ALKYNYLHALOCARBENES.

1. GENERATION OF ALKYNYLCHLORO- AND ALKYNYLBROMOCARBENES FROM ALKYNYLCHLOROBROMO- AND ALKYNYLDIBROMOMETHANES, THEIR MULTIPLICITY AND PHILICITY*

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The action of t-BuOK on alkynyldihalomethanes RC=CCHBrX (I, R = Me, t-Bu, Ph; X = Br, Cl) in pentane at -20 to 0°C generates the corresponding alkynylhalocarbenes RC=CCX (II; X = Br, Cl) which in the presence of olefins give alkynylhalocyclo-propanes (V) in 26-70% yield. It has been shown for the example of the reaction of (methylethynyl-) and (tert-butylethynyl)bromocarbenes with cis-butene-2 that the cycloaddition is fully stereospecific. The selectivity index for (methyl-ethynyl)bromocarbene was experimentally determined as 0.48 which is evident for electrophilic character in this carbene.

Alkynyl carbenes $R(C=C)_n\ddot{C}H$ (n = 1, 2) having a basic triplet state are generated by photolysis of the corresponding alkynyldiazomethanes [2, 3] or by thermolysis of Li-salts of the tosylhydrazones of dialkynylketones [4]. Methoxycarbonyl- and bromosubstituted (4-methylpenten-3-yn-1-yl)carbenes have also been described, generated by photolysis of the corresponding 3,3-dimethyl-5-alkynyl-3H-pyrazoles [5].

Bearing in mind the similarity in electronegativity of the ethynyl group and halogen atoms, we have suggested that alkynyldihalomethanes might undergo α elimination of hydrogen halide under the action of bases, similarly to haloforms [6, 7], with the formation of a new class of carbene particles - alkynylhalocarbenes. This possibility was subsequently confirmed by quantum-chemical calculations [8].

$$\begin{array}{rcl} \mathrm{RC} \equiv \mathrm{CCHXY} & \xrightarrow{\mathrm{B}^{-}, -\mathrm{H}^{+}} & \mathrm{RC} \equiv \mathrm{CCXY} & \xrightarrow{-\mathrm{X}^{-}} & \mathrm{RC} \equiv \mathrm{CCY} \\ & \xrightarrow{+\mathrm{H}^{+}} & \mathrm{RC} \equiv \mathrm{CCXY} & \xrightarrow{+\mathrm{X}^{-}} & \mathrm{RC} \equiv \mathrm{CCY} \end{array}$$

With this objective, previously unknown alkynyldihalomethanes (I) were prepared and their reaction with t-BuOK in the presence of olefins studied.

The dihalides (I) were prepared by halogenation of the corresponding formylacetylenes (III) with an equimolar mixture of PCl_3 and BR_2 in the presence of catalytic quantities of pyridine ($(PCl_3 + Br_2)Py$) at -50 to -70°C in CH_2Cl_2 .

 $RC \equiv CCHO \xrightarrow{(PCI_{s}+Br_{2})Py} \xrightarrow{MeC \equiv CCHBr_{2} + MeBrC = C = CHBr} (Ia, X = Br) (IV)$ (III) $RC \equiv CCHO \xrightarrow{(IV)} (IV)$ $RC \equiv CCHBrX$ (I) R = Me (a), t-Bu(b), Ph (c); X = Br, CL.

Reaction with methylformylacetylene (IIIa) gave methyldibromomethylacetylene (Ia, X = Br) containing 1,3-dibromobuta-1,2-diene (IV) as an impurity. Reaction of t-butyl- (IIIb) and phenyl- (IIIc) formylacetylenes with ((PCl₃ + Br₂)Py) yielded a mixture of the corresponding dibromomethylacetylenes (Ib, c; X = Br) and bromochloromethylacetylenes (Ib, c; X = C1) which were separated by distillation (purity > 95%).

*For previous communication, see [1].

