods A and C.

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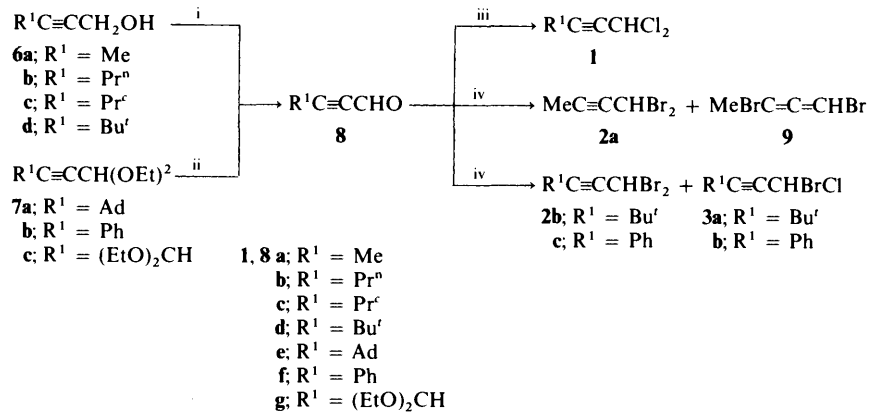


Scheme 2 Pr^c = cyclopropyl, Ad = adamantyl. *Reagents and conditions:* i, CrO_3–Py–HCl, CH_2Cl_2, 15–20 °C, 2.5 h; ii, HCO_2H, $CHCl_3$ or CH_2Cl_2, 40–45 °C; iii, PCl_5, Py (cat.), CH_2Cl_2 or $CHCl_3$, −20 °C, 20–40 min; iv, PCl_3–Br_2, Py (cat.), CH_2Cl_2, −50 °C, 30 min.

Table 1 Properties of 1,1-dichloroalk-2-ynes **1**

Compound (Formula)	Yield (%)	B.p./°C (*p*/mmHg)	δ_H(CCl_4; 60 MHz)[c] Cl_2CH	δ_H R^1	*m/z* (M^+)	ν_{max}/cm^{-1} (C≡C)	Found (%) (Required) C	H	Cl
1a ($C_4H_4Cl_2$)	55[a]	68–70 (90)	6.15 (q, *J* = 2.1 Hz)	1.19 (3 H, d, *J* = 2.1 Hz, Me)	126/124/122	2240	39.14 (39.07)	3.32 (3.28)	57.48 (57.66)
1b ($C_6H_8Cl_2$)	65[a]	90–92 (75)	6.12 (m)	0.95 (3 H, br t, *J* = 7.0 Hz, Me), 152 (2 H, m, CH_2), 2.29 (2 H, br t, *J* = 7.0 Hz, CH_2C≡)	154/152/150	2240	47.65 (47.71)	5.41 (5.34)	46.73 (46.95)
1c ($C_6H_6Cl_2$)	60[a]	82–83 (23)	6.17 (d, *J* = 2.0 Hz)	0.76 (4 H, m, 2 × CH_2), 1.23 (1 H, m, CH)	152/150/148	2240	48.23 (48.36)	4.02 (4.06)	47.40 (47.58)
1d ($C_7H_{10}Cl_2$)	60[a]	47–48 (13)	6.30 (s)	1.20 (9 H, s, 3 × Me)	168/166/164	2235	50.87 (50.94)	6.06 (6.11)	42.83 (42.96)
1e ($C_{13}H_{16}Cl_2$)	75[b]	m.p. 45	6.10 (s)	1.50–2.10 (15 H, m, Ad)	246/244/242	2235	64.15 (64.21)	6.72 (6.63)	28.96 (29.16)
1f ($C_9H_6Cl_2$)	60[b]	76–78 (1)	6.33 (s)	7.26 (5 H, m, Ph)	188/186/184	2225	58.53 (58.42)	3.21 (3.27)	38.23 (38.32)
1g ($C_8H_{12}Cl_2O_2$)	50[b]	64–65 (1)	6.20 (d, *J* = 2.0 Hz)	6.18 (6 H, t, *J* = 7.0 Hz, 2 × Me), 3.55 (4 H, m, 2 × CH_2), 5.18 (1 H, d, *J* = 2.0 Hz, CH)	169/167/165 (M^+ − EtO), 141/139/177 (M^+ − EtO − C_2H_4)	absent	45.44 (45.52)	5.66 (5.73)	33.51 (33.59)

[a] Based on the corresponding alcohol **6**. [b] Based on the corresponding acetal **7**. [c] For compound **1e** δ_H($CDCl_3$; 250 MHz).

The formation of product **12** from compound **1g** on reaction with base (in contrast with **1a–f**) is possibly the result of stabilization of the anion **4** [R^1 = $(EtO)_2CH$, X = Y = Cl] in the mesomeric form $(EtO)_2CH\bar{C}{=}C{=}CCl_2$ due to the influence of ethoxy groups.

