Organic Chemistry

Alkynylhalocarbenes
4.* Generation of (alk-1-ynyl)halocarbenes from 3-substituted 1,1,1,3-tetrahalopropanes under the action of bases**

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When treated with KOH under phase-transfer catalysis or with Bu^{t}OK, 3-substituted (alkyl or phenyl) 1,1,3-tribromo-1-fluoropropanes **1a—c** exclusively generate previously unknown (alk-1-ynyl)fluorocarbenes **5a—c**, which react with olefins to give 1-(alk-1-ynyl)-1-fluorocyclopropanes **6a—h** in 12—69% yields. Under analogous conditions, 3-alkyl- and 3-aryl-3-bromo-1,1,1-trichloropropanes **2a—c** selectively afford (alk-1-ynyl)chlorocarbenes **7a—c**, which are trapped by olefins to form the corresponding 1-(alk-1-ynyl)-1-chlorocyclopropanes **8a—k** in 35—70% yields. (Phenylethynyl)chlorocarbene **7a** is also selectively generated from 1,1,1,3-tetrachloro-3-phenylpropane (**3a**) upon its treatment with Bu^{t}OK. With an excess of 2,3-dimethylbut-2-ene or 2-methylpropene, carbene **7a** yields 1-chloro-1-(phenylethynyl)cyclopropanes **8a** or **8c**, respectively. In contrast, 1,1,1,3-tetrachloroheptane **3b** and 3-alkyl- and 3-phenyl-1,1,1,3-tetrabromopropanes **4a,c,f** react with bases in the presence of olefins to give, along with the corresponding 1-(alk-1-ynyl)-1-halocyclopropanes **8a,c,d** and **11a—f**, vinylidenecyclopropanes **12a,c—g**, which suggests the generation, under these conditions, both (alk-1-ynyl)halocarbenes **7b** and **9a—c** and vinylidenecarbenes **10** and **11a—c**. The composition and structures of intermediate products in the reactions of tetrahalides **1b**, **2a**, **2b**, **3a**, and **3b** with Bu^{t}OK were determined and the mechanisms for carbene generation in these reactions were proposed.

Key words: 3-substituted 1,1,1,3-tetrahalopropanes; dehydrohalogenation, phase-transfer catalysis, (alk-1-ynyl)halocarbenes, (alk-1-ynyl)halocyclopropanes, cycloaddition.

Earlier,[1,4—6] we have proposed a general method for the generation of (alk-1-ynyl)halocarbenes by alkaline solvolysis of 1,1-dihaloalk-2-ynes. This method affords (alk-1-ynyl)chloro- and (alk-1-ynyl)bromocarbenes with alkyl, cycloalkyl, phenyl, and trimethylsilyl substituents at the triple bond. Our recent studies[2,3] revealed that alkaline solvolysis of accessible 3-substituted 1,1,1,3-tetrahalopropanes **1—4** also yields (alk-1-ynyl)halocarbenes. This paper presents detailed data on the reactions of vari-

* For Part 3, see Ref. 1.
** Preliminary results have been published previously.[2,3]

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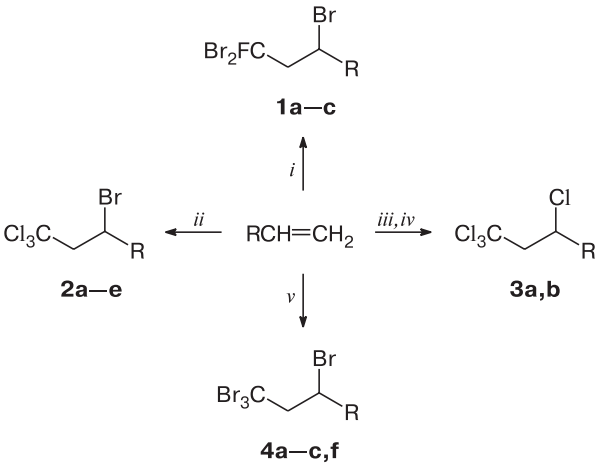
Scheme 1



R = Ph (**a**), Bu (**b**), Bu^t (**c**), $(Et_2O)_2CH$ (**d**), 4-ClC_6H_4 (**e**), Me (**f**).

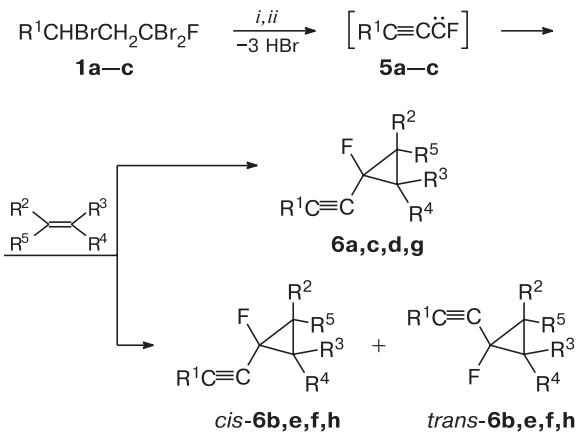
Reagents and conditions: *i*) CBr_3F, AIBN; *ii*) CCl_3Br, AIBN; *iii*) CCl_4, $(PhCOO)_2$; *iv*) CCl_4, MeCN, $CuCl_2$, Et_2NH_2Cl; *v*) CBr_4, CCl_4, AIBN.

ous tetrahalides **1**—**4** with bases in the presence of olefins as traps for carbenes generated under these conditions.

The starting tetrahalides **1**—**4**, except for **3a**, were prepared by free radical addition of the corresponding tetrahalomethanes to accessible terminal olefins.[7] To do this, the latter were heated with a two- to fivefold molar excess of a tetrahalomethane for 4—10 h in the presence of catalytic amounts of azodiisobutyronitrile (AIBN) or dibenzoyl peroxide (Scheme 1). 1,1,1,3-Tetrachloro-3-phenylpropane (**3a**) was synthesized by addition of CCl_4 to styrene, with a mixture of $CuCl_2$ and Et_2NH_2Cl as a catalyst.[8]

The reactions of 3-alkyl- and 3-phenyl-1,1,3-tribromo-1-fluoropropanes **1a**—**c** with KOH in CH_2Cl_2 at 20—40 °C or with Bu^{t}OK in hexane at 20 °C proceed through successive elimination of three HBr molecules to give the corresponding (alk-1-ynyl)fluorocarbenes **5a**—**c**, which represent a new class of highly reactive carbenes. Their trapping by alkenes (2-methylpropene, 2,3-dimethylbut-2-ene, or styrene) affords previously unknown alkynylfluorocyclopropanes **6a**—**h** in 12—69% yields (Scheme 2, Table 1). As expected, alkenes that are unsymmetrical relative to the plane of the π-orbitals of the double bond gave cyclopropanes **6b,e,f,h** as mixtures of *cis*- and *trans*-isomers.

Scheme 2

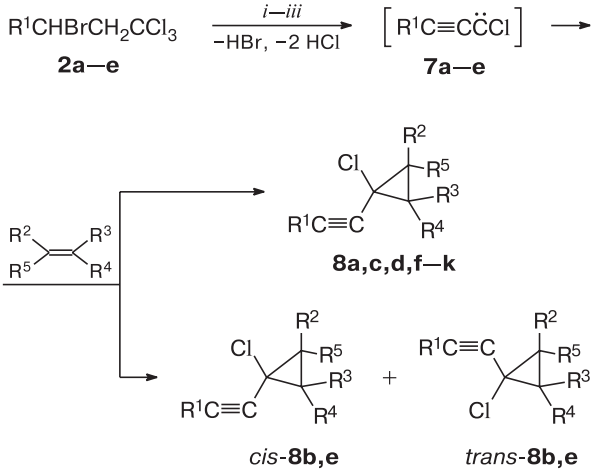


1a, 5a: R^1 = Ph; **1b, 5b:** R^1 = Bu^n; **1c, 5c:** R^1 = Bu^t.

	R^1	R^2	R^3	R^4	R^5
6a	Ph	Me	Me	Me	Me
6b	Ph	—$(CH_2)_4$—		H	H
6c	Bu	Me	Me	Me	Me
6d	Bu	H	Me	Me	H
6e	Bu	—$(CH_2)_4$—		H	H
6f	Bu	Ph	H	H	H
6g	Bu^t	Me	Me	Me	Me
6h	Bu^t	—$(CH_2)_4$—		H	H

Reagents and conditions: *i*) Bu^{t}OK, hexane, 20—60 °C; *ii*) KOH, BTEAC (cat.), CH_2Cl_2, 20 °C.

Scheme 3



2a, 7a: R^1 = Ph; **2b, 7b:** R^1 = Bu^n; **2c, 7c:** R^1 = Bu^t; **2d, 7d:** R^1 = $(EtO)_2CH$; **2e, 7e:** R^1 = 4-ClC_6H_4.

	R^1	R^2	R^3	R^4	R^5
8a	Ph	Me	Me	Me	Me
8b	Ph	H	Me	Me	Me
8c	Ph	H	Me	Me	H
8d	Bu	Me	Me	Me	Me
8e	Bu	Ph	H	H	H
8f	Bu	H	Me	Me	H
8g	Bu^t	Me	Me	Me	Me
8h	$(EtO)_2CH$	Me	Me	Me	Me
8i	$(EtO)_2CH$	H	Me	Me	H
8j	4-ClC_6H_4	Me	Me	Me	Me
8k	4-ClC_6H_4	H	Me	Me	H

Reagents and conditions: *i*) Bu^{t}OK, hexane, 20—60 °C; *ii*) KOH, BTEAC (cat.), CH_2Cl_2, 20—40 °C; *iii*) Bu^{t}OK, benzene, 80 °C.

Table 1. Reactions of 3-substituted 1,1,3-tribromo-1-fluoropropanes **1a—c** and 3-substituted 3-bromo-1,1,1-trichloropropanes **2a—e** with bases in the presence of alkenes $R^2R^4C{=}CR^3R^5$

Source of the carbene	Base, solvent[a]	τ[b] /h	T /°C	Carbene	Alkene				Product (*trans*-to-*cis* ratio)	Yield (%)	B.p./°C (*p*/Torr) M.p./°C
					R^2	R^3	R^4	R^5			
1a	A	0.5	20	**5a**	Me	Me	Me	Me	**6a**	50[c]	—
	B	2	20	**5a**	—$(CH_2)_4$—		H	H	**6b** (4.5 : 1)	69[d]	140—150 (2)
1b	B	10	20	**5b**	Me	Me	Me	Me	**6c**	48[d]	130—140 (20)
	A	3	20	**5b**	H	Me	Me	H	**6d**	41[d]	110—120 (25)
	B	8	20	**5b**	—$(CH_2)_4$—		H	H	**6e** (3.7 : 1)	54[d]	150—170 (12)
	B	12	20	**5b**	Ph	H	H	H	**6f** (3.5 : 1)	49[d]	110—130 (2)
1c	A	8	65—70	**5c**	Me	Me	Me	Me	**6g**	43[d]	130—150 (90)
	A	8	65—70	**5c**	—$(CH_2)_4$—		H	H	**6h** (4.4 : 1)	6[d]	103—105 (14)
2a	A	1	20	**7a**	Me	Me	Me	Me	**8a**	48[c]	59—60
	A	1	20	**7a**	H	Me	Me	Me	**8b** (1.4 : 1)	45[d]	120—123 (2)
	A	1	20	**7a**	H	Me	Me	H	**8c**	43[c]	—
	B	2	20	**7a**	Me	Me	Me	Me	**8a**	70[e]	—
	B	8	20	**7a**	H	Me	Me	H	**8c**	34[d]	110—111 (2)
2b	A	3	65—70	**7b**	Me	Me	Me	Me	**8d**	52[d]	150—160 (10)[g]
	B	32	40—45	**7b**	Ph	H	H	H	**8e** (3.5 : 1)	49[d]	130—140 (1)[g]
	A	48	20	**7b**	H	Me	Me	H	**8f**	35[d]	130—140 (15)[g]
2c	C	32	80	**7c**	Me	Me	Me	Me	**8g**	48[e]	—
2d	A	8	20	**7d**	Me	Me	Me	Me	**8h**	37[c]	—
	A	8	20	**7d**	H	Me	Me	H	**8i**	35[c]	—
2e	A	1	20	**7e**	Me	Me	Me	Me	**8j**	46[c]	—
	A	1	20	**7e**	H	Me	Me	H	**8k**	42[c]	—

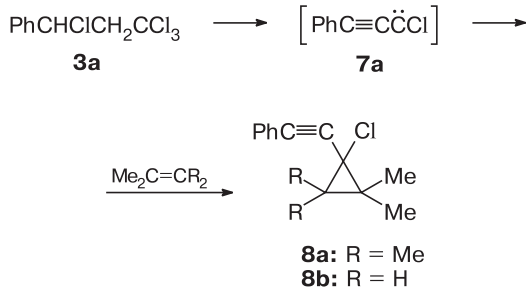
[a] A for Bu^{t}OK in hexane, B for KOH/BTEAC(cat.) in CH_2Cl_2, and C for Bu^{t}OK in benzene.
[b] Reaction time.
[c] The product was isolated by column chromatography.
[d] The product was isolated by vacuum distillation.
[e] Determined from the GLC data with the use of an internal standard.
[g] The bath temperature for vacuum microdistillation.