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Initial dihalo- methanes of RC=CCHBrX		Olefins R'R'C=CR'R'				1-Alkyny1-1-halocyclopropanes				
R	x	R1	R²	R3	R4	compound	yield, % of theory	bp, °C (mm), mp, °C*	Z/E isomer ratio	
Me Me t-Bu t-Bu t-Bu Ph t-Bu t-Bu Ph	Br Br Br Br Br Cl Cl	H Me Me H Me Ph H H Me H	Me Me Me Me H Me Me Me Me	Me H Me Me H H Me Me Me Me	H H H H H H H H H H H H	(Va) (Vb) (Vc) (Vd) (Ve) (Vf) (Vf) (Vf) (Vi) (Vi) (Vj) (Vk)	26 40 41 56 40 59 50 60 70 56		1:1,7 1:1 1:2,5 1:3 - -	

TABLE 1. Yields and Properties of 1-Alkynyl-1-halocyclopropanes

In the reaction between t-BuOK and (Ia-c; X = Br) α elimination of HBr occurs with the formation of alkynylbromocarbenes (II, X = Br) which are intercepted by olefins. Both liquid olefins and those which are gases under normal conditions enter into reaction with equal success forming the corresponding l-alkynyl-l-bromocyclopropanes (Va-h) in yields of 25-60%. As might be expected, unsymmetrically substituted olefins form cyclopropanes (Vb, c, f, g) as a mixture of E and Z isomers (Table 1).



(I), (I1): R = Me(a), t-Bu (b), Ph (c). X = Br, Cl. R^1 , R^2 , R^3 , $R^4 = H$, Me, Ph.

Similar reactions with bromochloromethylacetylenes (Ib, c; X = Cl) yielded alkynylchlorocyclopropanes (Vi-k) in yields of 56-70%; the corresponding bromocyclopropanes were completely absent which is evidence that alkynylchlorocarbenes (IIb, c; X = Cl) are formed exclusively under these conditions (cf. [6]).

The structure of the cyclopropanes (Va-k) was proved by chromatography-mass spectrometry, and IR and PMR spectroscopy (Table 2). Thus, a quite intense molecular ion peak is observed in the mass spectra of these compounds having a doublet with a separation of 2 mass units and relative intensities of 1:1 and 3:1, respectively, resulting from the different isotopes of Cl and Br. The IR spectra show absorption bands in the 2225-2255 cm⁻¹ region from the C=C bond. Identification of the Z and E isomers of cyclopropanes (Vb, c, f, g) was effected by comparing the chemical shifts of the protons of the substituents at the carbon atoms of the cyclopropane ring. Thus, for the Z isomers the chemical shift of the proton signals of the R¹ and R² substituents located in the cis position relative to the halogen atom will be greater, as a result of stronger deshielding by the latter, than for the E isomers.

Carbenes (IIa, b; X = Br) react fully stereospecifically with cis-butene-2; according to Skell's hypothesis [9, 10] this is evidence of a singlet ground state. It should be noted that in all the cases which we studied no products of the resonance addition of carbenes

TABLE 2. Spectra of Cyclopropanes (Va)-(Vk)