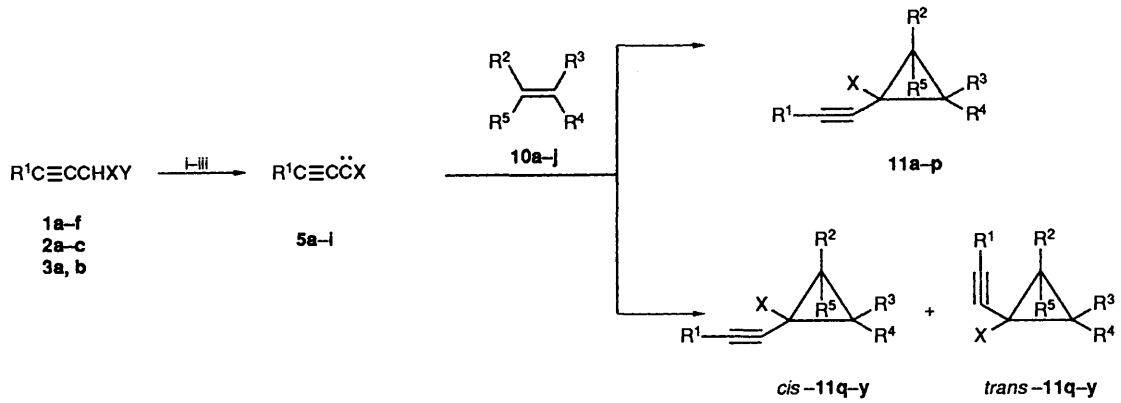
$$(EtO)_2CHC{\equiv}CCHCl_2 \xrightarrow{\text{i or ii}} (EtO)_2CHCH{=}C{=}CCl_2$$
1g **12**

Scheme 3 *Reagents and conditions:* i, powdered KOH, BTEAC (cat.), CH_2Cl_2, *ca.* 20 °C; ii, Bu^{t}OK, pentane, −10 °C

The addition of carbene **5c** to (*Z*)- and (*E*)-but-2-enes was found to be *cis*-stereospecific, *i.e.* the *cis* relationship of R^2 and R^3 and of R^4 and R^5 in the substrate alkene were preserved in the product cyclopropanes. In accordance with the Skell hypothesis[17] this carbene must be a singlet. Since all of the carbenes **5** have related structures one may assume a singlet nature for this species. It should be noted that no products resulting from the addition of carbenes **5** to alkenes *via* C-3 were found. This observation is consistent with the bent structure of carbenes **5**, which prevents delocalization of the π and n electrons:[1] $R\overset{3}{C}{\equiv}\overset{2}{C}(Cl)\overset{1}{C}: \longleftrightarrow :\overset{3}{C}(R)\overset{2}{C}{\equiv}\overset{1}{C}Cl$, and also provides indirect evidence for the singlet nature of this species.

Experimental evidence for the electrophilicity of carbenes **5** was provided by means of relative rate studies of bromo(methylethynyl)carbene **5g** with a set of standard alkenes, which are summarized in Table 4 together with the relative reactivity of dichlorocarbene[18] under similar conditions. A plot of $\log(k_i/k_o)$ for carbene **5g** *vs.* $\log(k_i/k_o)$ for dichlorocarbene in the standard manner gives a Moss carbenic selectivity index[19] of *m* = 0.48 (correlation coefficient 0.986) for carbene **5g**. The relative reactivity data of Table 4 and the corresponding *m* = 0.48 clearly establish carbene **5g** as an electrophile. It is unlikely that the nature of substituents at the acetylene bond will significantly change the character of alkynylcarbenes **5**, therefore all of these carbenes should be regarded as electrophilic.

Table 2 Generation of carbenes **5** and their addition to alkenes **10** with formation of cyclopropanes **11**



