Chloro(4-methylpent-3-en-1-ynyl)carbene: IR spectrum, structure, photochemical transformations, and reactions with alkenes

V. D. Gvozdev, K. N. Shavrin, E. G. Baskir, M. P. Egorov, and O. M. Nefedov*

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 119991 Moscow, Russian Federation. Fax: +7 (499) 135 5328. E-mail: vgvozdev2006@yandex.ru

A comprehensive study of previously unknown chloro(4-methylpent-3-en-1-ynyl)carbene generated by photolysis of newly synthesized 5-chloroethynyl-3,3-dimethyl-3*H*-pyrazole was carried out both in low-temperature argon matrix and in solution at room temperature. Irradiation at 330 nm < λ < 380 nm causes the pyrazole to undergo a selective transformation to 1-chloro-3-diazo-5-methylhexa-4-en-1-yne. Photolysis of the latter at λ >520 nm leads to elimination of dinitrogen, thus producing the title carbene. Key structural parameters of this species were determined using matrix IR spectroscopy and quantum chemical calculations. It was established that the more stable state of the carbene is a singlet one. Further phototransformations of chloro(4-methylpent-3-en-1-ynyl)carbene lead to formation of isomeric 6-chloro-2-methylhexa-1,3-diene-5-yne. A preparative method for the synthesis of alkynylchlorocyclopropanes with yields up to 76% was proposed. It is based on photolysis of 5-chloroethynyl-3,3-dimethyl-3*H*-pyrazole in benzene in the presence of excess amounts of various alkenes. The possibility of using this approach for selective cyclopropanation of double bonds in the presence of hydroxyl groups in the substrate molecule was demonstrated taking 3-methylbut-2-enol as an example.

Key words: 3*H*-pyrazoles, photolysis, matrix isolation, matrix IR spectroscopy, alkynylchlorocarbenes, alkynylchlorocyclopropanes, addition reactions.

Carbenes are intermediate species with a lone pair on carbon. Similarly to ions and radicals, they also belong to key intermediates of numerous chemical reactions.[1—3] The most characteristic reaction of carbenes and related carbenoids, *viz.*, cycloaddition to alkenes, represents a direct and versatile method for the synthesis of various cyclopropanes.[4,5] Recently, these strained structures have attracted ever-increasing attention as building blocks for the synthesis of various classes of organic compounds.[6—8] Ethynylcarbenes, where the formal carbene center is adjacent to the triple bond, are of interest to both theoretical research (since this combination allows one to gain a better insight into the nature of conjugation) and synthetic chemistry (first of all, as key intermediates of the synthesis of strained ethynylcyclopropanes). These species and their isomers, *viz.*, cyclopropenylidenes, are involved in processes occurring in interstellar medium,[9,10] in combustion,[11,12] and during photolysis of polymers.[13,14] Highly reactive ethynylcarbenes readily enter into addition reactions and are used in synthetic organic chemistry for, *e.g.*, the synthesis of functionalized alkynylcyclopropanes[15—21] that possess valuable pharmacological properties[22—24] and play an important role in biochemical processes. Reactions of alkynylcyclopropanes proceeding with retention or transformation of the three-carbon rings are widely used[25—32] in the synthesis of carbo- and heterocyclic structures belonging to various classes of chemical compounds.

In the last three decades the simplest ethynylcarbene HC≡C(H)C: and its alkyl-substituted analogues have been intensively studied in a number of research groups by spectroscopic and theoretical methods.[33—38] The simplest mono- and dichloro-substituted ethynylcarbenes generated by photolysis of corresponding mono- and dichlorocyclopropenylidenes in inert matrices were detected by IR spectroscopy.[39] 5-Methylhexa-1,2,4-triene-1,3-diyl, a triplet carbene bearing both vinyl and ethynyl groups,[40] as well as a similar singlet carbene containing a methylthio fragment at the carbene center were studied earlier in our laboratory.[41,42] It was shown that substituents have a strong impact on the structure, spectral characteristics, and pathways of further photochemical transformations of these carbenes. Their thorough studies made it possible to observe both reactions typical of ethynylcarbenes and processes characteristic of methylthio- and vinyl-substituted carbenes.