	•			ht vpalle					I
Com- pound	F	Ē.	R2	R3	Å.	× .	PMR spectra (250 MHz, CDCl ₃ , 6, ppm, J, Hz) $\frac{Mass spec}{3^{5}Cl and}$	rum IR spectrum v, cm ⁻¹ (C≡C)	(
(Va)	CH3	ιH	CH ₃ ²	CH ₃ 3	ъ Н	Br	$\begin{bmatrix} 1,05 & d & (H^2, J_1, 4=5,9), \\ 0,05 & 0,01, 0,01, 0 \\ 0,01, 0,01, 0 \\ 0$	2255	
E-(Vb)	CH,	CH3 ¹	CH ₃ ²	H ³	۰H	Br	$1,03^{\circ}$ (3H, CH ₃ ⁻¹ , 1,88 > (3H, CH ₃) $1,18^{\circ}$ (6H, CH ₃ ⁻¹ , CH ₃ ⁻¹ , 1,58 m (2H, H ³ & H ⁴), 1,938 186	2250	
Z-(Vb)	CH3	CH3 ¹	CH ₃ ²	H ³	,H	Br	$\begin{bmatrix} 1, H_{3}, CH_{3}, CH_{3}, \delta, CH_{3}, \delta, CH_{3}^{2}, 1.21 \text{ m} (2H, H^{3}\delta, H^{4}), 1.86s \end{bmatrix}$ 186	2250	
E-(Vc)	CH3	CH31	CH ₃ ²	CH ₃ ³	'n,	Br	1.091 , CH_{3} , CH_{3} , L_{44} , $e_{6,5}$, $1,11 \le (3H, CH_{3}^2)$, $1.21 \le 200$	2240	
$Z^{-}(V_{C})$	CH3	CH3	CH3 ²	CH ₃ ³	'nH	Br	(17) , 1.50 \approx (art, CH_3), 1.93 \approx (art, CH_3) 0.92 $=$ (14, 2, 1, 1=6,5), 1.11 $=$ (3H, CH_3), 1.13 \approx (3H, 200	2240	
(PA)	CH,	CH ₃ 1	CH32	CH ₃ ³	CH3	Br	$\begin{array}{c} CH_{3}^{(H)}, 1.21^{-3}, (2H, CH_{3}^{-3}), 1.095^{-6}, (2H, CH_{3}^{-1}), 1.92^{-8}, (3H, CH_{3}^{-1}), (3H, C$	2245	
(Ae)	t-C,H.	ιH	CH3 ²	CH3 ³	,H	Br	$1.08 \rightarrow 0.01$, $J_{1,1} = 8,0$, $1,12 \rightarrow 0.1$, $1,21 \approx (9H, 3CH_3)$, $228 \rightarrow 0.000$, $228 \rightarrow 0.000$, 2000 , 20	2236	
E-(Vf)	t-C,H,	CH3 ^t	CH ₃ ²	H3	Η	Br	1.0° S (301, CH_3°), 1.0° S (301, CH_3°), 1.24 S (91, $3CH_3$), 1.57 m 228	2235	
Z-(Vf)	t-C,H,	CH31	CH ₃ ²	H ³	۰H	Br	$\begin{array}{c} 228, 11, 15, 26, 17, 17, 18, 18, 18, 18, 18, 18, 18, 18, 18, 18$	2235	
E-(VB)	t-CtHs	CeH,	H ²	нз	,H	Br	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2240	
Z-(V B)	1-C,H	C ₆ H,	H²	εH	Ή	В	$\begin{array}{c} C_{6}H_{3}, \\ 1,29 & (9H. \ 3CH_{3}), \ 1,75 \ d.d \\ 1,77 \ d.d \\ H^{2}, \ J_{3,i}=9,5), \ 2,58 \ d.d \\ (H^{2}, \ J_{3,i}=9,5), \ 2,58 \ d.d \\ (H^{4}), \ 7,34 \ m \\ (5H, \ m) \end{array}$	2240	
(4A)	CeH,	Ĥ	CH ₃ ²	CH ₃ ³	,H	Br	$\begin{bmatrix} 0.611.9 \\ 1.26 & d \\ 0.01 & 0.01 \end{bmatrix}$, 1,36 d (H ¹), 1,41 s (3H, CH ₃ ³), 1,47 s 248	2225	
(Vi)	<i>t</i> -C,H,	Ĥ	CH ₃ ²	CH ₃ 3	۶H	C	$\begin{array}{c} \begin{array}{c} 101, \ CH_{3}^{-1} \\ 1,01 \\ 1,01 \\ 0,0 \\ 0$	2235	
(tv)	ι-C,H	CH ₃ 1	CH ₃ ²	CH ₃ ³	CH ₃ 4	C	$\frac{1.50}{1.07} \lesssim (12H, CH_3^{-1}), Lio3 \lesssim (CH_3^{-1}), CH_3^{-1}), CH_3^{-1} \lesssim (12H, CH_3^{-1}), CH_3^{-1} \lesssim (12H, CH_3^{-1}), 1,15 \lesssim (9H, 212)$	2235	
(Vk)	CeH5	Ĥ	CH ₃ ²	CH ₃ ³	H4	Ū,	$\begin{bmatrix} J_{119} & (H^4, J_{4,4}=6), I_{128} & (H^4), I_{139} & s & (3H, CH_3^3), \\ I_{142} & (3H, CH_3^2), T_{21}-7,40m & (5H, C_6H_3) \end{bmatrix} = 204$	2230	