Carbene precursors	Reaction conditions[a]	Carbene			Alkene					Product (*cis*:*trans*)[b]	Yield (%)
			R^1	X		R^2	R^3	R^4	R^5		
1a	iii	**5a**	Me	Cl	**10a**	Me	H	H	Me	**11a**	41
1a	i	**5a**	Me	Cl	**10a**	Me	H	H	Me	**11a**	<5
1b	i	**5b**	Pr^n	Cl	**10a**	Me	H	H	Me	**11b**	60
1c	i	**5c**	Pr^c	Cl	**10a**	Me	H	H	Me	**11c**	80
1d	i	**5d**	Bu^t	Cl	**10a**	Me	H	H	Me	**11d**	53
3a	i	**5d**	Bu^t	Cl	**10a**	Me	H	H	Me	**11d**	64
3a	iii	**5d**	Bu^t	Cl	**10a**	Me	H	H	Me	**11d**	60
1e	i	**5e**	Ad	Cl	**10a**	Me	H	H	Me	**11e**	94
1f	iii	**5f**	Ph	Cl	**10a**	Me	H	H	Me	**11f**	60
1f	i	**5f**	Ph	Cl	**10a**	Me	H	H	Me	**11f**	<5
3b	iii	**5f**	Ph	Cl	**10a**	Me	H	H	Me	**11f**	56
2a	iii	**5g**	Me	Br	**10a**	Me	H	H	Me	**11g**	26
2b	i	**5h**	Bu^t	Br	**10a**	Me	H	H	Me	**11h**	54
2b	iii	**5h**	Bu^t	Br	**10a**	Me	H	H	Me	**11h**	56
2c	iii	**5i**	Ph	Br	**10a**	Me	H	H	Me	**11i**	50
2c	i	**5i**	Ph	Br	**10a**	Me	H	H	Me	**11i**	<5
1c	i	**5c**	Pr^c	Cl	**10b**	Me	H	Me	H	**11j**	78
1c	i	**5c**	Pr^c	Cl	**10c**	H	$[CH_2]_2$		H	**11k**	80
1a	iii	**5a**	Me	Cl	**10d**	H	$[CH_2]_3$		H	**11l**	30
1a	i	**5a**	Me	Cl	**10d**	H	$[CH_2]_3$		H	**11l**	<5
1b	ii	**5b**	Pr^n	Cl	**10d**	H	$[CH_2]_3$		H	**11m**	60
1c	ii	**5c**	Pr^c	Cl	**10d**	H	$[CH_2]_3$		H	**11n**	65
2a	iii	**5g**	Me	Br	**10e**	Me	Me	Me	Me	**11o**	44
1d	i	**5d**	Bu^t	Cl	**10e**	Me	Me	Me	Me	**11p**	77
3a	i	**5d**	Bu^t	Cl	**10e**	Me	Me	Me	Me	**11p**	70
2a	iii	**5g**	Me	Br	**10f**	Me	Me	H	H	*cis,trans*-**11q** (1:1.7)	40
1c	i	**5c**	Pr^c	Cl	**10f**	Me	Me	H	H	*cis,trans*-**11r** (1:3)	84
2b	i	**5h**	Bu^t	Br	**10f**	Me	Me	H	H	*cis,trans*-**11s** (1:2.5)	40
2a	ii	**5g**	Me	Br	**10g**	Me	Me	Me	H	*cis,trans*-**11t** (1:1)[c]	41
1b	i	**5b**	Pr^n	Cl	**10h**	Bu^n	H	H	H	*cis,trans*-**11u** (1:2.5)[c]	35
1c	ii	**5c**	Pr^c	Cl	**10i**	$[CH_2]_4$		H	H	*cis,trans*-**11v** (1:4)	42
1d	i	**5d**	Bu^t	Cl	**10i**	$-[CH_2]_4-$		H	H	*cis,trans*-**11w** (1:3.4)[c]	93
1d	i	**5d**	Bu^t	Cl	**10j**	Ph	H	H	H	*cis,trans*-**11x** (1:2.3)	57
2b	i	**5d**	Bu^t	Br	**10j**	Ph	H	H	H	*cis,trans*-**11y** (1:3)	60

[a] i, Method A; ii, method B; iii, method C (see the Experimental section). [b] Ratios were determined by GLC. [c] Ratio was determined from the ^1H NMR spectrum of the distilled product.

Experimental

GLC analysis of the starting material and products was carried out on a LCM-8 MD flame ionization gas chromatograph with an integrator I-02 using the following 200 × 0.3 cm columns: (1) 5% SP-2100 on Inerton, 20 mesh; (2) 5% ES-30 on Chromaton N-AW-DMCS, 20 mesh; (3) 15% Carbowax-6000 on Chromaton N-AW-DMCS, 20 mesh. Preparative work was performed on an LCP-71 gas chromatograph using a 200 × 10 cm column with 15% Carbowax-6000 on Chromaton N-AW-DMCS, 30 mesh. ^1H NMR spectra were recorded on a Tesla BS-467 (60 MHz) or a Bruker WM-250 (250 MHz) spectrometer using 3–10% CCl_4 or $CDCl_3$ solutions with tetramethylsilane (TMS) as an internal standard. ^{13}C NMR spectra were obtained on a Bruker AM-300 (70 MHz) spectrometer. Coupling constant values J are given in Hz. IR spectra were recorded for a thin films or for CCl_4 solutions on a UR-20 or a Specord M-80 spectrophotometer. Mass spectra were determined on a Varian MAT CH-6 mass spectrometer and either a Varian MAT 111 (column 300 × 3 cm, SE-30 on Chromaton W) or a Finnigan MAT INCOS-50 gas chromatograph–mass spectrometer (capillary column RSL-200, 30 m × 0.25 mm).

The following compounds were prepared according to previously described procedures: but-2-ynol **6a**,[20] hex-2-ynol **6b**,[20] 4,4-dimethylpent-2-ynol **6d**,[20] 3-cyclopropylprop-2-ynol **6c**,[21] 1,1-diethoxy-3-phenylprop-2-yne **7b**,[22] 1,1,4,4-tetraethoxybut-2-yne **7c**.[13] The complex Py–CrO_3–HCl was prepared as described in ref. 23.

Table 3 Properties of cyclopropanes **11**.