Analogously, when treated with bases, 3-alkyl- and 3-aryl-3-bromo-1,1,1-trichloropropanes **2a—e** selectively generate the corresponding (alk-1-ynyl)chlorocarbenes **7a—e**, which react with olefins to give alkynylchlorocyclopropanes **8a—k** in 35—70% yields (Scheme 3, see Table 1). Cyclopropanes **8b,e** were obtained as mixtures of *cis*- and *trans*-isomers.

(Phenylethynyl)chlorocarbene (**7a**) was generated by treating 1,1,1,3-tetrachloro-3-phenylpropane (**3a**) with an excess of Bu^{t}OK in hexane at 20 °C in the presence of 2-methylpropene and 2,3-dimethylbut-2-ene; the corresponding cyclopropanes **8a,c** were selectively obtained in 58 and 66% yields, respectively.

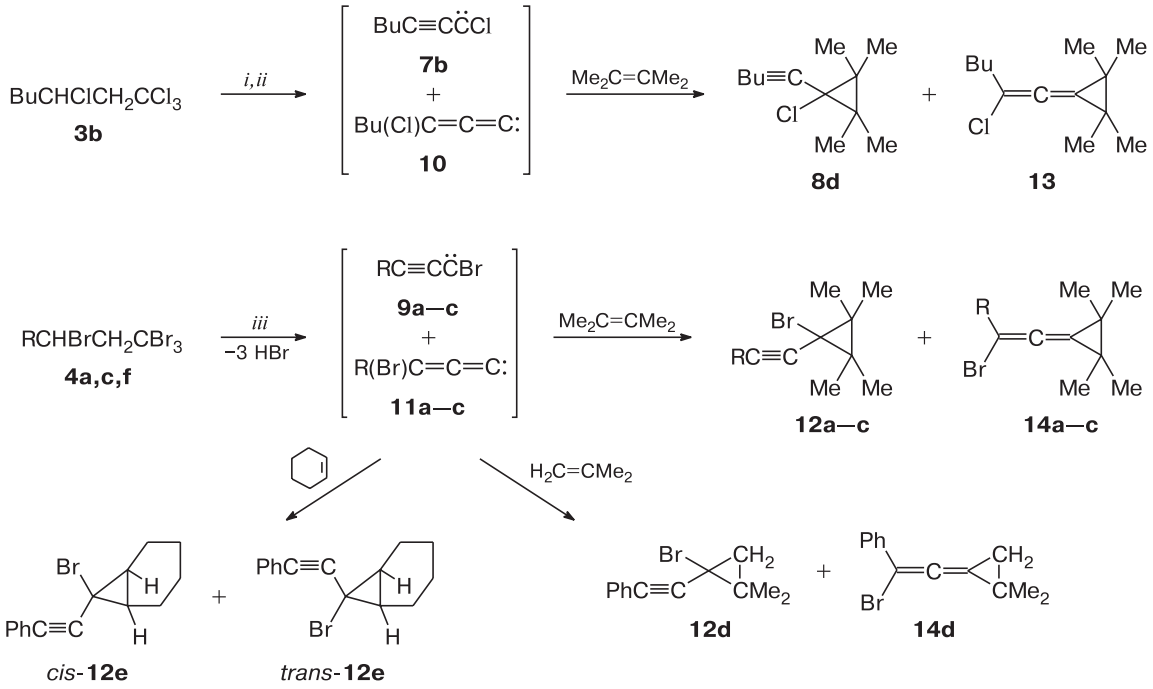
The reactions of 1,1,1,3-tetrachloroheptane (**3b**), 1,1,1,3-tetrabromo-3-phenylpropane (**4a**), 1,1,1,3-tetrabromo-4,4-dimethylpentane (**4c**), and 1,1,1,3-tetrabromobutane (**4f**) with Bu^{t}OK in hexane or benzene at 20 °C give, along with (alk-1-ynyl)halocarbenes **7b** (from **3b**) and **9a—c** (from **4a**, **4c**, and **4f**), halovinylidenecarbenes **10** and **11a—c**. Their generation becomes evi-

Scheme 4



Reagents and conditions: Bu^{t}OK, hexane, 20 °C.

Scheme 5



R = Ph (**4a, 9a, 11a, 12a, 14a**), Bu^t (**4c, 9b, 11b, 12b, 14b**), Me (**4f, 9c, 11c, 12c, 14c**).

Reagents, conditions, and yields: *i*) Bu^{t}OK, hexane, 20 °C; *ii*) KOH, BTEAC (cat.), CH_2Cl_2, 20—40 °C; the total yield of compounds **8d** and **13** was 48—55%; *iii*) Bu^{t}OK, benzene, 20 °C.

dent while analyzing the reaction products, namely, 1-(alk-1-ynyl)-1-halocyclopropanes **8d** and **12a—e** and halovinylidenecyclopropanes **13** and **14a—d**, which were formed in the presence of alkenes in total 34—55% yields (Scheme 5, Table 2). Individual 1-bromo-1-(phenylethynyl)cyclopropanes **12a,d** were isolated in 33—51% yields (**12a** by recrystallization from methanol and **12d** by distillation *in vacuo*). Unlike alkyne **12d**, isomeric vinylidenecyclopropane **14d** could not be distilled, probably, because of its instability. Note that the reaction mixture obtained from tetrabromide **4a** with Bu^{t}OK in hexane in the presence of cyclohexene contained no bromovinylidenecyclopropane like adduct **13** (GLC and ^{1}H NMR data), which is probably due to its low stability and decomposition during the reaction. Only 7-bromo-7-(phenylethynyl)norcarane **12e** was isolated by vacuum distillation and characterized as a mixture of *trans*- and *cis*-isomers.

Treatment of tetrachloride **3b** with KOH in CH_2Cl_2 in the presence of an excess of 2,3-dimethylbut-2-ene at 40—45 °C gave the same products **8d** and **13** as with Bu^{t}OK. The total yield of these cyclopropanes remained virtually unchanged, but the content of allene **13** in the reaction mixture increased from 20 to 50%.

Unlike the reactions of tetrabromide **4a** with Bu^{t}OK, which mostly yield, in the presence of olefins, 1-(alk-1-ynyl)-1-bromocyclopropanes **12a,d,e** (see Table 2), its reaction with KOH under conditions of phase-transfer catalysis in the presence of 2,3-dimethylbut-2-ene gave a 1.6 : 1 mixture of 1-[(bromo)phenylvinylidene]-2,2,3,3-tetramethylcyclopropane (**14a**) and 2,2,3,3-tetramethyl-1-(phenylvinylidene)cyclopropane (**15**) (NMR and MS data) in total 45% yield. This indicates that both bromo(phenyl)vinylidenecarbene (**11a**) and phenylvinylidenecarbene (**16**) are generated under these conditions (Scheme 6).

1,1,1,3-Tetrabromoheptane (**4b**) reacts with Bu^{t}OK in benzene at 20 °C in the presence of an excess of 2-methylpropene to give a mixture of three products in the 5 : 5 : 1 ratio in total 26% yield, which were identified as 1-bromo-1-(hex-1-ynyl)-2,2-dimethylcyclopropane (**12f**), 1-(butyl)bromovinylidene-2,2-dimethylcyclopropane (**14e**), and 1-bromo-1-(hex-1-enyl)-2,2-dimethylcyclopropane (**17**) (NMR and MS data). When diethyl ether or THF were used instead of benzene, a mixture of the same cyclopropanes was obtained in total 27—31% yield, but the ratio between them was different (see Table 2). The results obtained suggest that tetrabromide **4b** generates, under the above conditions, carbenes **9d**, **11d**, and **18** (see Scheme 6).

The structures of the cyclopropanes synthesized were proved by elemental analysis, GL-MS, and ^{1}H and

Table 2. Reactions of 3-substituted 1,1,1,3-tetrachloropropanes **3a,b** and 3-substituted 1,1,1,3-tetrabromopropanes **4a—f** with bases in the presence of alkenes $R^2R^4C{=}CR^3R^5$

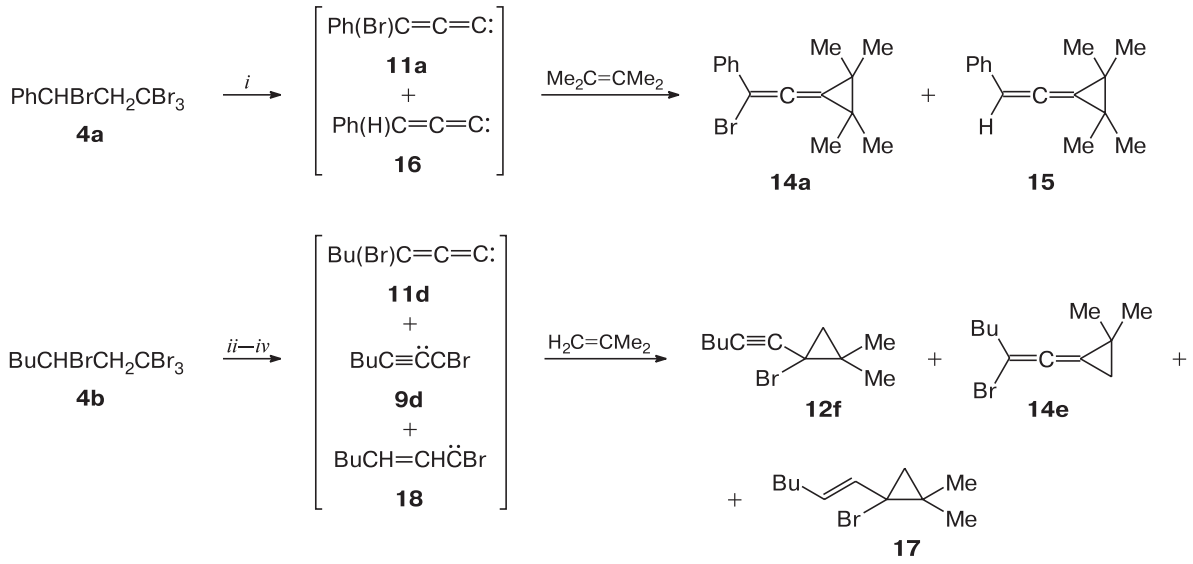
Starting compound	Base, solvent[a]	τ[b] /h	*T* /°C	Carbene	Alkene				Product (ratio)	Total yield (%)	B.p./°C (*p*/Torr) M.p./°C
					R^2	R^3	R^4	R^5			
3a	A	1	20	**7a**	Me	Me	Me	Me	**8a**	66[c]	58—60
	A	48	20	**7a**	H	Me	Me	H	**8c**	58[d]	110—120 (2)[e]
3b	A	48	20	**7b**, **10**	Me	Me	Me	Me	**8d** : **13** (4 : 1)	50[d]	150—160 (10)[e]
	B	80	40—45	**7b**, **10**	Me	Me	Me	Me	**8d** : **13** (1.1 : 1)	48[d]	150—160 (10)[e]
4a	C	1	20	**9a**, **11a**	Me	Me	Me	Me	**12a** : **14a** (8 : 1)	33[f] (pure **12a**)	—
	C	1	20	**9a**, **11a**	H	Me	Me	H	**12d** : **14d** (10 : 1)	51[d] (pure **12d**)	118—120 (1)
	C	1	20	**9a**	$-(CH_2)_4-$		H	H	**12e** (5 : 1)[g]	34[d]	155—158 (1)
	B	4	20	**11a**, **16**	Me	Me	Me	Me	**14a** : **15** (1.6 : 1)	45[c]	—
4b	C	2	20	**9d**, **11d**, **18**	H	Me	Me	H	**12f** : **14e** : **17** (5 : 5 : 1)	26[d]	120—130 (10)[e]
	D	2	20	**9d**, **11d**, **18**	H	Me	Me	H	**12f** : **14e** : **17** (5 : 4 : 1)	31[d]	120—130 (12)[e]
	E	2	20	**9d**, **11d**, **18**	H	Me	Me	H	**12f** : **14e** : **17** (15 : 1 : 6)	27[d]	120—130 (10)[e]
4c	C	2	80	**9b**, **11b**	Me	Me	Me	Me	**12b** : **14b** (1 : 1.4)	24[f]	—
4f	C	4	20	**9c**, **11c**	Me	Me	Me	Me	**12c** : **14c** (2.4 : 1)	23[d]	100—110 (10)[e]

[a] A for Bu^{t}OK in hexane, B for KOH/BTEAC(cat.) in CH_2Cl_2, C for Bu^{t}OK in benzene, D for Bu^{t}OK in Et_2O, and E for Bu^{t}OK in THF.
[b] Reaction time.
[c] The product was isolated by column chromatography.
[d] The product was isolated by distillation.
[e] The bath temperature for vacuum microdistillation.
[f] The product was isolated by recrystallization from methanol.
[g] The ratio of *trans*- to *cis*-isomers.

^{13}C NMR data (Tables 3—8). The mass spectra of bromo- and chlorocyclopropanes contain rather intense molecular ion peaks composed of characteristic isotopic doublets spaced at 2 amu (their intensity ratios are 1 : 1 and 1 : 3, respectively). The ^{13}C NMR spectra of alkynes **6**, **8**, and **12** show signals at δ 73—95 characteristic of the triple bond, while the ^{13}C NMR spectra of vinylidenecyclopropanes **13** and **14** contain signals at δ 95—110 and 180—186 characteristic of the terminal and central carbon atoms in the allenic fragment, respectively. The ^{1}H NMR spectra of the cyclopropanes obtained also show signals for the protons, which are characteristic of substituents at the cyclopropane fragment and the multiple bonds in these compounds.