*Recorded on a Tesla BS 467 (60 MHz), solvent CCl $_{\rm t}.$

	:(CCl ₂	:CBrC=CMe	
Olefin	K/K_0	$\log K/K_0+1$	K/K _o	$\lg K/K_0+1$
2,3-Dimethylbutene-2 2-Methylbbutene-2 Isobutylene cis-Butene-2	7,41 3,05 1 0,23	1,87 1,48 1 0,36	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	1,49 1,21 1 0,77

TABLE 3. Values of K/K_0 and $\log K/K_0 + 1$ for (Methylethynyl)bromocarbene (IIa; X = Br) and Dichlorocarbene

(II) to olefins at the C³ atom was detected. This points to a marked absence of propargyl conjugation [2], characteristic for triplet alkynyl carbenes, from the singlet carbenes (II).

$$:C^1XC^2 \equiv C^3R(II) \leftarrow \to XC^1 \equiv C^2(R)C^3:$$

With the object of establishing the philicity of the new carbenes, we used the method of [11] to study the competing reactions of the (methylethynyl)bromocarbene (IIa, X = Br) generated from (Ia, X = Br) by the action of t-BuOK in pentane at -10°C with pairs of methyl-substituted ethylenes taken in tenfold molar excess and isobutylene used as a standard. The ratio K/K_0 was calculated on the basis of GLC results. The values obtained for K/K_0 and $\log K/K_0 + 1$ for (IIa; X = Br) and analogous data for dichlorocarbene [12] taken as standard are set out in Table 3. The experimental value of the selectivity index found for (IIa; X = Br), determined according to [11], was 0.48, which is evidence of the electrophilic character of this carbene.

EXPERIMENTAL

Analysis of the starting materials and products was carried out by GLC on an LKhM-8MD chromatograph with a flame ionization detector or a katharometer and I-02 integrator. Columns were 200 \times 0.3 cm with either 5% SP-2100 on AW-HMDS Inerton or 5% Carbowax 6000 on N-AW-DMCS Chromatone; carrier gas was 30 ml/min helium. PMR spectra were recorded on a Tesla BS 467 (60 MHz) and a Bruker WM 250 (250 MHz) using 3-10% solutions in CCl₄ or CDCl₃ with TMS as internal standard. Chromatography-mass spectrometry was carried out on a Finnigan MAT INCOS-50 instrument (RSL-200 capillary column 30 m \times 0.25 mm). IR spectra were run on a Specord M 80 and a Perkin Elmer 577 as solutions in CCl₄.

Phenylformylacetylene was prepared by the method of [13], and butyne-2-ol-1 and 4,4-dimethylpentyn-2-ol-1 by the method of [14]. The complex C_5H_5N/CrO_3HC1 was prepared according to [15].

<u>Alkynyldibromo- and Alkynylbromochloromethanes (I; X = Br, Cl) (general method)</u>. To a suspension of 72.8 g (0.34 mole) C_5H_5N/CrO_3HCl complex in 450 ml CH_2Cl_2 was added, over 15 min at 10-15°C, 0.2 mole hydroxymethylacetylene and the mixture stirred at the same temperature until all the initial alcohol had disappeared (~2.5 h, GLC monitoring) and then filtered through a layer of neutral Al_2O_3 . The filtrate was cooled to -70°C and 1.6 g (0.02 mole) pyridine added followed by a $PCl_3 + Br_2$ mixture prepared by adding 32.4 g (0.2 mole) Br_2 to a solution of 27.4 g (0.2 mole) PCl_3 in 90 ml CH_2Cl_2 at -20°C and then stirring for 1 h at 0°C. The mixture was stirred at -50 to -70°C until all the aldehyde had disappeared (~40 min, GLC monitoring). Anhydrous $NaHCO_3$ (180 g) was then added, and the temperature taken up to -5°C and held there for 16 h. The precipitate was filtered off, the filtrate passed through silica gel, the solvent evaporated on a rotary evaporator and the residue distilled in vacuum. Compounds (Ia, b) were prepared by this method.