Compound (Formula)	B.p./°C (p/mmHg)	δ_H($CDCl_3$; 250 MHz)[b] R[1]	R[2]	R[3]	R[4]	R[5]	m/z (M^+)	ν_{max}/cm^{-1} (C≡C)	Found (%) (Required) C	H
11a ($C_8H_{11}Cl$)	59–61 (25)	1.80 (3 H, s, Me)	1.23 (3 H, s, Me)	0.93 (1 H, d, J = 6.0)	0.89 (1 H, d, J = 6.0)	1.20 (3 H, s, Me)	144/142	2235	67.25 (67.37)	7.73 (7.77)
11b ($C_{10}H_{15}Cl$)	77–79 (40)	0.71–1.1 (3 H, m, Me), 1.5 (2 H, m, CH_2), 2.2 (2 H, m, $CH_2C\equiv$)	1.28 (3 H, s, Me)	0.7–1.1 (2 H, m, H^3 and H^4, overlapped Me in R^1)		1.25 (3 H, s, Me)	172/170	2245	70.32 (70.37)	8.82 (8.86)
11c ($C_{10}H_{13}Cl$)	62–63 (3)	0.60–0.88 (4 H, m, 2 × CH_2), 1.28 (1 H, m, CH)	1.30 (3 H, s, Me)	1.01 (2 H, br s, H^3 and H^4)		1.23 (3 H, s, Me)	170/168	2230	71.20 (71.21)	7.74 (7.77)
11d ($C_{11}H_{17}Cl$)	40–43 (1)	1.22 (9 H, s, 3 × Me)	1.33 (3 H, s, Me)	1.04 (1 H, d, J = 7.5)	1.01 (1 H, d, J = 7.5)	1.26 (3 H, s, Me)	186/184	2235	71.46 (71.53)	9.23 (9.28)
11e[a] ($C_{17}H_{23}Cl$)		1.5–2.1 (15 H, m, Ad)	1.25 (3 H, s, Me)	0.91 (2 H, br s, H^3 and H^4)		1.18 (3 H, s, Me)	264/262	2230	77.74 (77.69)	8.80 (8.82)
11f ($C_{13}H_{13}Cl$)	107–108 (1)	7.21–7.40 (5 H, m, Ph)	1.42 (3 H, s, Me)	1.28 (1 H, d, J = 6.0)	1.19 (1 H, d, J = 6.0)	1.39 (3 H, s, Me)	206/204	2230	76.23 (76.28)	6.39 (6.40)
11g ($C_8H_{11}Br$)	61–62 (37)	1.88 (3 H, s, Me)	1.35 (3 H, s, Me)	1.11 (1 H, d, J = 5.9)	1.05 (1 H, d, J = 5.9)	1.27 (3 H, s, Me)	188/186	2255	51.20 (51.36)	5.85 (5.93)
11h ($C_{11}H_{17}Br$)	69–70 (5)	1.21 (9 H, s, 3 × Me)	1.37 (3 H, s, Me)	1.17 (1 H, d, J = 8.0)	1.08 (1 H, d, J = 8.0)	1.28 (3 H, s, Me)	230/228	2235	57.73 (57.65)	7.52 (7.48)
11i ($C_{13}H_{13}Br$)	113–115 (1)	7.20–7.45 (5 H, m, Ph)	1.47 (3 H, s, Me)	1.36 (1 H, d, J = 6.0)	1.26 (1 H, d, J = 6.0)	1.41 (3 H, s, Me)	250/248	2225	62.76 (62.67)	5.35 (5.26)
11j ($C_{10}H_{13}Cl$)	78–79 (6)	0.58–0.77 (4 H, m, 2 × CH_2), 1.22 (1 H, m, CH)	1.16 (3 H, d, J = 7.0, Me)	0.93 (1 H, dq, J = 7.0, 6.0)	1.10 (3 H, d, J = 7.0, Me)	0.83 (1 H, dq, J = 7.0, 6.0)	170/168	2230	71.23 (71.21)	7.76 (7.77)
11k ($C_{10}H_{11}Cl$)	68–70 (2)	0.58–0.86 (4 H, m, 2 × CH_2), 1.20 (1 H, m, CH)	1.62 (1 H, d, J = 5.5)	0.95–1.16 (4 H, m, 2 × CH_2)		1.58 (1 H, d, J = 5.5)	168/166	2240	72.04 (72.07)	6.63 (6.65)
11l ($C_9H_{11}Cl$)	106–108 (43)	1.88 (3 H, br s, Me)	1.14 (1 H, br d, J = 6.1)	1.95–2.20 (4 H, m, 2 × CH_2), 2.20–2.35 (2 H, m, CH_2)		1.07 (1 H, br d, J = 6.1)	156/154	2240	69.86 (69.90)	7.14 (7.17)
11m ($C_{11}H_{15}Cl$)	63–65 (6)	0.97 (3 H, br t, J = 7.1, Me), 1.5 (2 H, m, CH_2), 1.8–2.6 (2H, m, $CH_2C\equiv$)	1.15 (1 H, d, J = 6.0)	1.8–2.6 (6 H, m, 3 × CH_2)		1.05 (1 H, d, J = 6.0)	184/182	2250	72.22 (72.32)	8.24 (8.28)
11n ($C_{11}H_{13}Cl$)	78–79 (2)	0.60–0.83 (4 H, m, 2 × CH_2), 1.20 (1 H, m, CH)	1.14 (1 H, d, J = 6.0)	1.85–2.65 (6 H, m, 3 × CH_2)		1.06 (1 H, d, J = 6.0)	182/180	2235	73.10 (73.13)	7.28 (7.25)
11o ($C_{10}H_{15}Br$)	62–63 (7)	1.92 (3 H, s, Me)	1.21 (6 H, s, Me^2 and Me^3)		1.18 (6 H, s, Me^4 and Me^5)		218/216	2245	55.71 (55.83)	6.94 (7.03)
11p ($C_{13}H_{21}Cl$)	M.p. 85	1.15 (9 H, s, 3 Me)	1.07 (12 H, s, Me^2, Me^3, Me^4 and Me^5)				202/200	2230	73.24 (73.39)	9.91 (9.95)