The *trans*- and *cis*-isomers of (alk-1-ynyl)fluorocyclopropanes **6b,e,f,h** were distinguished by comparing vicinal H—F coupling constants in their ^{1}H and ^{19}F NMR spectra and considering that $J_{H,F}(trans) < J_{H,F}(cis)$ for cyclopropanes[9] (see Tables 3—5). The other NMR signals were assigned to the corresponding *cis*- and *trans*-isomers from their integral intensities. When the *trans*-to-*cis* ratio only slightly differed from unity, the content of one of the isomers in the mixture was increased by column chromatography or distillation. An analysis of the ^{1}H NMR spectra of these compounds shows that signals for the protons in the *cis*-substituents relative to the F atom are shifted downfield compared to signals for analogous substituents in the *trans*-position. This difference for the *cis*- and *trans*-isomers is due to a strong deshieldzing effect of the fluorine atom and correlate with our previous data[5] for (alk-1-ynyl)bromo- (**12**) and (alk-1-ynyl)chlorocyclopropanes (**8**). It was used to identify the *trans*- and *cis*-isomers of new halocyclopropanes **8b,e** and **12e**.

Scheme 6



Reagents, conditions, and yields: *i*) KOH, BTEAC (cat.), CH_2Cl_2, 20—40 °C; the total yield of **14a**+**15** was 45%; *ii*) Bu^{t}OK, benzene, 20 °C; *iii*) Bu^{t}OK, Et_2O, 20 °C; *iv*) Bu^{t}OK, THF, 20 °C; the total yield of **12f**+**14e**+**17** was 26—31%.

Table 3. ^{19}F NMR spectra ($CDCl_3$, 188 MHz) of (alk-1-ynyl)fluorocyclopropanes **6a—h**

Compound	δ (*J*/Hz)	Compound	δ (*J*/Hz)
6a	−192.0 s	*trans*-**6e**	−162.4 t (*J* = 19)
trans-**6b**	−164.6 t (*J* = 19)	*cis*-**6e**	−198.3 s
cis-**6b**	−199.7 s	**6g**	−175.4 s
6c	−191.0 s	*trans*-**6h**	−162.8 t (*J* = 19)
6d	−181.6 d (*J* = 18.3)	*cis*-**6h**	−197.9 s

To elucidate the pathways through which the discovered carbenes are generated, we tried to determine the structures of intermediate products in the reactions of 3-substituted 1,1,1,3-tetrahalopropanes **1—4** with bases. It was shown that treatment of both 3-bromo-1,1,1-trichloro-3-phenylpropane (**2a**) and 1,1,1,3-tetrachloro-3-phenylpropane (**3a**) with Bu^{t}OK (0.5 equiv.) at room temperature for 30 min affords a mixture containing, along with the starting tetrahalide, 1,1,3-trichloro-3-

Table 4. Elemental analysis data for (alk-1-ynyl)halocyclopropanes **6a—h**, **8a—k**, and **12a,d,e**

Compound	Found / Calculated (%)		Molecular formula
	C	H	
6a	83.35 / 83.29	8.09 / 7.92	$C_{15}H_{17}F$
6b	83.89 / 84.08	7.17 / 7.06	$C_{15}H_{15}F$
6c	79.36 / 79.54	10.97 / 10.78	$C_{13}H_{21}F$
6d	78.74 / 78.52	10.24 / 10.18	$C_{11}H_{17}F$
6e	80.60 / 80.37	10.06 / 9.86	$C_{13}H_{19}F$
6f	83.47 / 83.29	7.67 / 7.92	$C_{15}H_{17}F$
6g	79.28 / 79.54	10.54 / 10.78	$C_{13}H_{21}F$
6h	80.19 / 80.37	9.75 / 9.86	$C_{13}H_{19}F$
8a	77.24 / 77.41	7.46 / 7.36	$C_{15}H_{17}Cl$
8b	76.91 / 76.88	6.74 / 6.91	$C_{14}H_{15}Cl$
8c	67.13 / 67.43	5.91 / 6.04	$C_{13}H_{13}Cl$
8d	73.51 / 73.39	9.82 / 9.95	$C_{13}H_{21}Cl$
8e	77.23 / 77.41	7.52 / 7.36	$C_{15}H_{17}Cl$
8f	71.70 / 71.53	9.38 / 9.28	$C_{11}H_{17}Cl$
8g	73.22 / 73.39	10.17 / 9.95	$C_{13}H_{21}Cl$
8h	64.89 / 64.98	9.04 / 8.96	$C_{14}H_{23}O_2Cl$
8i	62.59 / 62.47	8.52 / 8.30	$C_{12}H_{19}O_2Cl$
8j	67.13 / 67.43	5.91 / 6.04	$C_{15}H_{16}Cl_2$
8k	65.21 / 65.29	5.24 / 5.06	$C_{13}H_{12}Cl_2$
12a	65.17 / 64.99	6.32 / 6.18	$C_{15}H_{17}Br$
12d	62.61 / 62.85	5.22 / 5.33	$C_{13}H_{13}Br$
12e	65.61 / 65.47	5.67 / 5.49	$C_{15}H_{15}Br$

Table 5. ^{1}H NMR spectra ($CDCl_3$, 200.13 MHz, δ, *J*/Hz) of (alk-1-ynyl)halocyclopropanes **6a—h**, **8a—k**, and **12a—f**

Compound	^{1}H NMR				
	R^1	R^2	R^3	R^4	R^5
6a	7.30—7.50 (m, 5 H)	1.22 (s, 12 H, 4 Me)			
trans,cis-**6b**	7.30—7.60 (m, 5 H)	1.20—2.10 (m, 12 H, 4 CH_2 and 2 CH)			
6c	0.89 (t, 3 H, CH_3, J = 7.3); 1.25—1.60 (m, 4 H, 2 CH_2); 2.28 (dt, 2 H, $CH_2C\equiv$, J = 6.5, $J_{H,F}$ = 6.5)	1.05 (d, 6 H, 2 Me, J = 2.2); 1.08 (d, 6 H, 2 Me, J = 1.5)			
6d	0.91 (t, 3 H, CH_3, J = 7.4); 1.25—1.60 (m, 4 H, 2 CH_2); 2.28 (dt, 2 H, $C\underline{H}_2C\equiv$, J = 6.7, $J_{H,F}$ = 6.7)	0.94 (dd, 1 H, CH_2, J = 6.5, $J_{H,F}$ = 18.3)	1.21 (d, 3 H, CH_3, $J_{H,F}$ = 2.0)	1.15 (d, 3 H, CH_3, $J_{H,F}$ = 2.3)	0.73 (dd, 1 H, CH_2, J = 6.5, $J_{H,F}$ = 7.8)
trans-**6e**	0.89 (t, 3 H, CH_3, J = 7.3); 1.05—1.60 (m, 4 H, 2 CH_2); 2.22 (dt, 2 H, $CH_2C\equiv$, J = 6.5, $J_{H,F}$ = 6.5)	1.03—1.95 (m, 10 H, 4 CH_2 and 2 CH)*			
cis-**6e**	0.91 (t, 3 H, CH_3, J = 7.3); 1.05—1.60 (m, 4 H, 2 CH_2); 2.33 (dt, 2 H, $CH_2C\equiv$, J = 6.7, $J_{H,F}$ = 6.7)	1.03—1.95 (m, 10 H, 4 CH_2 and 2 CH)*			
trans-**6f**	0.76 (t, 3 H, CH_3, J = 7.3); 1.00—1.80 (m, 4 H, 2 CH_2); 2.07 (dt, 2 H, $CH_2C\equiv$, J = 6.8, $J_{H,F}$ = 6.8)	7.10—7.35 (m, 5 H)	1.00—1.80 (m, 2 H, CH_2)*		2.68 (ddd, 1 H, CH, J = 8.6, J = 17.7, J = 6.2)
cis-**6f**	0.91 (t, 3 H, CH_3, J = 7.3); 1.00—1.80 (m, 4 H, 2 CH_2); 2.26 (dt, 2 H, $CH_2C\equiv$, J = 6.8, $J_{H,F}$ = 6.8)	7.10—7.35 (m, 5 H)	1.00—1.80 (m, 2 H, CH_2)*		2.41 (ddd, 1 H, CH, J = 2.5, J = 8.5, J = 11)
6g	1.24 (s, 9 H, Bu^t)	1.07 (d, 6 H, 2 Me, J = 2.2); 1.10 (d, 6 H, 2 Me, J = 1.5)			
trans-**6h**	1.27 (s, 9 H, Bu^t)	1.10—1.90 (m, 12 H, 4 CH_2 and 2 CH)			
cis-**6h**	1.21 (s, 9 H, Bu^t)	1.10—1.90 (m, 12 H, 4 CH_2 and 2 CH)			
8a	7.28—7.50 (m, 5 H)	1.28 (s, 6 H, 2 Me); 1.31 (s, 6 H, 2 Me)			
trans-**8b**	1.22, 1.25 (both s, 6 H, CMe_2); 1.25—1.45 (m, 4 H, CH, CH$\underline{Me}$)				
cis-**8b**	1.22, 1.26 (both s, 6 H, CMe_2); 1.25—1.45 (m, 4 H, CH, CH$\underline{Me}$)				
8c	7.20—7.40 (m, 5 H, Ph)	1.28 (d, 1 H, J = 6)	1.42 (s, 3 H, Me)	1.39 (s, 3 H, Me)	1.19 (d, 1 H, J = 6)
8d	0.91 (t, 3 H, CH_3, J = 7.0); 1.20—1.55 (m, 4 H, 2 CH_2); 2.27 (t, 2 H, $CH_2C\equiv$, J = 7.0)	1.18 (s, 12 H, 4 Me)			
trans-**8e**	0.81 (t, 3 H, CH_3, J = 7.1); 1.00—2.00 (m, 4 H, 2 CH_2); 2.19 (t, 2 H, $CH_2C\equiv$, J = 7.0)	7.20—7.50 (m, 5 H)	1.00—2.00 (m, 2 H)*		2.80 (dd, 1 H, J = 8.0, J = 10)
cis-**8e**	0.97 (t, 3 H, CH_3, J = 7.1); 1.00—2.00 (m, 4 H, 2 CH_2); 2.29 (t, 2 H, $CH_2C\equiv$, J = 7.0)	7.20—7.50 (m, 5 H)	1.00—2.00 (m, 2 H)*		2.75 (dd, 1 H, J = 8.5, J = 9.5)
8f	0.88 (t, 3 H, CH_3, J = 7.1); 1.2—1.6 (m, 4 H, 2 CH_2); 2.23 (t, 2 H, $CH_2C\equiv$, J = 7.0)	1.05 (d, 1 H, J = 5.9)	1.31 (s, 3 H, Me)	1.23 (s, 3 H, Me)	1.00 (d, 1 H, J = 5.9)
8g	1.15 (s, 9 H, 3 Me)	1.07 (s, 12 H, 4 Me)			
8h	1.22 (t, 6 H, 2 $CH_2C\underline{H}_3$, J = 7); 3.40—3.72 (m, 4 H, 2 $C\underline{H}_2O$); 5.32 (s, 1 H, CH)	1.17 (s, 6 H, 2 Me); 1.23 (s, 6 H, 2 Me)			
8i	1.18 (t, 6 H, 2 $CH_2C\underline{H}_3$, J = 7); 3.40—3.70 (m, 4 H, 2 $C\underline{H}_2O$); 5.24 (s, 1 H, CH)	1.12 (d, 1 H, J = 6.5)	1.27 (s, 3 H, Me)	1.22 (s, 3 H, Me)	1.02 (d, 1 H, J = 6.5)
8j	7.20—7.40 (m, 4 H, Ph)	1.25 (s, 6 H, 2 Me); 1.28 (s, 6 H, 2 Me)			
8k	7.20—7.40 (m, 4H)	1.26 (d, 1 H, J = 5.9)	1.40 (s, 3 H, Me)	1.37 (s, 3 H, Me)	1.18 (d, 1 H, J = 5.9)
12a	7.20—7.50 (m, 5 H, Ph)	1.34 (s, 6 H, 2 Me); 1.35 (s, 6 H, 2 Me)			
12b	1.22 (s, 9 H, 3 Me)	1.17 (s, 6 H, 2 Me); 1.21 (s, 6 H, 2 Me)			
12c	1.92 (s, 3 H, Me)	1.19 (s, 6 H, 2 Me); 1.20 (s, 6 H, 2 Me)			
12d	7.20—7.40 (m, 5 H, Ph)	1.38 (d, 1 H, J = 6)	1.48 (s, 3 H, Me)	1.42 (s, 3 H, Me)	1.27 (d, 1 H, J = 6)
trans,cis-**12e**	7.20—7.50 (m, 5 H, Ph)	1.10—2.20 (m, 10 H, 4 CH_2 and 2 CH)			
12f	0.92 (t, 3 H, CH_3, J = 7.1); 1.20—1.60 (m, 4 H, 2 CH_2); 2.24 (t, 2 H, $C\underline{H}_2C\equiv$, J = 6.9)	1.14 (d, 1 H, CH_2, J = 5.9)	1.26 (s, 3 H, CH_3); 1.35 (s, 3 H, CH_3)		1.09 (d, 1 H, CH_2, J = 5.9)

* Overlap with signals for the Bu group.