In a continuation of these investigations it was of interest to study similar chlorocarbenes since they are of great importance for organic synthesis and widely used to obtain various cyclopropanes. Note that the presence of a halogen (*e.g.*, chlorine) atom at the carbene center favors stabilization of the singlet state of the carbene.[43—45] The aim of

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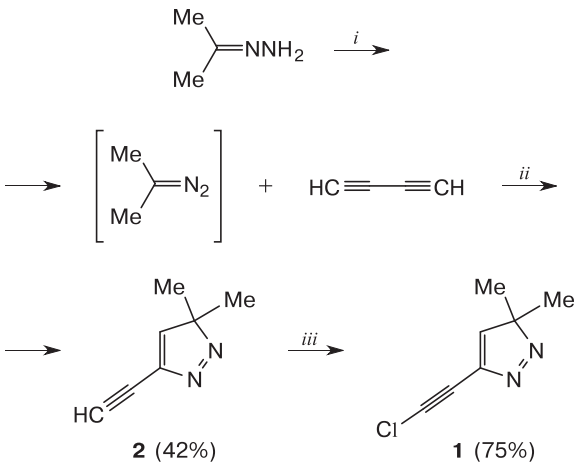
this work was to carry out a comprehensive study of (i) previously unknown chloro(4-methylpent-3-en-1-ynyl)-carbene and products of its photoisomerization by matrix IR spectroscopy and (ii) preparative-scale reactions of this carbene, which is photolytically generated in solution at room temperature, with various alkenes.

Results and Discussion

The starting pyrazole **1** was synthesized following Scheme 1. In the first stage, a solution of 2-diazopropane in diethyl ether prepared by the oxidation[46] of acetone hydrazone was subjected to the cycloaddition reaction with butadiyne synthesized following a known procedure.[47] The product, 5-ethynyl-3,3-dimethyl-3*H*-pyrazole (**2**), was isolated by vacuum sublimation followed by recrystallization from hexane in 42% yield (purity ~98%; no noticeable amount of the adduct of 2-diazopropane at both triple bonds as impurity). Pyrasole **2** was converted to the target compound **1** *via* chlorination of terminal alkynes,[48] which involves treatment of a substrate with a mixture of CCl_4 and potassium carbonate in the presence of catalytic amounts of tetrabutylammonium fluoride (TBAF). Unlike arylacetylenes that undergo quantitative conversion to corresponding chloroalkynes after 2 h under these conditions,[49] a complete conversion of ethynylpyrazole **2** required stirring for 96 h and the addition of extra amount of K_2CO_3 (see Scheme 1). As a result, chloroethynylpyrazole **1** was isolated in 75% yield (purity >95%).

Scheme 1

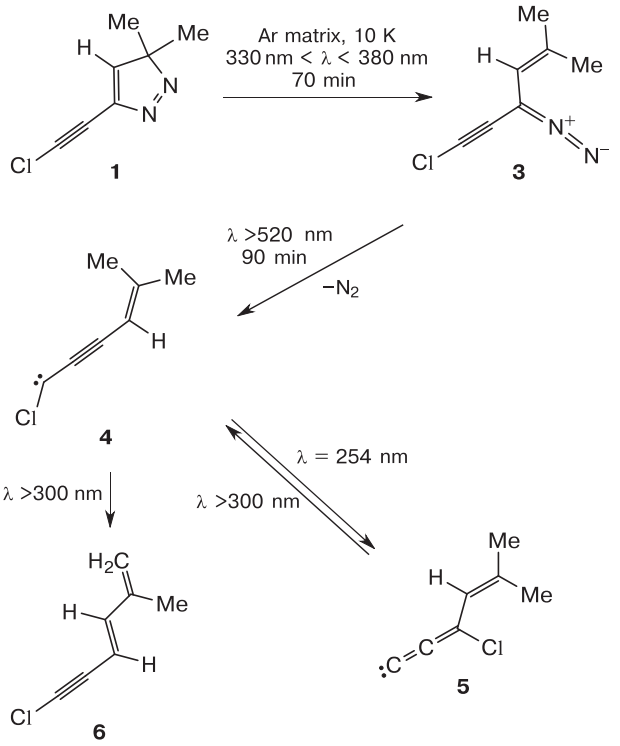


Reactants and conditions: *i*. HgO, KOH, Et_2O, 20 °C; *ii*. Et_2O, −50→20 °C; *iii*. CCl_4, Bu_4NF, K_2CO_3, 20 °C, 96 h.

Published data[50—52] and our experience[40—42] show that ethynyl-substituted pyrazoles are convenient selective sources for photogeneration of vinylethynylcarbenes.