Table 3 (*continued*)

Compound (Formula)	B.p./°C (*p*/mmHg)	δ_H(CDCl$_3$; 250 MHz)[b] R^1	R^2	R^3	R^4	R^5	*m/z* (M$^+$)	ν_{max}/cm^{-1} (C≡C)	Found (%) (Required) C	H
11q ($C_8H_{11}Br$)	90–94 (47)							2250	51.18 (51.36)	5.84 (5.93)
cis		1.86 (3 H, s, Me)	1.19 (6 H, m, Me^2 and Me^3)		1.21 (2 H, m, H^4 and H^5)		188/186			
trans		1.93 (3 H, s, Me)	1.18 (6 H, m, Me^2 and Me^3)		1.58 (2 H, m, H^4 and H^5)		188/186			
11r ($C_{10}H_{13}$)	86–91 (6)						170/168	2230	71.18 (71.21)	7.77 (7.77)
cis		0.58–0.78 (4 H, m, 2 × CH_2), 1.19 (1 H, m, CH)	0.98 (6 H, m, Me^2 and Me^3)		1.29 (2 H, m, H^4 and H^5)					
trans		0.58–0.80 (4 H, m, 2 × CH_2), 1.24 (1 H, m, CH)	0.96 (6 H, m, Me^2 and Me^3)		1.44 (2 H, m, H^4 and H^5)		170/168	2230		
11s ($C_{11}H_{17}Br$)	45–48 (3)							2235	57.69 (57.65)	7.51 (7.48)
cis		1.20 (9 H, s, 3 × Me)	1.08 (6 H, m, Me^2 and Me^3)		1.48 (2 H, m, H^4 and H^5)		230/228			
trans		1.24 (9 H, s, 3 × Me)	1.04 (6 H, m, Me^2 and Me^3)		1.57 (2 H, m, H^4 and H^5)		230/228			
11t ($C_9H_{13}Br$)	79–82 (13)							2240	53.62 (53.75)	6.44 (6.52)
cis		1.89 (3 H, s, Me)	1.11 (3 H, d, J = 6.5, Me)	1.13 (3 H, s, Me)	1.27 (3 H, s, Me)	0.92 (1 H, q, J = 6.5, H)	202/200			
trans		1.93 (3 H, s, Me)	1.09 (3 H, d, J = 6.5, Me)	1.11 (3 H, s, Me)	1.35 (3 H, s, Me)	1.21 (1 H, q, J = 6.5, H)	202/200			
cis-, *trans*-**11u** ($C_{12}H_{19}Cl$)	78–83 (2)	0.7–1.1 (6 H, m, Me^1 and Me^2), 1.1–1.9 (11 H, m, CH_2^1, 3 × CH_2^2, H^3, H^4 and H^5), 2.0–2.4 (2 H, m, CH_2^1C≡)					200/198	2235	72.49 (72.52)	9.61 (9.64)
cis-, *trans*-**11v** ($C_{12}H_{15}Cl$)	92–96 (2)	0.6–1.0 (4 H, m, 2 × CH_2^1), 1.1–2.1 (11 H, m, CH^1, 4 × $CH_2^{2,3}$, H^4 and H^5)					196/194	2240	74.00 (74.03)	7.72 (7.77)
cis-, *trans*-**11w** ($C_{13}H_{19}Cl$)	97–100 (20)	1.21 (9 H, s, 3 × Me^1 in *trans*-isomer), 1.24 (9 H, s, 3 × Me^1 in *cis*-isomer), 0.8–1.6 (10 H, m, 4 × $CH_2^{2,3}$, H^4 and H^5)					212/210	2235	74.05 (74.09)	9.06 (9.09)
11x ($C_{15}H_{17}Cl$)	131–134 (13)							2240	77.34 (77.41)	7.32 (7.36)
cis		1.24 (9 H, s, 3 × Me)	7.2–7.4 (5 H, m, Ph)	1.80–2.04 (2 H, m, H^3 and H^4)		2.93 (1 H, dd, J = 8.1, 10.4)	232/234			
trans		1.01 (9 H, s, 3 × Me)	7.2–7.4 (5 H, m, Ph)	1.08–2.04 (2 H, m, H^3 and H^4)		2.77 (1 H, dd, J = 7.6, 9.6)	232/234			
11y ($C_{15}H_{17}Br$)	105–108 (1)							2240	65.09 (64.99)	6.20 (6.18)
cis		1.29 (9 H, s, 3 × Me)	7.2–7.4 (5 H, m, Ph)	1.75 (1 H, dd, J = 6.0, 8.0)	1.77 (1 H, dd, J = 6.0, 9.5)	2.58 (1 H, dd, J = 8.0, 9.5)	278/276			
trans		1.03 (9 H, s, 3 × Me)	7.2–7.4 (5 H, m, Ph)	1.76 (1 H, dd, J = 6.5, 7.5)	1.87 (1 H, dd, J = 6.5, 9.5)	2.88 (1 H, dd, J = 7.5, 9.5)	278/276			