Table 6. ^{13}C NMR spectra ($CDCl_3$, 50.32 MHz, δ, *J*/Hz) and mass spectra of (alk-1-ynyl)halocyclopropanes **6a—h**, **8a—k**, and **12a—f**

Compound	^{13}C NMR				MS, *m/z*
	C≡C	*cyclo*-C_3	R^1	$R^2—R^5$	
6a	83.5 (d, ≡<u>C</u>CF, *J* = 32.5); 89.8 (d, Ph<u>C</u>≡, *J* = 10.2)	27.7 (d, 2 <u>C</u>Me_2, *J* = 11.5); 80.3 (d, CF, *J* = 215)	122.6 (d, C(1), *J* = 3); 128.2, 128.4, 131.6	15.5 (d, 2 Me, *J* = 8.6); 19.0 (2 Me)	216 $[M]^+$
trans-**6b**	82.6 (d, ≡<u>C</u>CF, *J* = 30); 93.4 (d, ≡<u>C</u>CH_2, *J* = 10)	22.4 (d, 2 CH, *J* = 13.5); 76.9 (d, CF, *J* = 208)	122.3 (d, C(1), Ph, *J* = 3); 128.4, 128.7, 131.6 (Ph)	19.0 (2 CH_2); 20.8 (d, 2 CH_2, *J* = 3)	214 $[M]^+$
cis-**6b**	87.4 (d, ≡<u>C</u>CF, *J* = 30); 85.9 (d, ≡<u>C</u>CH_2, *J* = 10)	21.3 (d, 2 CH, *J* = 13.5); 73.0 (d, CF, *J* = 208)	128.3, 128.5, 131.7 (Ph)	17.7 (d, 2 CH_2, *J* = 3); 21.4 (d, 2 CH_2, *J* = 2)	
6c	74.2 (d, ≡<u>C</u>CF, *J* = 33); 90.8 (d, ≡<u>C</u>CH_2, *J* = 10)	26.6 (d, 2 <u>C</u>Me_2, *J* = 12); 80.6 (d, CF, *J* = 214)	13.6 (CH_3); 18.7 (d, CH_2, *J* = 2.4); 22.0, 30.8 (2 CH_2)	15.6 (d, 2 Me, *J* = 10); 19.1 (2 Me)	196 $[M]^+$
6d	75.7 (d, <u>C</u>CF, *J* = 31.2); 89.3 (d, <u>C</u>≡CCF, *J* = 9.4)	23.3 (d, <u>C</u>Me_2, *J* = 11.7); 26.7 (d, CH_2, *J* = 12.2); 76.2 (d, <u>C</u>F, *J* = 207.6)	13.6 (CH_3); 18.6, 21.9, 30.6 (3 CH_2)	19.0 (d, (<u>C</u>H_3)$_2$C, *J* = 9.5); 22.6 ((<u>C</u>H_3)$_2$C)	168 $[M]^+$
trans-**6e**	73.4 (d, ≡<u>C</u>CF, *J* = 30); 94.7 (d, ≡<u>C</u>CH_2, *J* = 10)	21.3 (d, 2 CH, *J* = 14); 77.1 (d, CF, *J* = 203)	13.5 (CH_3); 18.8 (d, CH_2, *J* = 2); 21.9, 30.6 (2 CH_2)	18.9 (2 CH_2); 20.6 (d, 2 CH_2, *J* = 2)	194 $[M]^+$
cis-**6e**	78.7 (d, ≡<u>C</u>CF, *J* = 30); 86.6 (d, ≡<u>C</u>CH_2, *J* = 10)	20.5 (d, 2 CH, *J* = 14)	13.5 (CH_3); 18.5 (d, CH_2, *J* = 2)*	17.6 (d, 2 CH_2, *J* = 3); 21.4 (d, 2 CH_2, *J* = 2)	
trans-**6f**	74.2 (d, ≡<u>C</u>CF, *J* = 30); 91.4 (d, ≡<u>C</u>CH_2, *J* = 10)	20.2 (d, CH_2, *J* = 14); 30.0 (d, CH, *J* = 11); 73.7 (d, CF, *J* = 213)	13.4 (CH_3); 18.4 (d, C<u>H</u>$_2$, *J* = 2.5); 21.6, 30.2 (2 CH_2)	126.6, 128.0, 128.1 (Ph); 136.2 (C(1), Ph)	216 $[M]^+$
cis-**6f**	77.4 (d, ≡<u>C</u>CF, *J* = 32); 87.8 (d, ≡<u>C</u>CH_2, *J* = 9)	30.8 (d, CH, *J* = 11); 19.6 (d, CH_2, *J* = 13.5); 70.6 (d, CF, *J* = 213)	13.6 (CH_3); 18.6 (d, C<u>H</u>$_2$, *J* = 2.5); 22.0, 30.5 (2 CH_2)	126.8, 128.2, 128.5 (Ph); 134.7 (C(1), Ph)	
6g	73.4 (d, ≡<u>C</u>CF, *J* = 33); 99.1 (d, ≡<u>C</u>—Bu^t, *J* = 10)	26.5 (d, 2 <u>C</u>Me_2, *J* = 12); 80.2 (d, CF, *J* = 213)	27.8 (d, <u>C</u>(CH_3)$_3$, *J* = 2); 31.0 (3 CH_3)	15.5 (d, 2 Me, *J* = 10); 19.0 (2 Me)	196 $[M]^+$
trans-**6h**	72.0 (d, ≡<u>C</u>CF, *J* = 31); 102.7 (d, ≡<u>C</u>—Bu^t, *J* = 10)	21.4 (d, 2 CH, *J* = 13); 76.9 (d, CF, *J* = 204)	27.9 (d, <u>C</u>(CH_3)$_3$, *J* = 2); 30.9 (3 CH_3)	18.9 (2 CH_2); 20.7 (d, 2 CH_2, *J* = 3)	194 $[M]^+$
cis-**6h**	74.1 (d, ≡<u>C</u>CF, *J* = 30); 98.3 (d, ≡<u>C</u>—Bu^t, *J* = 10)	20.7 (d, 2 CH, *J* = 13); 79.5 (d, CF, *J* = 203)	27.5 (d, <u>C</u>(CH_3)$_3$, *J* = 2); 30.9 (3 CH_3)	17.7 (d, 2 CH_2, *J* = 3); 21.4 (d, 2 CH_2, *J* = 2)	
8a	85.2, 88.0	30.2 (2 <u>C</u>Me_2); 49.7 (CCl)	123.0 (C(1)); 128.2, 128.3	18.8 (2 Me); 19.7 (2 Me)	232, 234 $[M]^+$
trans-**8b**	82.8, 86.0	10.0 (CHMe); 28.9 (<u>C</u>Me_2); 45.3 (CCl)	122.8 (C(1)) 128.3, 128.4,	17.3, 24.0, 32.1 (3 Me)	218, 220 $[M]^+$
cis-**8b**	86.6, 89.9	9.5 (CHMe); 27.7 (<u>C</u>Me_2); 45.2 (CCl)	122.9 (C(1)) 131.7, 131.8	16.3, 25.0, 34.4 (3 Me)	
8d	80.7, 83.7	29.8 (2 <u>C</u>Me_2); 48.4 (CCl)	18.6 (2 Me); 60.7 (2 CH_2); 91.4 (CH)	15.1 (2 Me); 19.6 (2 Me)	212, 214 $[M]^+$
trans-**8e**	77.6, 87.1	25.0 (CH_2); 35.2 (CHPh); 33.5 (CCl)	13.6 (CH_3); 18.5, 21.6, 30.3 (3 CH_2)	136.1 (C(1))	128.1, 128.7, 129.3 232, 234 $[M]^+$

(*to be continued*)

Table 6 (*continued*)

Compound	^{13}C NMR				MS, *m/z*
	C≡C	*cyclo*-C_3	R^1	R^2—R^5	
cis-**8e**	82.7, 84.4	23.8 (CH_2); 36.4 (CHPh); 34.1 (CCl)	13.9 (CH_3); 18.6 (CH_2); 22.0, 30.6 (2 CH_2)	133.7 (C(1)) 126.7, 128.0, 128.3	
8f	79.6, 84.4	25.4 ($\underline{C}Me_2$); 31.8 (CH_2); 41.5 (CCl)	13.5 (CH_3); 18.5, 21.9, 30.7 (2 CH_2)	22.1, 23.1 (2 Me)	184, 186 $[M]^+$
8g	77.1, 94.2	28.8 (2 CMe_2); 49.9 (CCl)	27.7 (CMe_3); 31.1 (3 Me)	18.8 (2 Me); 19.6 (2 Me)	212, 214 $[M]^+$
8h	80.7, 83.7	29.8 (2 $\underline{C}Me_2$); 48.4 (CCl)	18.6 (2 Me); 60.7 (2 CH_2); 91.4 (CH)	15.1 (2 Me); 19.6 (2 Me)	258, 260 $[M]^+$, 213, 215 $[M - EtOH]^+$
8i	78.8, 84.8	25.9 ($\underline{C}Me_2$); 31.8 (CH_2); 39.8 (CCl)	14.8 (2 Me); 60.4, 60.5 (2 CH_2); 91.0 (CH)	21.7 (2 Me); 22.8 (2 Me)	230, 232 $[M]^+$, 185, 187 $[M - EtOH]^+$
8j	84.1, 89.1	30.4 (2 $\underline{C}Me_2$); 49.5 (CCl)	121.5 (C(1)); 128.6, 133.0 (4 CH); 134.2 (CCl)	18.8 (2 Me); 19.7 (2 Me)	266, 268 $[M]^+$
8k	82.3, 90.0	26.7 ($\underline{C}Me_2$); 32.6 (CH_2); 40.8 (CCl)	121.2 (C(1)); 128.6, 133.0 (4 CH); 134.4 (CCl)	22.2, 23.3 (2 Me)	238, 240 $[M]^+$
12a	85.6, 89.3	30.1 (2 $\underline{C}Me_2$); 43.2 (CBr)	123.1 (C(1)); 128.2, 128.3, 131.8 (Ph)	19.5 (2 Me); 21.4 (2 Me)	276, 278 $[M]^+$
12b	78.5, 94.7	28.8 (2 $\underline{C}Me_2$); 44.1 (CBr)	27.8 ($\underline{C}Me_3$); 31.1 (3 Me)	18.7 (2 CH_2); 21.4 (2 CH_2)	256, 258 $[M]^+$
12c	78.8, 82.1	29.0 (2 $\underline{C}Me_2$); 44.7 (CBr)	4.0 (Me)	19.4 (2 Me), 21.4 (2 Me)	214, 216 $[M]^+$
12d	83.6, 90.3	26.1 ($\underline{C}Me_2$); 30.2 (CBr); 33.2 (CH_2)	122.8 (C(1)); 128.3, 128.4, 131.8	22.8 (Me); 24.9 (Me)	248, 250 $[M]^+$
trans-**12e**	87.4, 89.3	28.0 (2 CH); 34.7 (CBr)	122.8 (C(1)) 128.2, 128.3,	20.1 (2 CH_2); 20.7 (2 CH_2)	274, 276 $[M]^+$
cis-**12e**	80.5, 93.4	25.3 (2 CH); 29.9 (CBr)	122.9 (C(1)) 128.4, 128.5	20.6 (2 CH_2); 24.6 (2 CH_2)	
12f	81.1, 84.9	22.7 ($\underline{C}Me_2$); 32.7 (CH_2); 31.2 (CBr)	13.6 (CH_3); 18.7, 22.0, 30.8 (3 CH_2)	22.8 (Me); 24.9 (Me)	228, 230 $[M]^+$

* The other signals overlap signals for *trans*-**6e**.