Photolysis of pyrazole **1** isolated in Ar matrix with UV light (λ 350 nm, a 330—380 nm filter) for 70 min at 10 K led to a 95% decrease in the intensities of the bands at 2236, 2231, and 2225 cm^{-1} in the spectrum of the starting compound **1** and to the appearance of a very strong band at 2052 cm^{-1} corresponding to antisymmetric stretching vibration, ν_{as}, of the C≡C triple bond and diazo group. Besides, the intensities of about 30 new bands increase synchronously. Among these bands, there are two bands of medium intensity observed at 821 and 757 cm^{-1}. They are well reproduced in the B3LYP/aug-cc-pVTZ calculations of the 1-chloro-3-diazo-5-methylhex-4-en-1-yne conformer (**3**) with *syn*-arranged vinyl and diazo groups (Scheme 2, Fig. 1, curves *1* and *2*).

Scheme 2



According to TD DFT calculations using the M06 functional, a very strong band with a maximum at 284 nm and a very weak band near 561 nm should appear in the UV region of the spectrum of the diazo compound **3**. However, the decomposition proceeds much more selectively upon irradiation with visible light, just like in the case of a similar diazo compound bearing a methylthio substituent.[41] Photolysis of the diazo compound **3** at λ >520 nm for 90 min causes a more than 95% decrease in the intensities of the corresponding spectral bands and simultaneous appearance of new bands (Table 1, see also Fig. 1, curves *2* and *3*) that can be assigned to singlet chloro(4-methylpent-3-en-1-ynyl)carbene **4**, as follows from comparison with the results of the B3LYP/aug-cc-pVTZ calculations.

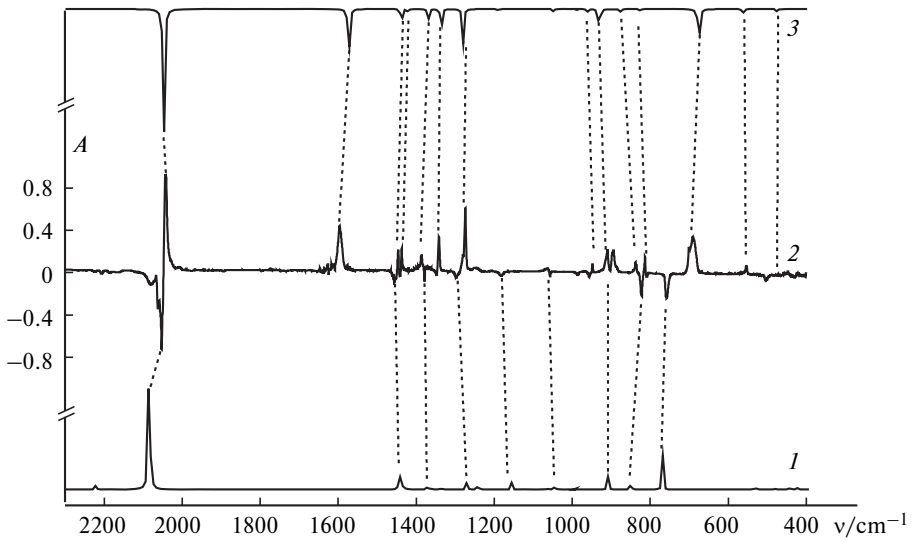
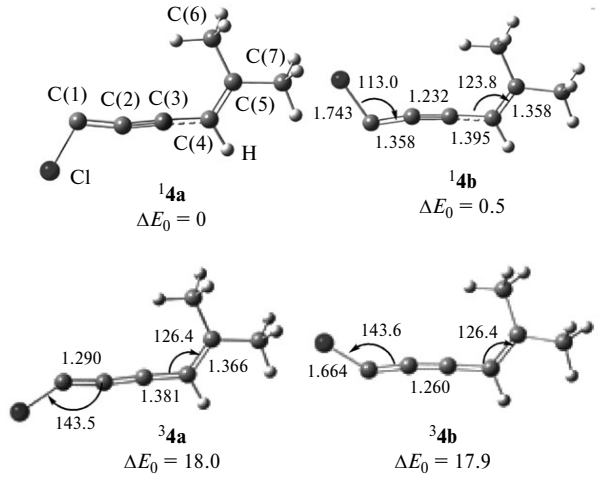


Fig. 1. Calculated IR spectrum of diazo compound **3** (*1*); difference IR spectrum (*2*) obtained by subtracting the IR spectrum ("down" bands) recorded before irradiation of the diazo compound **3** isolated in Ar matrix at 10 K from the spectrum ("up" bands) recorded after UV irradiation at $\lambda > 520$ nm for 90 min; and theoretically calculated IR spectrum of carbene **4** (*3*). The theoretical spectra obtained from B3LYP/aug-cc-pVTZ calculations were scaled using a scale factor of 0.9681 for $\nu > 1000$ cm^{-1} and a scale factor of 1.0028 for $\nu < 1000$ cm^{-1}.