[a] Purified by chromatography on silica gel in hexane. [b] For compounds **11a**, **b**, **c**, **e**, **k**, **m**, **p**, **u**, **v** δ_H(CCl$_4$; 60 MHz).

Synthesis of 1,1-*Dichloroalk*-2-*ynes* **1a–d** *from Prop*-2-*ynols* **6a–d** (*General Procedure*).—Alcohols **6a–d** (0.25 mol) were added at 10–15 °C over 15 min to a suspension of the complex Py–CrO_3–HCl (76.8 g, 0.36 mol) in CH_2Cl_2 (500 cm^3). The reaction mixture was stirred at ambient temperature for 2.5 h. After being cooled to −10 °C the mixture was filtered through neutral Al_2O_3. To the resulting solution at −20 °C pyridine (2 g, 0.025 mol) and then powdered PCl_5 (48 g, 0.23 mol) were added. The reaction mixture was stirred at −20 °C for 20–30 min and neutralized with $NaHCO_3$ (105 g, 1.25 mol). The mixture was kept at 0–5 °C for 16 h and the solid was filtered off. After evaporation of the filtrate the residue was distilled *in vacuo*.

1,1-Dichlorobut-2-yne **1a**, 1,1-dichlorohex-2-yne **1b**, 1,1-dichloro-3-cyclopropylprop-2-yne **1c** and 1,1-dichloro-4,4-dimethylpent-2-yne **1d** were obtained in this way. The yields and properties of these compounds are given in Table 1.

Synthesis of 1,1-*Dichloroalk*-2-*ynes* **1e–g** *from Propargyl Acetals* **7a–c** (*General Procedure*).—A solution of formic acid (90 cm^3, 2.3 mol) in $CHCl_3$ (85 cm^3) was added to a solution of the acetal (0.1 mol) and $CHCl_3$ (120 cm^3) at 40–45 °C. After being cooled to 20 °C the mixture was washed with water until a pH of 6 was achieved and dried over $MgSO_4$. The resulting solution of the aldehyde in $CHCl_3$ then was chlorinated with PCl_5 as described above. 3-Adamantyl-1,1-dichloroprop-2-yne **1e**, 1,1-dichloro-3-phenylprop-2-yne **1f** and 1,1-dichloro-4,4-diethoxybut-2-yne **1g** were obtained according to this procedure. The yields and properties of these compounds are given in Table 1.

Synthesis of 1,1-*Dibromoalk*-2-*ynes* **2a–c** *and* 1-*Bromo*-1-*chloroalk*-2-*ynes* **3a, b** *from Alcohols* **6** (*General Procedure*).—To a suspension of the complex Py–CrO_3–HCl (72.8 g, 0.34 mol) in CH_2Cl_2 (450 cm^3) at 10–15 °C was added the alcohol **6** over 15 min. The mixture was stirred at ambient temperature for 2.5 h and filtered through neutral Al_2O_3. Pyridine (1.6 g, 0.02 mol) and then a mixture of PCl_3 and Br_2 [obtained previously by addition of Br_2 (32.4 g, 0.2 mol) to a solution of PCl_3 (27.4 g, 0.2 mol) in CH_2Cl_2 (90 cm^3) at −20 °C and subsequent stirring for 1 h at 0 °C] were added to the filtrate at −70 °C. The mixture was stirred at −50 °C until the starting aldehyde disappeared (monitored by GLC, *ca.* 40 min) and worked up with $NaHCO_3$, as described above. After removal of the solid, the resulting solution was filtered through silica gel. The solvent was evaporated off and the residue was distilled *in vacuo* to yield compounds **2** and **3**.

1,1-*Dibromobut*-2-*yne* **2a**. As described above, starting from alcohol **6a** (14.02 g, 0.2 mol) a mixture (14.83 g, 35%) of compound **2a** and 1,3-dibromobuta-1,2-diene **9** was obtained in a 2:1 ratio, b.p. 80–89 °C at 25 mmHg. After distillation compound **2a** was isolated, b.p. 87–89 °C at 25 mmHg; ν_{max}/cm^{-1} 2247 (C≡C); δ_H(250 MHz; $CDCl_3$) 2.04 (3 H, d, J = 3, CH_3) and 6.07 (1 H, q, J = 3, C≡CH); *m*/*z* 133/131 (M^+ − Br), 81/79, 52 (M^+ − 2Br), 51 (M^+ − Br − HBr) (Found: C, 22.6; H, 1.9. $C_4H_4Br_2$ requires C, 22.67; H, 1.90%).