Table 7. ^{1}H NMR spectra ($CDCl_3$, 200.13 MHz, δ, *J*/Hz) of (organyl)halovinylidenecyclopropanes **13** and **14a—e**

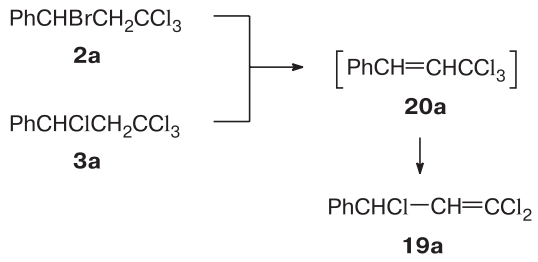
Compound	^{1}H NMR		
	R^1	R^2, R^5	R^3, R^4
13	0.89 (t, 3 H, CH_3 in Bu, *J* = 7); 1.20—1.55 (m, 4 H, 2 CH_2); 2.36 (t, 2 H, —$C\underline{H}_2$CCl=, *J* = 7)	1.26 (s, 6 H, 2 Me); 1.29 (s, 6 H, 2 Me)	
14a	7.15—7.60 (m, 5 H, Ph)	1.43 (s, 6 H, 2 Me); 1.47 (s, 6 H, 2 Me)	
14b	1.16 (s, 9 H, 3 Me)	1.25 (s, 6 H, 2 Me); 1.28 (s, 6 H, 2 Me)	
14c	2.31 (s, 3 H, Me)	1.27 (s, 12 H, 4 Me)	
14d	7.15—7.60 (m, 5 H, Ph)	1.78 (s, 2 H, CH_2)	1.42 (3 H, Me); 1.45 (s, 3 H, Me)
14e	0.91 (t, 3 H, CH_3 in Bu, *J* = 7); 1.20—1.55 (m, 4 H, 2 CH_2); 2.47 (t, 2 H, —$C\underline{H}_2$CBr=, *J* = 7)	1.52 (d, 1 H, CH_2, *J* = 7.3); 1.49 (d, 1 H, CH_2, *J* = 7.3)	1.29 (s, 3 H, Me); 1.27 (s, 3 H, Me)

Table 8. ^{13}C NMR spectra ($CDCl_3$, 50.32 MHz, δ) and mass spectra (*m/z*) of (organyl)halovinylidenecyclopropanes **13** and **14a—e**

Compound	^{13}C NMR					MS
	C=C=C	=C=	*cyclo*-C_3	R^1	R^2—R^5	
13	107.3, 107.6	180.8	13.9 ($\underline{C}H_3CH_2$—); 21.0, 21.1, 21.8, 29.3, 29.5, 36.9 (2 $\underline{C}Me_2$, 2 C($\underline{C}H_3$), $\underline{C}H_2$—$\underline{C}H_2$—$\underline{C}H_2$ in Bu)			212, 214 $[M]^+$
14a	94.7, 106.1	186.0	32.1 (2 $\underline{C}(Me)_2$)	125.9, 128.2, 128.8 (Ph); 135.9 (C(1))	21.1 (2 Me); 21.6 (2 Me)	214, 216 $[M]^+$
14b	105.7, 108.1	180.3	29.0 ($\underline{C}Me_2$)	29.1 (3 Me); 37.6 ($\underline{C}Me_3$)	20.9 (2 Me); 21.0 (2 Me)	256, 258 $[M]^+$
14c	90.1, 105.8	182.0	29.3 ($\underline{C}Me_2$)	26.4 (Me)	20.9 (2 Me); 21.3 (2 Me)	214, 216 $[M]^+$
14d			—			248, 250 $[M]^+$
14e	96.2, 98.0	183.4	13.9 ($\underline{C}H_3CH_2$—); 21.7, 22.5, 23.9, 24.7, 30.3, 31.2 ($\underline{C}Me_2$, 2 C($\underline{C}H_3$), CH_3—$\underline{C}H_2$—$\underline{C}H_2$— in Bu, CH_2 in *cyclo*-C_3H_2); 38.5 ($\underline{C}H_2CBr$=)			228, 230 $[M]^+$

phenylprop-1-ene (**19a**) (Scheme 7). The latter was obtained in the individual state in 28% yield by refluxing tetrahalide **2a** with triethylamine for 8 h. Note that the formation of trichloride **19a** from **2a** (and possibly from **3a**) is most probably due to the allylic rearrangement[10] of 1,1,1-trichloro-3-phenylprop-2-ene (**20a**) initially formed through elimination of HBr.

Scheme 7



Reagents and conditions: Bu^tOK (0.5 equiv.), hexane, 20 °C.

The treatment of trichloride **19a** with an excess of Bu^tOK in the presence of excess 2,3-dimethylbut-2-ene gave the corresponding cyclopropane **8a** in 46% yield. During the course of the reaction, 3,3-dichloro-1-phenylprop-2-yne (**21a**) and 1,1-dichloro-3-phenylpropa-1,2-diene (**22a**) were detected in the reaction mixture. These compounds proved to be identical with authentic samples obtained in an independent way (GLC data).

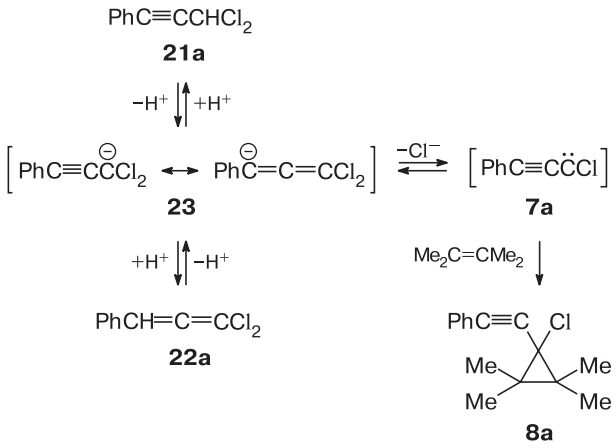
We found[5] that treatment of 3,3-dichloro-1-phenylprop-2-yne (**21a**) with a deficient amount of Bu^tOK in hexane at ~20 °C yields a mixture of dichloride **21a** and allene **22a** in the ratios from 5 : 1 to 1 : 1, depending on the amount of the base and the reaction time. However, the conversion of the starting alkyne **21a** into allene **22a** was incomplete since the reaction mixture, for $Bu^tOK > 0.5$ equiv., undergoes significant resinification, and no increase in the content of **22a** resulted. The presence of allene **22a** in the reaction mixture was proved by ^1H NMR spectroscopy. The spectrum of the reaction mixture shows a singlet at δ 6.57 corresponding to the allene proton and a multiplet for the phenyl protons at δ 7.30—7.50. Its ^{13}C NMR spectrum exhibits a signal at δ 200.9 for the sp-hybridized carbon atom in the allene fragment, a signal at δ 127 for the CCl_2 group, and a signal at δ 106 for the =CH group, which, without proton decoupling, appears as a doublet with a coupling constant of 165 Hz. Allene **22a** is rather labile and decomposes almost completely even in deuterochloroform at ~20 °C over a few days (GLC and ^1H NMR data).

The resulting mixture of compounds **21a** and **22a** react with Bu^tOK and an excess of 2,3-dimethylbut-2-ene to give 1-chloro-2,2,3,3-tetramethyl-1-(phenylethynyl)cyclopropane (**8a**) in 55% yield; the reaction mixture contained no starting dichlorides. When the initial ratio between dichlorides **21a** and **22a** was changed from 3 : 1 to 1 : 1, the yield of cycloadduct **8a** remained unchanged, being the same as for dichloride **21a** used alone (55%).

Hence, it can be concluded that cyclopropane **8a** is formed both from dichloroalkyne **21a** and from dichloroallene **22a**. Apparently, when treated with Bu^tOK, both lose the proton to give anion **23**, which is transformed, through the elimination of the chloride anion, into chloro(phenylethynyl)carbene **7a**; the latter is trapped by 2,3-dimethylbut-2-ene (Scheme 8).

Moreover, using the Moss method,[11] we demonstrated that the carbenes generated from both dichloride **21a** and trichloro bromide **2a** are of the same nature. For this purpose, we used the method of competitive reactions to determine the relative reactivities (k_i/k_0) of carbene **7a** generated under the action of Bu^tOK from the above halides with respect to a set of methylolefins with 2-methylpropene as a reference ($k_i/k_0 = 1$). The results obtained are given in Table 9. While comparing the relative reactivities of chloro(phenylethynyl)carbene generated from dichloride **21** and that from tetrahalide **2a**, one can see that they are equal to within the measure-

Scheme 8



Reagents and conditions: Bu^{t}OK, hexane, 20 °C, 30—90 min.

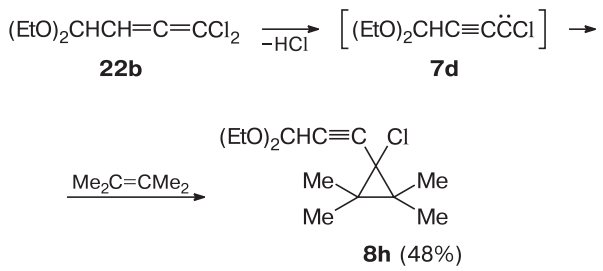
Table 9. Relative reactivity of chloro(phenylethynyl)carbene **7a** generated from dichloride **21a** (A) and from trichloro bromide **2a** (B)

Alkene	A	B
2-Methylpropene	1.0	1.0
2-Methylbut-2-ene	2.1±0.13	1.9±0.15
2,3-Dimethylbut-2-ene	4.9±0.21	5.0±0.17
cis-But-2-ene	0.34±0.02	0.36±0.03

ment error, which confirms the identity of the resulting intermediates.

Direct evidence that 1,1-dihalo-3-organyl-1,2-dienes **22** are precursors of (alk-1-ynyl)halocarbenes was provided[5] by the generation of chloro(3,3-diethoxyprop-1-ynyl)carbene (**7d**) in the reaction of 1,1-dichloro-4,4-diethoxybuta-1,2-diene (**22b**) with Bu^{t}OK. Its trapping by 2,3-dimethylbut-2-ene afforded the corresponding cyclopropane **8h** in 48% yield (Scheme 9).

Scheme 9



Reagents and conditions: Bu^{t}OK, hexane, 20 °C.

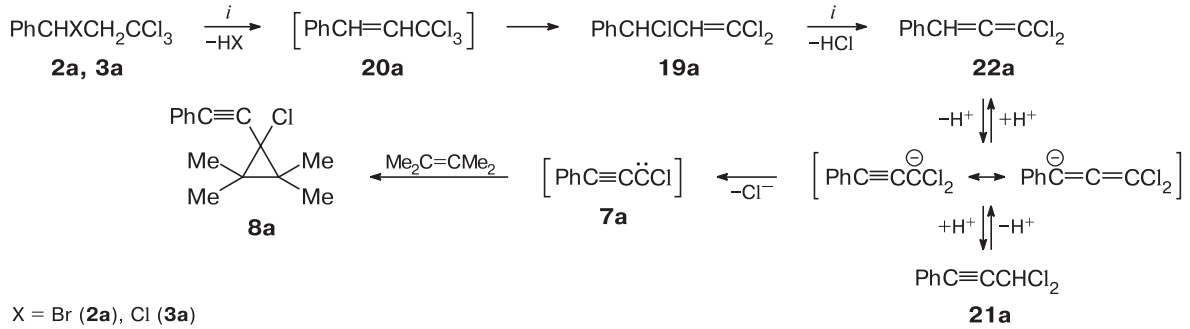
Thus, the results obtained indicate that the reactions of halides **2a** and **3a** with Bu^{t}OK in the presence of alkenes follow Scheme 10, proceeding through an equilibrium mixture of dichloroallene **22a** and dichloroalkyne **21a**.

When 1,1,3-tribromo-1-fluoroheptane (**1b**) was treated with an equimolar amount of Bu^{t}OK in the absence of olefins, the reaction mixture contained, along with the starting halide, *trans*-1,1-dibromo-1-fluorohept-2-ene (**24**) and the *E*- and *Z*-isomers of 1,3-dibromo-1-fluorohept-1-ene (**25**) in the ratio 1 : 1.8 : 0.9 : 0.75, respectively. Addition of Bu^{t}OK to the resulting mixture gave 1-bromo-1-fluorohepta-1,2-diene (**26**) and 1-bromo-1-fluorohept-2-yne (**27**).

The structures of all intermediate halides were proved by ^{1}H and ^{19}F NMR spectroscopy and GL-MS analysis. The configuration of the double bond in compounds **24** and **25** was determined from the values of vicinal H—H (for **24**) and H—F (for **25**) coupling constants.

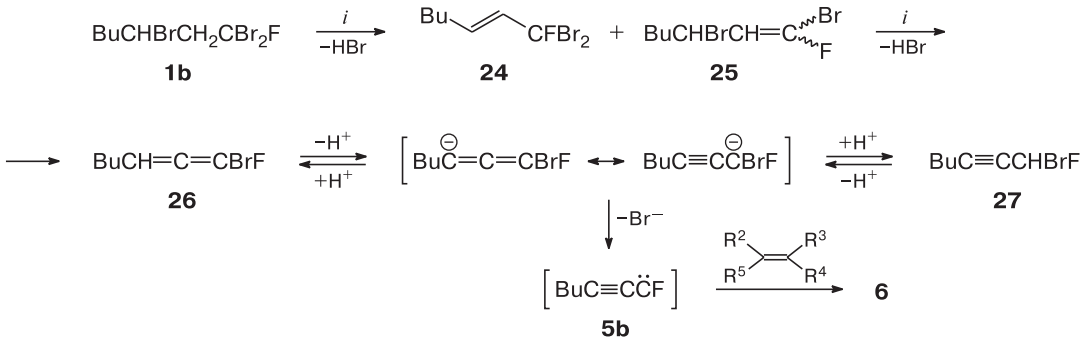
It should be noted that a set of signals corresponding to the CH=CH fragment in compound **24** has a very complex structure since the both protons have close chemical shifts and there are a lot of H—H and H—F spin-spin couplings. To calculate precise chemical shifts and coupling constants, we calculated the

Scheme 10



Reagents and conditions: *i*) Bu^{t}OK, hexane, 20 °C.

Scheme 11



Reagents and conditions: *i*) Bu^{t}OK, hexane, 20—60 °C.

spectrum* and corrected the initial parameters to minimize a discrepancy between the calculated and experimental data. Based on the coupling constant between the olefinic protons (15.5 Hz), obtained by this iterative procedure, we unambiguously assigned the *trans*-structure to alkene **24**.