As should be expected from analysis of the literature data,[53,54] the chlorine atom favors stabilization of the singlet species ^{1}**4** compared to the triplet one ^{3}**4**. According to G4(MP2) calculations (Fig. 2), the zero-point vibrational energy of the singlet species ^{1}**4a** is 18 kJ mol^{-1} lower than that of the triplet species ^{3}**4a** (ΔE_0 = 18 kJ mol^{-1}, *cf.* 0.6 kJ mol^{-1} obtained from B3LYP/aug-cc-pVTZ calculations). The energy difference between the carbenes *anti*-^{1}**4a** and *syn*-^{1}**4b** is very small (0.5 kJ mol^{-1}). These species have close geometric parameters (except the torsion angle) and spectroscopic characteristics. The geometric parameters of carbenes ^{1}**4** and ^{3}**4** differ appreciably. In the singlet species ^{1}**4**, the electron density is to a greater extent localized on the C(1) atom and the C(2)—C(3) bond is shortened, whereas in the triplet one, ^{3}**4**, the electron density is distributed between the C(1), C(2), and C(3) atoms, which manifests itself in elongation of the central bond, C(2)—C(3), and shortening of the adjacent bonds, C(1)—C(2) and C(3)—C(4).



^{1}**4a** $\Delta E_0 = 0$ ^{1}**4b** $\Delta E_0 = 0.5$

^{3}**4a** $\Delta E_0 = 18.0$ ^{3}**4b** $\Delta E_0 = 17.9$

Fig. 2. Geometric parameters of carbene **4** in the singlet (^{1}**4a**, ^{1}**4b**) and triplet (^{3}**4a**, ^{3}**4b**) states obtained from B3LYP/aug-cc-pVTZ calculations. The bond lengths are given in Å, the angles are given in degrees, and the energy difference ΔE_0 calculated using the G4(MP2) method with inclusion of zero-point vibrational energy is given in kJ mol^{-1}.

A very strong band at 2044 cm^{-1} observed in the IR spectrum (see Fig. 1, curve *2*; Table 1) corresponds to the ν(C≡C) stretching vibration and confirms that the lone pair is essentially localized on the C(1) atom and carbene **4** is a singlet species. A strong band at 1597 cm^{-1} corresponds to the ν(C=C) stretching vibration of the vinyl group. Bands corresponding to C—H stretching vibrations overlap with those of the starting compound and final products and appear as small changes of the spectra in the region of 3000 cm^{-1}. The bands of medium intensity at 1437, 1385, and 1341 cm^{-1} correspond to deformation vibrations of methyl groups. The bands at 1274 and 895 cm^{-1} correspond to stretching vibrations of the central carbon chain, while a very strong band at 695 cm^{-1} corresponds to the C—Cl stretching vibration.

The UV spectrum of carbene **4** obtained from TD DFT calculations includes absorption bands with maxima near 250 and 330 nm. Irradiation of the matrix at $\lambda = 254$ nm causes the appearance of new bands at 1962 and 1966 cm^{-1} in the IR spectrum. Additional irradiation with filtered light of a high-pressure lamp (300 nm $< \lambda <$ 400 nm) leads to weakening of these bands and to disappearance of the

Table 1. Frequencies in the IR spectrum of chloro(4-methylpent-3-en-1-ynyl)carbene (**4**): experimental values (Ar matrix, 10 K) and results of B3LYP/aug-cc-pVTZ calculations