<u>1,1-Dibromobutyne-2 (Ia; X = Br)</u>. A 2:1 mixture (14.83 g, 35%) of (Ia; X = Br) and 1,3-dibromobutadiene-1,2 (IV) with bp 80-89°C/25 mm was obtained from 14.02 g (0.2 mole) butyn-2-ol-1; from this (Ia; X = Br) was isolated by distillation, bp 87-89°C/25 mm. PMR spectrum (250 MHz, CDCl₃, δ , ppm, J, Hz): 2.04 d (3H, CH₃, J = 3), 6.07 q (1H, C=CH, J = 3). Mass spectrum, m/z: 133, 131 [M⁺ - Br]; 81, 79, 52 [M⁺ - 2Br]; 51 [M⁺ - Br - HBr]. IR spectrum (ν , cm⁻¹): 2247 (C=C).

<u>Compound (IV)</u> was identified without isolating it from its mixture with (Ia; X = Br). PMR spectrum of (IV) (250 MHz, CDCl₃, δ , ppm, J, Hz): 2.43 d (3H, J = 3), 6.09 q (1H, C=CH, J = 3). Mass spectrum, m/z: 214, 212, 210 [M⁺]; 133, 131 [M⁺ - Br]; 81, 79, 52 [M⁺ - 2Br]; 51 [M⁺ - Br - HBr]. IR spectrum (ν , cm⁻¹): 1960 (C=C=C). <u>1, l-Dibromo- (Ib; X = Br) and l-Bromo-l-chloro-4,4-dimethylpentyne-2 (Ib; X = Cl)</u>. A 4:1 mixture (14.4 g, 30%) of (Ib; X = Br) and (Ib; X = Cl) with bp $53-64^{\circ}C/3$ mm was obtained from 22.5 g (0.2 mole) 4,4-dimethylpentyne-2-ol and was separated by distillation.

(Ib; X = Br), bp 64-65°C/3 mm. PMR spectrum (60 MHz, CCl₄, δ , ppm): 1.18 s (9H, 3CH₃), 5.94 s (1H, CHBr⁻). Mass spectrum, m/z: 175, 173 [M⁺ - Br]; 160, 158 [M⁺ - Br - CH₃]; 94 [M⁺ - 2Br, (100)]; 79, 77. IR spectrum (ν , cm⁻¹): 2235 (C=C).

(Ib; X = C1), bp 50-52°C/3 mm. PMR spectrum (60 MHz, CC1₄, δ , ppm): 1.17 s (9H, 3CH₃), 6.00 s (1H, CHC1Br). Mass spectrum, m/z: 131, 129 [M⁺ - Br]; 116, 114 [M⁺ - Br - CH₃]; 94 [M⁺ - Br - C1]; 79, 77 (100). IR spectrum (ν , cm⁻¹): 2235 (C=C).

<u>Dibromo- (Ic; X = Br) and Bromochloro(phenylethynyl)methane (Ic; X = Cl)</u>. An equimolar mixture (21.4 g, 43%) of (Ic; X = Br) and (Ic; X = Cl) with bp 106-125°C/1 mm was obtained from 26 g (0.2 mole) phenylformylacetylene in 250 ml CH_2Cl_2 , 27.4 g (0.2 mole) PCl₃, 32.4 g (0.2 mole) Br₂, and 1.6 g (0.02 mole) pyridine and was separated by distillation.

(Ic; X = Br), bp 125-126°C/1 mm. PMR spectrum (60 MHz, CC1₄, δ , ppm): 6.17 s (1H, CHBr₂), 7.28 m (5H, C₆H₅). Mass spectrum, m/z: 276, 274, 272 [M⁺], 195, 193 [M⁺ - Br], 114 [M⁺ - 2Br]. IR spectrum (ν , cm⁻¹): 2212 (C=C).

(Ic; X = Cl), bp 105-106°C/1 mm. PMR spectrum (60 MHz, CCl₄, δ , ppm): 6.30 s (1H, CHClBr), 7.28 m (5H, C₆H₅). Mass spectrum, m/z: 232, 230, 228 [M⁺]; 195, 193 [M⁺ - Cl]; 151, 149 [M⁺ - Br]; 114 [M⁺ - Br - Cl]. IR spectrum (ν , cm⁻¹): 2214 (C=C).