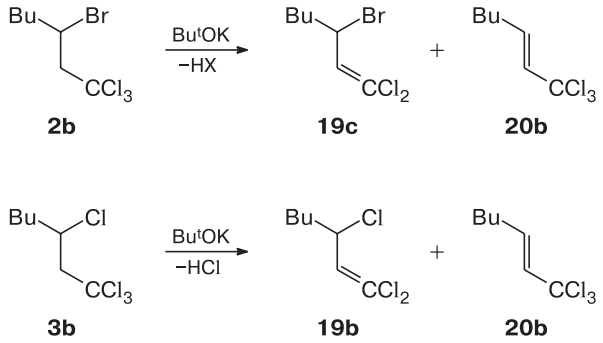
For the major isomer of compound **25** in the reaction mixture, $J_{H,F}$ = 28 Hz, while for the minor isomer this value was 10 Hz. Insofar as $J_{cis} < J_{trans}$ for fluoroalkenes,[9] *E*-halide **25** proves to be dominant.

The ^{1}H NMR spectrum of allene **26** contains a characteristic signal for the allene proton at δ 5.97 (td, $J_{H,F}$ = 1.6 Hz); this coupling constant is consistent with the ^{19}F NMR data for this compound. As expected, the ^{1}H NMR spectrum of alkyne **27** shows a doublet of triplets for the CHBrF group at δ 7 ($J_{H,F}$ = 52 Hz, $J_{H,H}$ = 1.7 Hz) because of the spin-spin coupling of the proton with the F atom and with the CH_2 group through the triple bond.

The data obtained suggest that carbene **5b** is generated from tetrahalides **1b** according to Scheme 11. Apparently, the generation of other (alk-1-ynyl)fluorocarbenes **5** occurs analogously.

Unlike halides **2a** and **3a**, compounds **2b** and **3b** react with a deficient amount of Bu^{t}OK (Scheme 12) to give a mixture of isomeric alkenes containing the terminal (**19b,c**) and internal double bond (**20b**) in the ratios 1 : 1.2 and 1 : 3.5, respectively. Their structures were determined from the ^{1}H NMR spectra of the reaction mixture. Trihalides **19b,c** give doublets for olefinic protons at δ 5.95—6.10 and doublets of triplets for the CHCl and CHBr groups at δ 4.6—4.8. The ^{1}H NMR spectrum of trichloroalkene **20b** with the internal double bond shows a set of signals (d and dt) characteristic of the olefinic protons in the CH=CH—CH_2 fragment. The vicinal coupling constant (15.5 Hz) indicates the *trans*-configuration of the double bond in **20b**.

Scheme 12



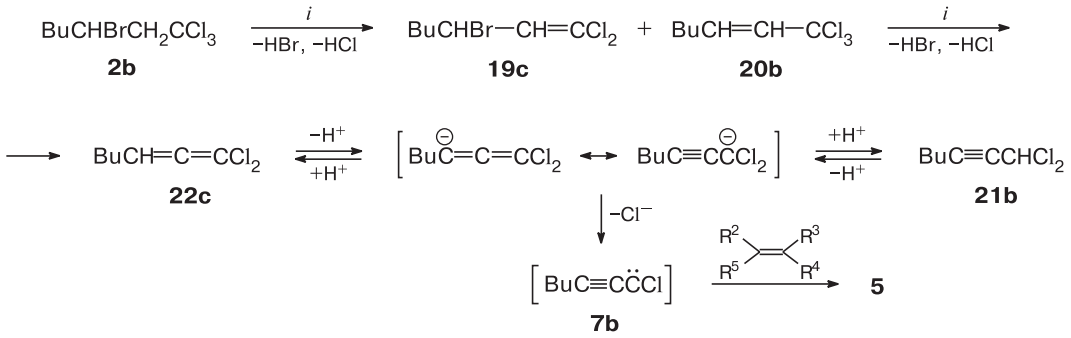
Reagents and conditions: Bu^{t}OK, hexane, 20 °C.

Further reactions of the mixtures obtained with Bu^{t}OK resulted in carbene generation, and intermediate products of their monodehydrohalogenation were not isolated or characterized. Insofar as tetrahalide **2b** selectively generates only chloro(hex-1-ynyl)carbene **7b** (see Scheme 3, Table 1), both chlorides **19c** and **20b** seem to be its precursors. Thus, carbene **7b** is probably generated by analogy with (alkyn-1-yl)fluorocarbene (see Scheme 11) through the formation of an equilibrium mixture of 1,1-dichlorohept-2-yne (**21b**) and 1,1-dichlorohepta-1,2-diene (**22c**) (Scheme 13).

The generation of butyl(chloro)vinylidenecarbene (**10**) in the reaction of tetrachloride **3b** with Bu^{t}OK (see Scheme 5) most probably proceeds *via* dehydrochlorination of trichloride **19b** into 1,3-dichlorohept-1-yne (**28**), which undergoes γ-elimination of HCl, by analogy

* To determine the chemical shifts and the coupling constants for a multiplet corresponding to this fragment, the spectral parameters were calculated and corrected to minimize a discrepancy between the calculated and experimental data (the NUTS program, version 4.35). The resulting chemical shifts and coupling constants are δ($C(H)_2C\underline{H}_b$=) 5.95 ($J_{a,b}$ = 6.9 Hz, $J_{b,c}$ = 15.5 Hz, $J_{H,F}$ = −1 Hz); δ($CBr_2FC\underline{H}_c$=) 6.04 ($J_{a,c}$ = −1.5 Hz, $J_{b,c}$ = 15.5 Hz, $J_{H,F}$ = 16.4 Hz).

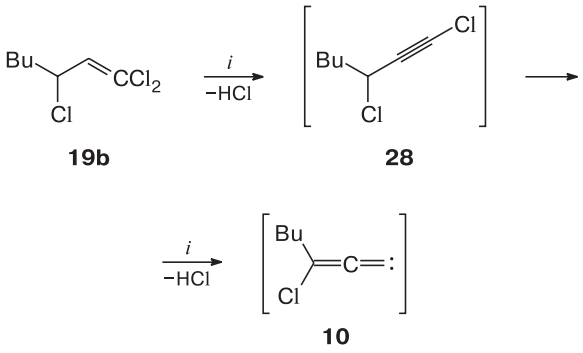
Scheme 13



Reagents and conditions: *i*) Bu^{t}OK, hexane, 20—60 °C.

with other vinylidenecarbenes,[12] to give carbene **10** (Scheme 14).

Scheme 14



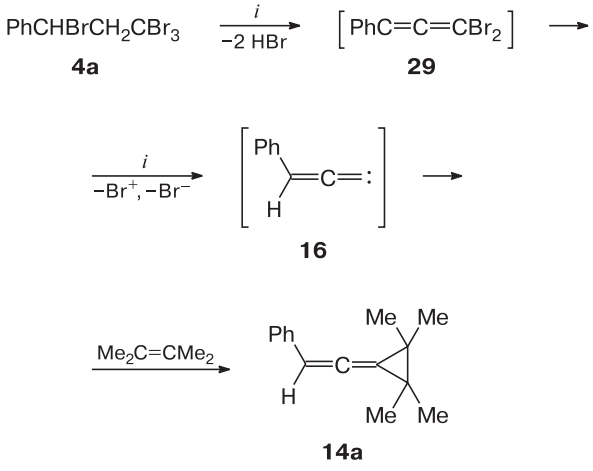
Reagents and conditions: *i*) Bu^{t}OK, hexane, 20—60 °C.

Apparently, the reactions of tetrabromides **4a,c,f** with Bu^{t}OK proceed analogously, generating (alk-1-ynyl)bromocarbenes **9a—c** and bromovinylidenecarbenes **11a—c** (see Scheme 5). These carbenes are trapped by alkenes to give isomeric bromine-containing cyclopropanes **12** and **14**. Phenylvinylidenecarbene (**16**) is most likely generated from tetrabromide **4a** under conditions of phase-transfer catalysis (see Scheme 6) *via* elimination of two HBr molecules followed by KOH-initiated debromination of intermediate 1,1-dibromo-3-phenylpropa-1,2-diene (**29**) (Scheme 15). The possibility of such processes has been reported earlier.[13]

The formation of small amounts of a third product, namely, cyclopropane **17**, from tetrabromide **4b** suggests the generation of (*trans*-hex-1-enyl)bromocarbene (**18**) (see Scheme 6), which can be due to partial debromination of intermediate *trans*-1,1,1-tribromohept-2-ene (**30**) under the action of Bu^{t}OK.

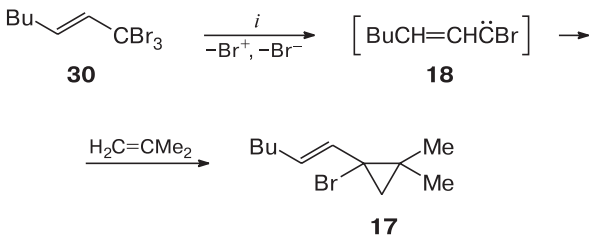
Hence, we found that the reactions of 3-alkyl- and 3-phenyl-1,1,3-tribromo-1-fluoropropanes with KOH (phase-transfer catalysis) or Bu^{t}OK exclusively give (alk-1-ynyl)fluorocarbenes, which belong to a new class of carbene intermediates. Under analogous conditions, 3-aryl- and 3-alkyl-3-bromo-1,1,1-trichloropropanes generate (alk-1-ynyl)chlorocarbenes. However, the behavior of 3-substituted 1,1,1,3-tetrachloro- or 1,1,1,3-tetrabromopropanes in the presence of bases is

Scheme 15



Reagents and conditions: *i*) KOH, CH_2Cl_2, BTEAC, 20 °C.

Scheme 16



Reagents and conditions: *i*) Bu^{t}OK, hexane, 20—60 °C.

largely determined by the nature of both the 3-substituent and the halogen atoms and also depend on the reaction conditions. When they are used as carbene sources, halovinylidenecarbenes are generated along with (alkyn-1-yl)halocarbenes; in some cases, vinylidene- and bromo(vinyl)carbenes are also formed. The mechanisms for these complex multistep reactions were proposed.

Experimental

GLC analysis of the starting reagents and the products was carried out on a Hewlett-Packard 5890 Series II instrument with a capillary column 30 m×0.153 mm and a Hewlett-Packard 3396A automated integrator. When the yields of the known compounds were determined by GLC, the products were identified by comparing their retention times with those of authentic samples. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AC-200p and Bruker AM-300 spectrometers in $CDCl_3$ with tetramethylsilane as the internal standard. IR spectra were recorded on a Perkin—Elmer 580 spectrophotometer in CCl_4. Mass spectra were recorded on a Finningan MAT INCOS-50 GL-MS spectrometer.

The starting 3-substituted 1,1,1,3-tetrahalopropanes **2a—e**, **3b**, and **4a—c,f** were prepared as described in Ref. 7; 1,1,1,3-tetrachloro-3-phenylpropane (**3a**) was obtained according to the known procedure.[8]

1,1-Dichloro-3-phenylprop-2-yne (**19a**) and 1,1-dichloro-4,4-diethoxybuta-1,2-diene (**22b**) were prepared as described earlier.[5] Tetrabromomethane,[14] tribromofluoromethane,[15] and bromotrichloromethane[16] were synthesized according to the known procedures.

Synthesis of 3-substituted 1,1,3-tribromo-1-fluoropropanes (1a—c). Azodiisobutyronitrile (50 mg, 0.3 mmol) was added to a mixture of a starting alkene (styrene, hex-1-ene, or 3,3-dimethylbut-1-ene) (10 mmol) and tribromofluoromethane (13.5 g, 50 mmol). The reaction mixture was heated at 75 °C for 4—12 h, and the excess of tribromofluoromethane was removed at atmospheric pressure (b.p. 106—108 °C) and then at 10—15 Torr. The product was isolated from the residue by vacuum distillation.

1,1,3-Tribromo-1-fluoro-3-phenylpropane (1a), b.p. 112—114 °C (1 Torr). The yield was 30% (from styrene). ^{1}H NMR, δ: 3.71—3.84 (m, 2 H, CH_2); 5.37 (dd, 1 H, CHBr, J = 6.2 Hz, J = 7.4 Hz); 7.30—7.50 (m, 5 H, Ph). ^{13}C NMR, δ: 47.7 (CHBr); 60.8 (d, $\underline{C}H_2CBr_2F$, J = 18 Hz); 92.3 (d, CBr_2F, J = 324 Hz); 127.7, 128.9, 129.0 (Ph); 140.2 (C(1), Ph).

1,1,3-Tribromo-1-fluoroheptane (1b), b.p. 83—84 °C (2 Torr). The yield was 78% (from hex-1-ene). ^{1}H NMR, δ: 0.93 (t, 3 H, CH_3, J = 7 Hz); 1.25—1.65 (m, 4 H, 2 CH_2); 1.70—2.05 (m, 2 H, $C\underline{H}_2$CHBr); 3.26 (ddd, 1 H, $C\underline{H}_2CFBr_2$, J = 17 Hz, J = 7.5 Hz, $J_{H,F}$ = 17 Hz); 3.43 (ddd, 1 H, $C\underline{H}_2CFBr_2$, J = 17 Hz, J = 6.2 Hz, $J_{H,F}$ = 23 Hz); 4.30 (ddt, 1 H, CHBr, J = 6.2 Hz, J = 7.5 Hz, J = 7 Hz). ^{13}C NMR, δ: 14.0 (Me); 21.9, 29.2, 38.2 (3 CH_2); 49.6 (CHBr); 60.4 (d, $\underline{C}H_2CBr_2F$, J = 18 Hz); 93.3 (d, CBr_2F, J = 323 Hz).