Symmetry	Tentative assignment[a]	Experiment, frequency[b]/cm^{-1}	Calculations	
			Frequency[c]/cm^{-1}	Intensity[d]
A″	$\nu_{as}(C(6)H_3)$, $\nu_{as}(C(7)H_3)$		3035	3
A′	$\nu_s(C(6)H_3)$, $\nu_s(C(7)H_3)$, ν(C(4)H)	2992 w	3023	34
A′	$\nu_s(C(6)H_3)$, $\nu_s(C(7)H_3)$, ν(C(4)H)	2947 w	3015	8
A″	$\nu_{as}(C(6)H_3)_2$, $\nu_{as}(C(7)H_3)$	2918 w	2964	14
A″	$\nu_{as}(C(6)H_3)$, $\nu_{as}(C(7)H_3)$		2959	0
A′	$\nu_s(C(6)H_3)$, $\nu_s(C(7)H_3)$	2880 w	2926	25
A′	$\nu_s(C(6)H_3)$, $\nu_s(C(7)H_3)$		2919	2
A′	ν(C(2)≡C(3))	2044 vs	2048	672
A′	ν(C(4)=C(5))	1597 s	1574	232
A″	$\delta_{as}(C(6)H_3)$, $\delta_{as}(C(7)H_3)$	1446 m	1442	17
A′	$\delta_s(C(6)H_3)$, $\delta_s(C(7)H_3)$, δ(C(4)H)	1437 m	1436	29
A′	$\delta_s(C(6)H_3)$, $\delta_s(C(7)H_3)$		1422	8
A″	$\delta_{as}(C(6)H_3)$, $\delta_{as}(C(7)H_3)$		1420	1
A′	$\delta_s(C(6)H_3)$, $\delta_s(C(7)H_3)$	1385 m	1370	41
A′	$\delta_s(C(6)H_3)$, δ(C(4)H)		1368	2
A′	δ(C(4)H), $\delta_s(C(6)H_3)$, $\delta_s(C(7)H_3)$	1341 m	1337	93
A′	$\nu_s(C(1)C(2))$, $\nu_s(C(3)C(4))$, δ(C(4)H)	1274 s	1280	126
A′	$\rho_s(C(6)H_3)$, $\rho_s(C(7)H_3)$	1205 vw	1191	6
A″	$\rho_{as}(C(6)H_3)$, $\rho_{as}(C(7)H_3)$	1072 vw	1067	1
A′	$\rho_s(C(6)H_3)$, $\rho_s(C(7)H_3)$	1058 w	1050	8
A″	$\rho_{as}(C(6)H_3)$, $\rho_{as}(C(7)H_3)$		992	5
A′	$\rho_s(C(6)H_3)$, $\rho_s(C(7)H_3)$	947 w 909 m	962	9
A′	$\nu_s(C(1)C(2))$, $\nu_s(C(3)C(4))$	895 m	931	115
A″	ω(C(4)H)	838 m	876	15
A′	$\nu_s(C(5)C(6))$, $\nu_s(C(5)C(7))$	813 m	826	12
A′	ν(C(1)Cl), δ(C(1)C(2)C(3))	691 s	676	192
A″	ω(C(1)C(2)C(3))		567	1
A′	δ(C(3)C(4)C(5)), δ(C(2)C(1)Cl)	553 vw	563	19
A′	δ(C(1)C(2)C(3)), ν (C(1)Cl)	447 vw	476	9

[a] Notations for vibration types: ν stands for stretching, δ stands for scissoring, ρ stands for rocking, and ω stands for wagging vibrations.

[b] Notations for vibrational band intensities: vs stands for very strong, s stands for strong, m stands for medium, w stands for weak, and vw stands for very weak.

[c] Frequencies were obtained from B3LYP/aug-cc-pVTZ calculations using a scale factor of 0.9681 for the range of 3500—1000 cm^{-1} or 1.0028 for the range of 1000—500 cm^{-1}.

[d] Intensity in km mol^{-1}.

weak bands at 1141, 1036, 1030, and 738 cm^{-1}. By analogy with the simplest chlorovinylidene[39] all these bands can be assigned to isomeric vinylidenecarbene **5** (see Scheme 2). Splitting of the bands near 1960 cm^{-1}, which are characteristic of the allene group, is indicative of the formation of two isomeric species with *syn*- and *anti*-arrangement of the vinyl and allene moieties. The formation of compound **5** can be explained by migration of the Cl atom to the C(3) atom, which was observed earlier[39] for ethynylcarbenes.

Exposure of carbene **4** to light with 300 nm < λ < 450 nm leads to synchronous weakening of the spectral bands corresponding to this species and to the appearance of new bands at 2208, 1442, 1370, 1366, 1318, 1229, 1116, 1021, 993 (w), 957, 895, and 717 cm^{-1}. The intensities of these bands increase upon irradiation with unfiltered light of the high-pressure mercury lamp and thus additionally substantiate that the bands correspond to a stable end product. By analogy with the vinylethynylcarbenes studied earlier[40,41] and based on comparison with the results of quantum chemical calculations, these bands can be assigned to 6-chloro-2-methylhexa-1,3-dien-5-yne (**6**) (see Scheme 2). The stretching vibration of the triple bond in this compound, ν(C≡C), appears as a band at 2008 cm^{-1}, while the wagging vibrations of the CH and CH_2 groups in the diene moiety appear as strong bands at 957 and 895 cm^{-1}.