Compound **9** was identified without being separated from the mixture, ν_{max}/cm^{-1} 1960 (C=C=C); δ_H(250 MHz; $CDCl_3$) 2.43 (3 H, d, J = 3, CH_3) and 6.09 (1 H, q, J = 3, C=CH); *m*/*z* 133/131 (M^+ − Br), 81/79, 52 (M^+ − 2Br) and 51 (M^+ − Br − HBr).

In the same way, starting from 4,4-dimethylpent-2-ynol **6d** (22.5 g, 0.2 mol) a mixture (14.4 g, 30%) of compounds **2b** and **3a** was obtained in the ratio 4:1 and were separated by distillation.

Compound **2b**, b.p. 64–65 °C at 3 mmHg; ν_{max}/cm^{-1} 2235 (C≡C); δ_H(60 MHz; CCl_4) 1.18 (9 H, s, 3 × CH_3) and 5.94 (1 H, s, $CHBr_2$); *m*/*z* 175/173 (M^+ − Br), 160/158 (M^+ − Br − CH_3), 94 (M^+ − 2Br) and 79/77 (Found: C, 33.25; H, 4.1. $C_7H_{10}Br_2$ requires C, 33.11; H, 3.97%).

Compound **3a**, b.p. 50–52 °C at 3 mmHg, ν_{max}/cm^{-1} 2235 (C≡C); δ_H(60 MHz; CCl_4) 1.17 (9 H, s, 3 × CH_3) and 6.00 (1 H, s, CHClBr); *m*/*z* 131/129 (M^+ − Br), 116/114 (M^+ − Br − CH_3), 94 (M^+ − Br − Cl) and 79/77 (Found: C, 40.0; H, 4.7. $C_7H_{10}BrCl$ requires C, 40.13; H, 4.81%).

1,1-*Dibromo*-3-*phenylprop*-2-*yne* **2c** *and* 1-*Bromo*-1-*chloro*-3-*phenylprop*-2-*yne* **3b**.—A mixture of PCl_3 and Br_2 [which had previously been obtained by addition of Br_2 (32.4 g, 0.2 mol) to a solution of PCl_3 (27.4 g, 0.2 mol) in CH_2Cl_2 (90 cm^3) at −20 °C and subsequent stirring for 1 h at 0 °C] was added to a solution of phenyl(formyl)acetylene **8f** (26 g, 0.2 mol) and pyridine (1.6 g, 0.02 mol), in CH_2Cl_2 (250 cm^3) at −50 °C. The mixture was stirred at −50 °C until the aldehyde **8f** disappeared (*ca.* 40 min, GLC monitoring) and treated with $NaHCO_3$ as described above. After removal of the solid, the resulting residue was filtered through silica gel. After evaporation the residue was distilled *in vacuo*, to yield an equimolar mixture of compounds **2c** and **3b**, b.p. 106–125 °C at 1 mmHg. The products were separated by distillation.

Compound **2c**, b.p. 125–126 °C at 1 mmHg; ν_{max}/cm^{-1} 2212 (C≡C); δ_H(60 MHz; CCl_4) 6.17 (1 H, s, $CHBr_2$) and 7.28 (5 H, m, C_6H_5); *m*/*z* 276/274/272 (M^+), 195/193 (M^+ − Br) and 114 (M^+ − 2Br) (Found: C, 39.6; H, 2.3. $C_9H_6Br_2$ requires C, 39.46; H, 2.21%).

Compound **3b**, b.p. 105–106 °C at 1 mmHg; ν_{max}/cm^{-1} 2214 (C≡C); δ_H(60 MHz; CCl_4) 6.30 (1 H, s, CHClBr) and 7.28 (5 H, m, C_6H_5); *m*/*z* 232/230/228 (M^+), 195/193 (M^+ − Cl), 151/149 (M^+ − Br) and 114 (M^+ − Br − Cl) (Found: C, 47.0; H, 2.55. C_9H_6BrCl requires C, 47.10; H, 2.64%).

Basic Solvolysis of 1,1-*Dihaloalk*-2-*ynes* **1** *in the Presence of Alkenes* (*General Procedure*).—*Method A*. The dichloride **1** (0.01 mol) was added to a suspension of an alkene (0.07–0.1 mol), powdered KOH (2.2 g, 0.04 mol) and BTEAC (0.1 g, 0.0005 mol) in CH_2Cl_2 (20 cm^3) at 5–20 °C for 15 min. The mixture was stirred at ambient temperature until the starting dichloride **1** had disappeared (2–4 h, GLC monitoring) and filtered. Thereafter, the solvent was evaporated off and the resulting residue was distilled *in vacuo*.