1,1,3-Tribromo-1-fluoro-4,4-dimethylpentane (1c), b.p. 80—82 °C (3 Torr). The yield was 58% (from 3,3-dimethylbut-1-ene). ^{1}H NMR, δ: 1.11 (s, 9 H, 3 Me); 3.26—3.41 (m, 2 H, CH_2CBr_2F); 4.00—4.07 (m, 1 H, CHBr). ^{13}C NMR, δ: 27.2 (3 Me); 36.3 ($\underline{C}Me_3$); 57.6 (d, $\underline{C}H_2CBr_2F$, J = 18 Hz); 61.0 (CHBr); 94.3 (d, CBr_2F, J = 324 Hz).

Synthesis of 1-(alk-1-ynyl)-1-fluorocyclopropanes (6a—h) and 1-(alk-1-ynyl)-1-chlorocyclopropanes (8a—k) from 3-substituted 1,1,3-tribromo-1-fluoropropanes (1a—c) and 3-substituted 3-bromo-1,1,1-trichloropropanes (2a—e) (general procedure). ***A*. Using Bu^{t}OK as a base.** A solution of a starting tetrahalide (2 mmol) in 1 mL of a solvent specified in Table 1 was added at ~20 °C to a mixture of Bu^{t}OK (1350 mg, 12 mmol) and a starting alkene (6 mmol) in 6 mL of the same solvent. The reaction mixture was stirred (the reaction duration and temperature are given in Table 1) until the reaction was completed (monitoring by GLC). Then the reaction mixture was treated with water, and the organic layer was separated. The organic material was extracted from the aqueous phase with ether (3×10 mL). The combined organic layers were dried with magnesium sulfate, and the solvent was removed. Cyclopropane **6** or **8** was isolated from the residue by vacuum distillation or by column chromatography in hexane (see Table 1). The yields, boiling points, and the ratios between the *cis*- and *trans*-isomers of compounds **6** and **8** are given in Table 1. Their spectral characteristics are presented in Tables 3—5.

***B*. Using KOH as a base.** A solution of a starting tetrahalide (2 mmol) in 1 mL of CH_2Cl_2 was added to a mixture of KOH (1.8 g, 30 mmol), one drop of water, BTEAC (50 mg), and a starting alkene (6 mmol) in CH_2Cl_2 (10 mL). The solvent was preliminarily refluxed over KOH with BTEAC and then distilled to remove an impurity of chloroform. The reaction mixture was stirred (the reaction duration and temperature are given in Table 1) until the reaction was completed (monitoring by GLC). The product was isolated as described above for Bu^{t}OK as a base (see Table 1). The yields, boiling points, and the ratios between the *cis*- and *trans*-isomers of cyclopropanes **6** and **8** are given in Table 1. Their spectral characteristics are presented in Tables 3—6.

Reaction of 1,1-dichloro-3-phenylprop-2-yne (21a) with a deficient amount of Bu^{t}OK. Generation of chloro(phenylethynyl)carbene (7a) from a mixture of dichloride 21a and 1,1-dichloro-3-phenylpropadiene (22a). Freshly prepared Bu^{t}OK (50 mg, 0.44 mmol) was added at ~20 °C to a solution of dichloride **21a** (185 mg, 1 mmol) in 3 mL of hexane. After 10 min, the content of the starting dichloride was reduced to 82%, and allene **22a** (18%) was detected in the reaction mixture (GLC data). The ratio of compound **21a** to **22a** became 1 : 1 after 30 min. When the reaction was carried out for a longer period of time or with a larger amount of Bu^{t}OK (in separate experiments), the relative content of allene **22a** in the mixture did not increase because of intense resinification. The mixture of the starting dichloride and allene **22a** was isolated by passing the reaction mixture through a thin layer of silica gel. The solution obtained was then used in reactions with Bu^{t}OK in the presence of 2,3-dimethylbut-2-ene. Product **22a** was characterized by the NMR spectra of the reaction mixture. ^{1}H NMR, δ: 6.57 (s, 1 H, PhC$\underline{H}$); 7.20—7.50 (m, 5 H, 2 Ph). ^{13}C NMR, δ: 106.1 (Ph$\underline{C}$H); 127.0 (CCl_2); 127.4, 129.8, 132.0 (Ph); 139.4 (C(1), Ph); 201.0 (=C=).

2,3-Dimethylbut-2-ene (252 mg, 3 mmol) and tridecane (100 mg) were added to a solution of the aforesaid 1 : 1 mixture of dichlorides **21a** and **22a**. The resulting mixture was analyzed by GLC with a pre-calibrated detector. The amount of dichlorides **21a** and **22a** in the mixture was determined from the ratio

of their peak areas to that of tridecane. Potassium *tert*-butoxide (224 mg, 2 mmol) was added, and the reaction mixture was kept for 30 min and treated with 5 mL of water. The organic layer was separated, and the organic material was extracted from the aqueous phase with hexane (2×5 mL). The combined organic layers were analyzed by GLC with a pre-calibrated detector. The yield of 1-chloro-2,2,3,3-tetramethyl-1-(phenylethynyl)cyclopropane (**8a**) (55% from both dichlorides **21a** and **22a**) was determined from the ratio of its peak area to that of tridecane. In an analogous reaction involving a 3 : 1 mixture of dichlorides **21a** and **22a**, the yield of cyclopropane **8a** was 56%.

When dichloride **21a** was used alone (instead of a mixture of chlorides **21a** and **22a**), the yield of cyclopropane **8a** was 60% (GLC data).

While carrying out an analogous reaction without addition of tridecane, cyclopropane **8a** (98 mg, 42%) was isolated from the reaction mixture by column chromatography in hexane. The purity of the product was >95% (GLC and ^{1}H NMR data).

Synthesis of 1-chloro-1-(3,3-diethoxyprop-1-ynyl)-2,2,3,3-tetramethylcyclopropane (8h). A solution of 1,1-dichloro-4,4-diethoxybuta-1,2-diene (**22b**) (560 mg, 2.65 mmol) in 1 mL of hexane was added at ~20 °C to a mixture of 2,3-dimethylbut-2-ene (670 mg, 8 mmol) and Bu^{t}OK (582 mg, 5.2 mmol) in 5 mL of hexane. The reaction mixture was stirred for 2 h and treated with water. The organic layer was separated, and the organic material from the aqueous phase was extracted with hexane (3×10 mL). The combined organic layers were dried with magnesium sulfate, and the solvent was evaporated. Column chromatography of the residue in hexane gave cyclopropane **8h** (327 mg, 48%). The spectral data of the product obtained are given in Tables 4 and 5.

Determination of the relative reactivity of chloro(phenylethynyl)carbene (7a) generated from 3,3-dichloro-1-phenylpropyne (21a) and 3-bromo-1,1,1-trichloro-3-phenylpropane (2a) under the action of Bu^{t}OK. ***A.*** Potassium *tert*-butoxide (110 mg, 1 mmol) was added to a solution of 2,3-dimethylbut-2-ene and 2-methylbut-2-ene (10—15 mmol) in 25 mL of benzene. The reaction mixture was cooled to −10 to −20 °C, and 2-methylpropene (350—650 mg, 7—12 mmol) was added using an evaporation—condensation method. The flask was hermetically sealed with a rubber plug and warmed to ~20 °C. A solution of the starting dichloride **21a** (1 mmol) in 1—2 mL of hexane was added. After 30 min, the reaction mixture was stratified by adding water, and the organic layer was analyzed five times by GLC. An outlier (if present) was rejected, while the other results were averaged. The mass fractions of cyclopropanes **8** were determined with a detector pre-calibrated against authentic samples. The data obtained were used to calculate k_i/k_0 for carbene **7a** with respect to a corresponding alkene by the formula $k_i/k_0 = (n_i/n_0)\ (m_0/m_i)$, where n_i/n_0 is the ratio between the obtained amounts of adducts of carbene **7a** with the *i*th alkene and with 2-methylpropene and m_0/m_i is the molar ratio of 2-methylpropene to the *i*th alkene. In each case, the data from two analogous experiments were averaged. The confidence interval was calculated according to a standard procedure.[17]

The k_i/k_0 value for *cis*-butene was determined in a separate experiment. In this case, the starting mixture was prepared by evaporation—condensation of *cis*-butene and 2-methylpropene after each other into a reaction flask cooled to −20 to −10 °C.

B. When chloro(phenylethynyl)carbene (**7a**) was generated from tetrahalide **2a** (200 mg, 0.66 mmol), the corresponding stoichiometric amount of Bu^{t}OK (220 mg, 2 mmol) was taken. The k_i/k_0 values obtained are given in Table 9.

Synthesis of cyclopropanes 8a and 8c by the reactions of 1,1,1,3-tetrachloro-3-phenylpropane (3a) with Bu^{t}OK in the presence of alkenes. The reaction was carried out according to the general procedure for the preparation of 1-(alk-1-ynyl)-1-chlorocyclopropanes (see above) with the use of Bu^{t}OK as a base. After the reaction was completed (over 1 h in hexane at ~20 °C), the reaction product was isolated by column chromatography in hexane (cyclopropane **8a**) or by vacuum microdistillation (cyclopropane **8c**). The yields of compounds **8a** and **8c** were 66 and 58%, respectively. Their ^{1}H NMR spectra are identical with those of the same cyclopropanes obtained from tetrahalide **2a**.

Reactions of 1,1,1,3-tetrachloroheptane (3b) with bases in the presence of 2,3-dimethylbut-2-ene. ***A.*** **Using Bu^{t}OK as a base.** A solution of tetrachloride **3b** (400 mg, 1.68 mmol) in 1 mL of hexane was added at ~20 °C to a mixture of Bu^{t}OK (1120 mg, 10 mmol) and 2,3-dimethylbut-2-ene (420 mg, 5 mmol) in 5 mL of hexane. The reaction mixture was stirred at ~20 °C for 48 h and then treated with water. The organic layer was separated, and the organic material was extracted from the aqueous phase with ether (3×10 mL). The combined organic layers were dried with magnesium sulfate, and the solvent was evaporated. Vacuum microdistillation (10 Torr, bath temperature 120—130 °C) of the residue gave a 4 : 1 mixture of isomeric cyclopropanes **8d** and **13** (170 mg, a total yield of 50%). The spectral characteristics of products **8d** and **13** are given in Tables 4—8.

B. **Using KOH as a base.** A solution of tetrachloride **3b** (800 mg, 3.36 mmol) in 1 mL of CH_2Cl_2 was added to a mixture of KOH (2.8 g, 50 mmol), one drop of water, BTEAC (50 mg, 0.22 mmol), 2,3-dimethylbut-2-ene (840 mg, 10 mmol), and CH_2Cl_2 (10 mL). The reaction mixture was stirred at ~20 °C for 80 h (monitoring by GLC) and then treated with water. The organic layer was separated, and the organic material was extracted from the aqueous phase with ether (3×10 mL). The combined organic layers were dried with magnesium sulfate, and the solvent was evaporated. Vacuum microdistillation (10 Torr, bath temperature 120—130 °C) of the residue gave a 1.1 : 1 mixture of isomeric cyclopropanes **8d** and **13** (325 mg, a total yield of 48%). The spectral characteristics of products **8d** and **13** are given in Tables 4—8.

Synthesis of 1-bromo-1-(phenylethynyl)cyclopropanes (12a,d,e) by the reactions of 1,1,1,3-tetrabromo-3-phenylpropane (4a) with Bu^{t}OK in the presence of alkenes. A solution of tetrabromide **4a** (4.36 g, 10 mmol) in 10 mL of benzene was added at ~20 °C to a mixture of Bu^{t}OK (5.6 g, 50 mmol) and a starting alkene (30 mmol) in 30 mL of benzene. The reaction mixture was stirred at ~20 °C for 1 h and then treated with water. The organic layer was separated, and the organic material was extracted from the aqueous phase with benzene (2×30 mL). The combined organic layers were dried with magnesium sulfate, and the solvent was evaporated. The residue was passed through an SiO_2 layer in hexane cooled to −10 °C, and the solvent was removed *in vacuo* (30—40 °C, 10—15 Torr).

With 2,3-dimethylbut-2-ene as the alkene, the residue contained, along with cyclopropane **12a**, vinylidenecyclopropane

14a (8%); in the case of 2-methylpropene, cyclopropane **12d** was accompanied by vinylidenecyclopropane **14d** (11%) (NMR and GLC data). Product **12a** was isolated by recrystallization from methanol, while cyclopropanes **12d,e** were purified by vacuum distillation. The yields, boiling and melting points, and the ratios of the *trans*- and *cis*-isomers for products **12a,d,e** are given in Table 2. The spectral characteristics of cyclopropanes **12a,d,e** and **14a,d** are presented in Tables 4—7.