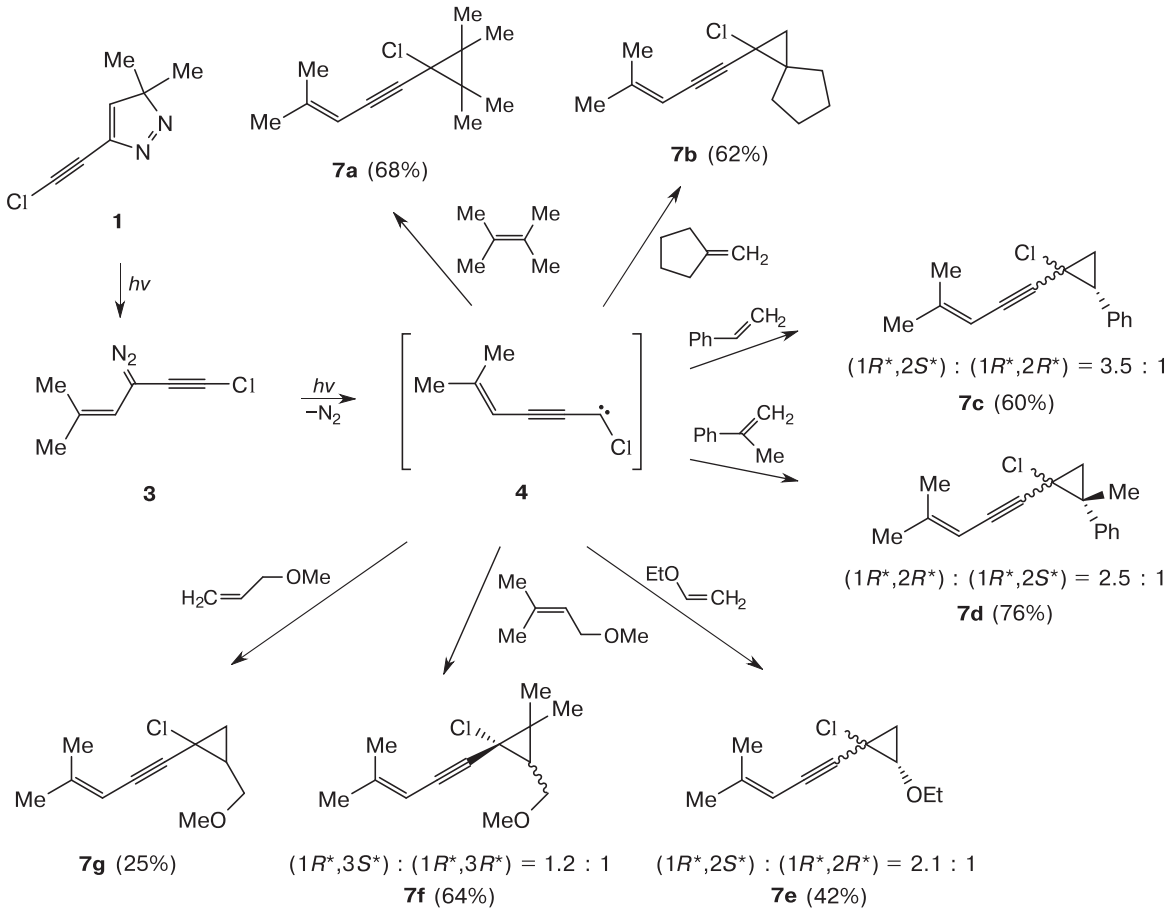
To assess the synthetic applicability of carbene **4** generated by the photodecomposition of pyrazole **1**, we studied this process in solution in the presence of various trapping agents.

Photolysis of pyrazole **1** under the action of unfiltered light of the 500-W high-pressure mercury lamp was carried out in benzene in the presence of 10—15-fold molar excess of an alkene (2,3-dimethylbut-2-ene, methylenecyclopentane, styrene, isopropenylbenzene, ethoxyethene, 3-methoxypropene, 1-methoxy-3-methylbut-2-ene) for 6—15 h at ~20 °C. The process leads to complete conversion of the starting compound accompanied by the evolution of nitrogen. According to NMR spectroscopy data, all the reactions yield corresponding chlorocyclopropanes **7a—g**. Note that adducts **7a—f** can be isolated in pure form (yields 42—76%) by flash chromatography on silica gel after evaporation of the solvent and excess alkene. As could be expected, reactions using asymmetrical (relative to the π-bond plane) olefins afford two stereoisomers **7c—g** that were characterized without separation (Scheme 3). Their configurations were determined by comparing the chemical shifts of the signals of the Me group in cyclopropane **7d** and protons in the phenyl (in **7c**), ethoxy (in **7e**) or methoxymethyl (in **7f**) substituents. From the published data[15,16] for other alkynylchlorocyclopropanes it follows that signals from these fragments *cis*-arranged relative to the Cl atom are shifted downfield owing to the deshielding effect of this atom.