Method B. The dichloride **1** was added to a suspension of the alkene (0.07–0.1 mol), powdered KOH (2.2 g, 0.04 mol) and BTEAC (0.1 g, 0.0005 mol) in hexane (20 cm^3) for 15 min. The mixture was stirred at 40–45 °C until the starting dichloride had disappeared (3–5 h, GLC monitoring) and filtered. The solvent was evaporated off and the residue was distilled *in vacuo*.

Method C. Compound **1** (0.01 mol) was added to a suspension of alkene (0.07–0.1 mol) and Bu^{t}OK (2.24 g, 0.02 mol) in pentane (10 cm^3) cooled to −20 °C. The reaction mixture was stirred at ambient temperature for 0.5 h. The temperature was then raised to 0 °C and stirring was continued until the starting dichloride had disappeared (GLC monitoring). The solid was filtered off through silica gel. After evaporation of the filtrate the residue was distilled *in vacuo*. The preparative data and

Table 4 Relative reactivities of bromo(methylethynyl)carbene **5g** and dichlorocarbene Cl_2C: towards alkenes

Alkene	MeC≡CC̈Br	Cl_2C:[a]
2,3-Dimethylbut-2-ene	3.12 ± 0.05	7.41
2-Methylbut-2-ene	1.64 ± 0.03	3.05
2-Methylpropene	1	1
(*Z*)-But-2-ene	0.59 ± 0.05	0.23

[a] *Via* $CHCl_3$, Bu^{t}OK.[18]

properties of cyclopropanes **11a–y** prepared in this way are given in Tables 2 and 3.

1,1-*Dichloro*-4,4-*diethoxybuta*-1,2-*diene* **12**.—As described above (method A), starting from the dichloride **1g** (1.8 g, 8.5 mmol) in the presence of alkene **10e**, the title compound **12** (1.2 g, 67%) was obtained, b.p. 56–58 °C at 1 mmHg; ν_{max}/cm^{-1} 1975 (C=C=C); *m/z* 165 ($M^+ - C_2H_5O$, 12%), 109 (28), 103 (70), 75 (52) and 47 (100); δ_H 1.17 (6 H, t, J = 7.0, 2 × CH_3), 3.50 (4 H, m, 2 × CH_2), 4.90 (1 H, d, J = 5.0, CH) and 5.53 (1 H, d, J = 5.0, CH=) (Found: C, 45.45; H, 5.7. $C_8H_{12}Cl_2O_2$ requires C, 45.52; H, 5.73%).

Similarly, starting from the dichloride **1g** (0.9 g, 4.25 mmol) and using method C only, the diene **12** (0.4 g, 44%) was again obtained.

Stereoselectivity of Addition of Chloro(cyclopropylethynyl)carbene **5c** *to* (Z)- *and* (E)-*But*-2-*enes*.—The reaction of the dichloride **1c** with (*Z*)-but-2-ene **10f** [>99% pure, (*E*)-but-2-ene **10b** impurity <1%] was carried out as above (method A). When the reaction was complete the mixture was analysed using GC [column (3), at 170 °C] and was found to contain *cis*- (66.7 ± 0.5%) and *trans*-isomers (33.1 ± 0.5%) of *cis*-1-chloro-1-cyclopropylethynyl-2,3-dimethylcyclopropane **11r** and only a trace amount of *trans*-2,3-dimethylcyclopropane **11j**, which evidently originated from **10b** in the starting alkene. The *cis*- and *trans*-isomers were separated by preparative GC at 180 °C and their structures were established by IR, ^1H NMR and mass spectrometry (see Table 2).

The reaction with (*E*)-but-2-ene **10b** [>99% pure, (*Z*)-but-2-ene **10f** impurity <1%] was carried out in a manner similar to that described for **10f**. GC analysis [column (3), at 170 °C] showed that *trans*-dimethylcyclopropane **11j** and only traces of cyclopropane *cis*-, *trans*-**11r** were formed. The properties and spectral data of **11j** are listed in Tables 2 and 3.

Relative Rate Determinations for Bromo(methylethynyl)carbene **5g** (*General Procedure*).—The dibromide **2a** (2.1 g, 0.01 mol) was added to a suspension of freshly sublimed Bu^{t}OK (2.24 g, 0.02 mol) in a solution of a binary mixture of the appropriate alkene [2,3-dimethylbut-2-ene, 2-methylbut-2-ene or (*Z*)-but-2-ene] (0.1 mol) and 2-methylpropene (5.6 g, 0.1 mol) in pentane (20 cm^3) at −10 °C under Ar. After being stirred for 30 min at the same temperature the mixture was analysed by means of analytical flame ionization GC coupled to an integrator [column (1), at 120 °C]. Six product ratios were determined for each pair of alkenes and averaged. The determined relative rates are summarized in Table 4. These were used for the calculation of Moss carbenic selectivity index, which is defined as the least-squares slope of $\log(k_i/k_o)$ for carbene **5g** *vs.* $\log(k_i/k_o)$ for dichlorocarbene, m = 0.48, correlation coefficient 0.986.

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