Reactions of 3-substituted 1,1,1,3-tetrabromopropanes 4b,c,f with Bu^{t}OK in the presence of alkenes. A solution of a starting tetrahalide (2 mmol) in 1 mL of a solvent specified in Table 2 was added at ~20 °C to a mixture of Bu^{t}OK (1350 mg, 12 mmol) and a starting alkene (6 mmol) in 5 mL of the same solvent. The reaction mixture was stirred (the reaction duration and temperature are given in Table 2) until the reaction was completed (monitoring by GLC). Then the reaction mixture was treated with water, and the organic layer was separated. The organic material was extracted from the aqueous phase with ether (3×10 mL). The combined organic layers were dried with magnesium sulfate and the solvent was evaporated. A mixture of the reaction products was isolated from the residue by vacuum distillation, recrystallization from methanol, or by column chromatography in hexane. When compounds **4c,f** were used, the resulting mixtures contained two components, namely, bromides **12b,c** and **14b,c**; with 1,1,1,3-tetrabromoheptane (**4b**) as the starting reagent, 1-bromo-1-(*trans*-hex-1-enyl)-2,2-dimethylcyclopropane (**17**) was detected along with bromides **12f** and **14e** (GLC and ^{1}H and ^{13}C NMR data). The composition of the mixtures obtained and the total yields and boiling points of the reaction products are given in Table 2. The spectral characteristics of cyclopropanes **12b,c,f** and **14b,c,e** are presented in Tables 4—8.

Compound 17. ^{1}H NMR, δ: 0.91 (t, 3 H, CH_3 in Bu, J = 7.0 Hz); 1.04 (s, 3 H, Me); 1.38 (s, 3 H, Me); 1.20—1.55 (m, 6 H, 3 CH_2); 2.06 (dt, 2 H, —C$\underline{H}_2$CH=, J = 6.5 Hz, J = 6.5 Hz); 5.64 (dt, 1 H, —CH_2C$\underline{H}$=, J = 15.2 Hz, J = 6.5 Hz); 5.79 (d, 1 H, CBrC$\underline{H}$=, J = 15.2 Hz). ^{13}C NMR, δ: 14.0 ($\underline{C}H_3CH_2$—); 21.4, 22.3, 22.8, 25.1, 26.2, 27.2, 31.3, 31.6 ($\underline{C}Me_2$, 2 C($\underline{C}H_3$), 4 CH_2, CBr); 131.3 and 133.6 ($\underline{C}$H=$\underline{C}$H). MS, m/z: 230, 232 $[M]^+$.

Reaction of 1,1,1,3-tetrabromo-3-phenylpropane (4a) with KOH in the presence of 2,3-dimethylbut-2-ene. A solution of tetrabromide **4a** (1 g, 2.3 mmol) in 1 mL of CH_2Cl_2 was added to a mixture of KOH (1.8 g, 30 mmol), benzyltriethylammonium chloride (50 mg), and 2,3-dimethylbut-2-ene (570 mg, 6.8 mmol) in 10 mL of CH_2Cl_2. The reaction mixture was stirred at ~20 °C for 2 h. The course of the reaction was monitored by GLC. Then the reaction mixture was treated with water, and the organic layer was separated. The organic material was extracted from the aqueous phase with ether (3×10 mL). The combined organic layers were dried with magnesium sulfate. Column chromatography of the residue on silica gel in hexane gave a 1.7 : 1 mixture of bromides **14a** and **15** (240 mg). The spectral characteristics of cyclopropane **14a** are given in Tables 7 and 8.

2,2,3,3-Tetramethyl-1-(phenylvinylidene)cyclopropane (15). ^{1}H NMR, δ: 1.40 (s, 6 H, 2 Me); 1.49 (s, 6 H, 2 Me); 6.20 (s, 1 H, CH=); 7.30—7.60 (m, 5 H, Ph). ^{13}C NMR, δ: 21.3 (2 CH_3); 22.0 (2 CH_3); 31.4 (2 $\underline{C}Me_2$); 95.8 (=CH—); 99.1 (=C in *cyclo*-C_3); 126.4, 127.1, 128.5 (Ph); 136.8 (C(1), Ph); 182.9 (=C=). MS, m/z: 198 $[M]^+$.

Reactions of 3-bromo-1,1,1-trichloro-3-phenylpropane (2a) and 1,1,1,3-tetrachloro-3-phenylpropane (3a) with a deficient amount of Bu^{t}OK. Potassium *tert*-butoxide (56 mg, 0.5 mmol) was added at ~20 °C to a solution of a starting tetrahalide (**2a** or **3a**) (1 mmol) in 5 mL of hexane. The reaction mixture was stirred for 60 min and then passed through a thin layer of silica gel; the sorbent was washed with hexane. After the solvent was evaporated, the residue contained the starting tetrahalide and 1,1,3-trichloro-3-phenylprop-1-ene (**19a**) in the ~1 : 1 ratio (GLC and NMR data). The latter was identified by comparing its ^{1}H and ^{13}C NMR spectra with those of an authentic sample (see below).

Synthesis of 1,1,3-trichloro-3-phenylprop-1-ene (19a). A mixture of tetrahalide **2a** (2.5 g, 8.2 mmol) and triethylamine (3.3 g, 33 mmol) was refluxed for 8 h. The reaction mixture was diluted with 20 mL of Et_2O and washed with aqueous 5% HCl. The organic material was additionally extracted from the aqueous layer with ether (10 mL). The combined organic layers were dried with magnesium sulfate, and the solvent was evaporated. Vacuum distillation of the residue gave product **19a** (0.5 g, 28%), b.p. 92—93 °C (2 Torr). ^{1}H NMR, δ: 5.72 (d, 1 H, CH, J = 10.2 Hz); 6.30 (d, 1 H, CH, J = 10.2 Hz); 7.20—7.50 (m, 5 H, Ph). ^{13}C NMR, δ: 58.4 (CHCl); 124.2 (=CCl_2); 126.9, 128.8, 128.9, 129.4 (Ph, —CH=); 138.4 (C(1), Ph). MS, m/z: 185, 187 $[M - Cl]^+$.

Synthesis of 1-chloro-2,2,3,3-tetramethyl-1-(phenylethynyl)cyclopropane (8a) from 1,1,3-trichloro-3-phenylprop-1-ene (19a). Chloride **19a** (152 mg, 0.687 mmol) was added at ~20 °C to a mixture of 2,3-dimethylbut-2-ene (290 mg, 3.4 mmol), Bu^{t}OK (310 mg, 2.74 mmol), and dodecane (100 mg) in 3 mL of hexane. Approximately two minutes after the addition was completed, the reaction mixture contained, along with the starting trichloride and cyclopropane **8a**, allene **22a** and alkyne **21a** in the 1 : 1 ratio; their total content was 6% (GLC data). The latter two compounds were identified by comparing their retention times with those of authentic samples (see the section "Reaction of dichloride **21a** with a deficient amount of Bu^{t}OK"). The reaction mixture was stirred for 30 min and analyzed by GLC, which showed the complete absence of the starting trichloride **19a** and intermediate compounds **21a** and **22a**. The yield of cyclopropane **8a** was determined from the ratio of its peak area with that of dodecane with a pre-calibrated detector. The yield of **8a** was 46%.

Reactions of 3-bromo-1,1,1-trichloroheptane (2b) and 1,1,1,3-tetrachloroheptane (3b) with a deficient amount of Bu^{t}OK. The reactions were carried out as described above for the reactions of halides **2a** and **3a** with Bu^{t}OK. After being treated with water, the reaction mixture contained the starting reagent (~50%) and products **19c** and **20b** in the 1 : 3.5 ratio (for **2b**) or products **19b** and **20b** in the 1 : 1.2 ratio (for **3b**) (NMR and GLC data). The products were identified from the ^{1}H NMR spectra of the resulting mixtures.

Compound 19b. ^{1}H NMR, δ: 0.91 (t, 3 H, CH_3 in Bu, J = 7.0 Hz); 1.20—2.00 (m, 6 H, 3 CH_2); 4.75 (dt, 1 H, CHCl, J = 11.1 Hz, J = 7.2 Hz); 6.10 (d, 1 H, CH=CCl_2, J = 11.1 Hz).

Compound 19c. ^{1}H NMR, δ: 0.91 (t, 3 H, CH_3 in Bu, J = 7.0 Hz); 1.20—2.00 (m, 6 H, 3 CH_2); 4.66 (dt, 1 H, CHBr, J = 11.1 Hz, J = 7.2 Hz); 5.98 (d, 1 H, CH=CCl_2, J = 11.1 Hz).

Compound 20b. ^{1}H NMR, δ: 0.92 (t, 3 H, CH_3 in Bu, J = 7.0 Hz); 1.20—1.55 (m, 4 H, 2 CH_2); 2.18 (dt, 2 H, —C$\underline{H}_2$CH=,

J = 7 Hz, J = 6.5 Hz); 6.11 (d, 1 H, $CHCCl_3$, J = 15.5 Hz); 6.27 (dt, 1 H, $CH_2C\underline{H}$=, J = 15.5 Hz, J = 7.2 Hz).

Reaction of 1,1,3-tribromo-1-fluoroheptane (1b) with Bu^{t}OK: identification of intermediate products. Potassium *tert*-butoxide (158 mg, 1.41 mmol) was added at ~20 °C to a solution of tetrahalide **1b** (500 mg, 1.41 mmol) in 5 mL of hexane. The reaction mixture was stirred for 15 min and then treated with water. The organic layer was separated, and the organic material was extracted from the aqueous phase with ether (3×10 mL). The combined organic layers were dried with magnesium sulfate, and the solvent was evaporated. The residue contained a mixture of the starting compound **1b**, *trans*-1,1-dibromo-1-fluorohept-2-ene (**24**), and isomeric *E*- and *Z*-1,3-dibromo-1-fluorohept-1-enes (**25**) in the 1 : 1.8 : 0.9 : 0.75 ratio (GLC and NMR data). The total yield was 340 mg.

Compound 24. ^{1}H NMR, δ: 0.88 (t, 3 H, CH_3 in Bu, J = 7 Hz); 1.20—1.55 (m, 4 H, 2 CH_2); 2.06 (dt, 2 H, —C$\underline{H}_2$CH=, J = 7 Hz, J = 6.5 Hz); 5.85—6.15 (m, 2 H, —CH=CH—). ^{19}F NMR, δ ($CFCl_3$): –51.8 (d, $CFBr_2$, J = 16.6 Hz). MS, m/z: 193, 195 $[M - Br]^+$.

Compound *E*-25. ^{1}H NMR, δ: 0.88 (t, 3 H, CH_3 in Bu, J = 7 Hz); 1.20—2.00 (m, 6 H, 3 CH_2); 4.72 (dt, 1 H, CHBr, J = 11.1 Hz, J = 7.2 Hz); 5.31 (dd, 1 H, CH=CFBr, J = 11.1 Hz, $J_{H,F}$ = 27.9 Hz). ^{19}F NMR, δ ($CFCl_3$): –69.2 (d, =CFBr, J = 27.9 Hz). MS, m/z: 193, 195 $[M - Br]^+$.

Compound *Z*-25. ^{1}H NMR, δ: 0.88 (t, 3 H, CH_3 in Bu, J = 7 Hz); 1.20—2.00 (m, 6 H, 3 CH_2); 4.48 (dtd, 1 H, CHBr, J = 10.9 Hz, J = 7.1 Hz, $J_{H,F}$ = 2.5 Hz); 5.71 (dd, 1 H, CH=CFBr, J = 10.9 Hz, $J_{H,F}$ = 10.9 Hz). ^{19}F NMR, δ ($CFCl_3$): –68.3 (dd, =CFBr, J = 10.9 Hz, J = 2.5 Hz). MS, m/z: 193, 195 $[M - Br]^+$.

The mixture of the halides obtained (340 mg) was dissolved in 5 mL of hexane, and Bu^{t}OK (120 mg, 1.07 mmol) was added at ~20 °C. After 30 min, the starting tetrahalide **1b** was completely consumed (GLC data), and the reaction gave, along with trihalides **24** and **25**, two new products identified as dihalides **26** and **27** in 12 and 5% yields, respectively. After 60 min, the reaction mixture contained *trans*-**24** (45%), the *E*-isomer of **25** (25%), the *Z*-isomer of **25** (3%), allene **26** (15%), and alkyne **27** (5.5%) (GLC data). When the mixture reacted with Bu^{t}OK for 90 min, the relative content of products **26** and **27** decreased to 12 and 5%, respectively. The reaction mixture was treated with water. The organic layer was separated, and the organic material was extracted from the aqueous phase with ether (3×10 mL). The combined organic layers were dried with magnesium sulfate, and the solvent was evaporated *in vacuo* at a bath temperature of no higher than 40 °C. The residue (164 mg) was analyzed by NMR spectroscopy and GL-MS spectrometry.

1-Bromo-1-fluorohepta-1,2-diene (26). ^{1}H NMR, δ: 0.92 (t, 3 H, CH_3 in Bu, J = 7 Hz); 1.20—1.60 (m, 4 H, 2 CH_2); 2.20—2.45 (m, 2 H, CH_2CH=); 5.97 (dt, 1 H, —CH=, J = 6.5 Hz, $J_{H,F}$ = 1.6 Hz). ^{19}F NMR, δ ($CFCl_3$): –95.4 (d, =CFBr, J = 1.6 Hz). MS, m/z: 150, 152 $[M - C_3H_6]^+$.

1-Bromo-1-fluorohept-2-yne (27). ^{1}H NMR, δ: 0.92 (t, 3 H, CH_3 in Bu, J = 7 Hz); 1.20—1.60 (m, 4 H, 2 CH_2); 2.20—2.45 (m, 2 H, $CH_2C\equiv$); 6.77 (dt, 1 H, —CHFBr, $J_{H,F}$ = 52 Hz, J = 1.7 Hz). ^{19}F NMR, δ ($CFCl_3$): –121.5 (d, —CHFBr, J = 52 Hz). MS, m/z: 113 $[M - Br]^+$.

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