The highest yields of cyclopropanes **7** were achieved using isopropenylbenzene having an electron-rich double bond as trapping agent. Styrene has a less nucleophilic double bond than isopropenylbenzene and reacts with slightly lower efficiency (yield of compound **7c** was 60%). Cyclopropanation in the presence of ethoxyethene is accompanied by resinification of the reaction mass and the yield of the corresponding ethoxycyclopropane **7e** is only 42%.

A comparison of the results of pyrazole **1** photolysis in the presence of 1-methoxy-3-methylbut-2-ene and 3-methoxypropene (they differ in two Me groups) also revealed a noticeable influence of electron-donor substituents at the alkene double bond. The reaction with the former alkene results in the corresponding cyclopropane **7f** in 64% yield, whereas the reaction with the latter affords a complex mixture containing ~25% of cyclopropane **7g** (based on NMR data for the reaction mass). Such a low yield prevented this compound from being isolated. It was identified in the reaction mass based on the characteristic pairs of signals of methoxymethyl and dimethylvinyl groups corresponding to two stereoisomers and on the presence of signals from protons at the trisubstituted cyclopropane ring that are consistent with the expected structure.

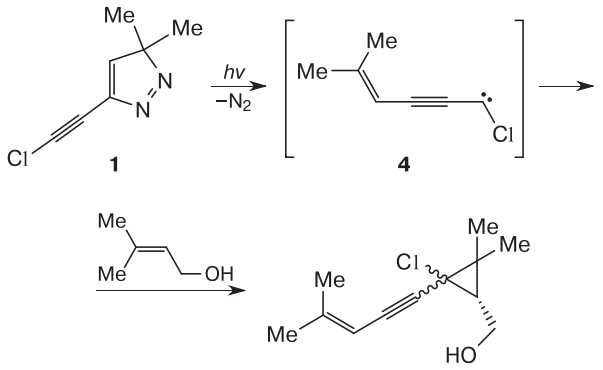
Scheme 3



These features are indicative of electrophilic character of carbene **4**, which agrees with the published data[15] for other alkynylhalocarbenes, and suggest that the species is prone to participation in side processes in the absence of active trapping agents. The latter differs carbene **4** from the previously studied[15,16] alkynylhalocarbenes with alkyl and aryl substituents at the triple bond that afford high yields of cyclopropane adducts with alkenes of different structure. Most probably, this feature is related to the side cycloaddition reactions of carbenes at the reactive trisubstituted double bond of the dimethylvinyl moiety. Note that structurally similar alkylthio(4-methylpent-3-en-1-ynyl)carbenes behave analogously (photolytic generation of these species was studied in our laboratory recently[41]).

Photolysis of pyrazole **1** in the presence of excess 3-methylbut-2-enol resulted in the corresponding alcohol **7h** (yield 56%) isolated as individual compound by vacuum microdistillation (Scheme 4). Based on the NMR spectra of the reaction mixture, no products of carbene **4** insertion into the O—H bond were formed. The possibility of selective cyclopropanation of the multiple bonds in the presence of hydroxyl groups in the substrate molecule is an important advantage of our method for generation of alkynylchlorocarbenes over the known solvolytic approaches.

Scheme 4



(1*R**,2*S**) : (1*R**,2*R**) = 1.15 : 1

7h (56%)

As shown above, the generation of carbene **4** proceeds *via* an intermediate, the diazo compound **3** representing the primary photoisomerization product of the starting pyrazole **1**. However, our attempts to detect the formation of **3** at ~20 °C by NMR monitoring of reaction mixtures during the photolysis of pyrazole **1** failed. Most probably, the formation of compound **3**, *i.e.*, the rate-limiting step of the overall process under our experimental conditions, proceeds much slower than subsequent elimination of nitrogen molecule. Carbene **4** thus generated readily reacts with alkenes.

Summing up, we proposed a simple and convenient photolytic approach to generation of previously unknown chloro(4-methylpent-3-en-1-ynyl)carbene. This labile species was detected by matrix isolation and characterized by IR spectroscopy. We established that carbene **4** has a singlet ground state and determined its geometric parameters and the pathways of further phototransformations. In addition, an original method was proposed for the synthesis of alkynylchlorocyclopropanes under mild conditions, based on preparative-scale photolysis of the previously unknown 5-chloroethynyl-3,3-dimethyl-3*H*-pyrazole.