<u>Reaction of (Alkyny1)dihalomethanes (I) with t-BuOK in the Presence of Olefin (general</u> <u>method</u>). To a mixture of 0.1 mole olefin and 0.02 mole t-BuOK in 10 ml pentane, cooled to -20° , was added over 5 min 0.01 mole (I); the mixture was stirred at this temperature for 0.5 h and the temperature raised to 0°C and stirred until (I) was completely consumed (GLC monitoring). The precipitate was filtered off and the filtrate passed through silica gel, evaporated on a rotary evaporator, and the residue distilled in vacuum.

Yields and properties of the products are given in Tables 1 and 2.

Determination of K/K_0 for (Methylethynyl)bromocarbene (IIa; X = Br). Competitive reactions of methyldibromomethylacetylene (Ia; X = Br) were carried out by the general method with the following pairs of olefins: isobutylene-cis-butene, isobutylene-2-methylbutene-2, isobutylene-2,3-dimethylbutene-2. The reaction products were analyzed by GLC on an LKhM-8MD chromatograph with a flame ionization detector and I-02 integrator. The column was 200 × 0.3 cm with 5% SP 2100 on N-AW-DMCS Inertone. The values of K/K_0 and $\log K/K_0 + 1$ for the carbene tested and similar data for :CCl₂ [12] are given in Table 3.

In addition, the method of least squares was used to determine the selectivity index (m) which is the tangent of the angle of slope of the line with coordinates: $x = (\log K/K_0 + 1)_{:CC1_2}$, $y = (\log K/K_0 + 1)_{:CBrC \equiv CMe}$; $m = 0.48 \pm 0.05$.

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REACTIONS OF [2 + 2 + 1]-CYCLOADDITION WITH THE PARTICIPATION

OF CYCLOPROPENES AND DICOBALT HEXACARBONYL COMPLEXES

OF ACETYLENES

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The reaction of dicobalt hexacarbonyl complexes of acetylene and its phenyl and dimethyl derivatives with the methyl ester of 1-methyl-2-(trimethylsilyl)-1-cyclopropene-3-carboxylic acid with adsorption on a silica gel or NaX zeolite surface leads to the formation of a mixture of bicyclo[3.1.0]hex-2-en-4-one and tricyclo[4.1.0.0², ⁴]heptan-5-one derivatives, whereby the yields and the composition of products are dependent on the type of the adsorbent. It has been found that under the reaction conditions partial isomerization of the bicyclo-[3.1.0]hex-2-en-4-one derivatives into substituted phenols occurs. Action of anhydrous KF and crown-ether in acetonitrile on the bicyclo[3.1.0]hex-2-en-4-one derivatives in acetonitrile leads to protodesilylation.

Alkenes are capable of reacting with dicobalt hexacarbonyl complexes (DCHCC) of acetylenes according to a [2 + 2 + 1]-cycloaddition scheme thus forming derivatives of cyclopenten-2-one (the Khand-Pauson reaction) [1]. The intramolecular variant of this reaction for the synthesis of several natural polycyclic compounds and their analogs [2] is particularly widely used. The intermolecular variant has less synthetic application because of the low activity and low regioselectivity of the cyclization of most alkenes under these reaction conditions [1-3]. However, a strained methylenecyclopropane readily undergoes the Khand-Pauson intermolecular reaction, and the process is characterized by high regioselectivity [4].

In the present work, we studied for the first time the possibility of the participation in this reaction of still another class of strained cycloolefins - cyclopropenes which are very active in cycloaddition reactions, including those catalyzed by transition metal compounds [5]. As the subjects of the investigation we chose 3,3-dimethylcyclopropene (I) as the most available and stable representative of cyclopropenes, and DCHCC of a series of acetylenes with different numbers of substituents at the triple bond - acetylene (IIa), phenylacetylene (IIb), and 2-butyne (IIc).

The reaction of (I) with DCHCC of phenylacetylene (IIb) was carried out under conditions previously developed by us for the reaction of (IIb) with methylenecyclopropane [4] (heating in a sealed ampul in the presence of chromatographic adsorbents). Under these conditions, a rapid conversion of (I) was observed, but the cycloaddition product according to Khand-Pauson (IV) formed in a yield of ~2% only, while the main reaction product was (III) a cyclodimerization product of the initial (I) with inclusion of the CO molecule.



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