Experimental

Experiments on matrix IR spectroscopy were carried out using a Displex CSW cryogenic closed-cycle system (APD Cryogenics, Inc., USA). The starting pyrazole was evaporated at 33 °C and co-deposited with argon (Kriotekhgaz, Moscow, Russia, 99.998%) taken in a large excess (~1 : 1000) onto the surface of a copper cube located inside the vacuum cryostat and cooled to 10 K through a high-vacuum Teflon® valve for 60—90 min. The cryostat was equipped with two optical windows, *viz.*, a KBr window for IR measurements and a CaF_2 window for UV photolysis. The substance under study and the inert gas was supplied using two independent lines. The temperature of the cooled surface was measured using a DT-470 silicon diode and a Lake Shore model 330-11 temperature controller. Photolysis of the matrix was carried out using a Philips low-pressure mercury lamp ($\lambda = 254$ nm, 11 W) or a DRSh-500 high-pressure mercury lamp (500 W) equipped with a water filter and a set of cutoff filters. Infrared spectra were recorded on a Bruker IFS-113v FT-IR spectrometer (Germany) equipped with a DTGS detector in the range of 4000—400 cm^{-1} in the reflectance mode with a resolution of 0.5 cm^{-1}.

Quantum chemical calculations were carried out using the Gaussian program.[55] The geometries and vibrational spectra were calculated using the B3LYP functional[56,57] and the aug-cc-pVTZ basis set.[58—60] Theoretical UV spectra were obtained from TD DFT calculations with the M06 functional[61] and the Def2TZVP basis set.[62] The anharmonicity effects in the theoretical IR spectra were included using the following scale factors: 0.9681 for the spectral range of 3500—1000 cm^{-1} and 1.0028 for the range of 1000—500 cm^{-1}.[63] Thermodynamic parameters were evaluated by the G4(MP2) method.[64,65] The ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer in $CDCl_3$ with the residual signal of the solvent as internal reference.

High-resolution mass spectra were recorded on a Bruker micrOTOF II instrument (positive ion mode, electrospray ionization, capillary voltage 4500 V). The mass scan range was m/z = 50—3000 D; both external and internal calibrations (Electrospray Calibrant Solution (Fluka)) were used. Solutions in acetonitrile were injected *via* a syringe, the flow rate was 3 μL min^{-1}, nitrogen was used as nebulizer gas (4 L min^{-1}), and the interface temperature was 180 °C.

Alkenes, except 1-methoxy-3-methylbut-2-ene, were commercially available products used as is. 1-Methoxy-3-methylbut-2-ene was synthesized by methylation of 3-methylbut-2-en-1-ol (prenyl alcohol) with iodomethane following a known procedure.[66] Butadiyne was synthesized by dehydrochlorination of 1,4-dichlorobut-2-yne under the conditions described in literature[47] and stored at −20 °C as a solution in diethyl ether, which was consumed within a few days. Acetone hydrazone was synthesized following a known procedure.[67]

5-Ethynyl-3,3-dimethyl-3*H*-pyrazole (2). In a three-neck flask equipped with a magnetic stir bar, dropping funnel and connected to a trap cooled with a mixture of dry ice and propan-2-ol, a suspension of red mercuric oxide (31.2 g, 114 mmol) in diethyl ether (70 mL) was prepared. Then, a 3 *M* KOH solution in ethanol (2.3 mL, 6.9 mmol) was added. The pressure in the system was reduced to 250—350 mbar and acetone hydrazone

(8.07 g, 112 mmol) was added dropwise over a period of 15 min. Then, the pressure was reduced again to ~15 mbar and the reaction mass was completely recondensed into the trap without heating (on a water bath at ~20 °C). A bright red solution of 2-diazopropane in ether was obtained. As the recondensation was completed, the solution was added to a solution of butadiyne (4 g, 80 mmol) in diethyl ether (50 mL) cooled to −50 °C; this was accompanied by discoloration, precipitation, and evolution of a small amount of nitrogen.

The solution thus obtained was warmed up to ~20 °C, the solvent was evaporated. Vacuum sublimation of the residue (12 mbar, bath temperature 80—100 °C) followed by recrystallization from hexane afforded pyrazole **2** (4.03 g, 42%) as bulk white crystals. The spectral data for the product were identical to those reported earlier.[68]

5-Chloroethynyl-3,3-dimethyl-3*H*-pyrazole (1). A mixture of pyrazole **2** (1.5 g, 12.5 mmol), CCl_4 (15 mL, 155 mmol), tetrabutylammonium fluoride (0.49 g, 1.87 mmol), and anhydrous freshly powdered potassium carbonate (3.45 g, 25 mmol) was stirred for 48 h using a magnetic stir bar at ~20 °C. Then, an additional amount of potassium carbonate (1.5 g, 10.8 mmol) was added and the mixture was stirred for an additional 48 h. The excess CCl_4 was evaporated and water (20 mL) and diethyl ether (30 mL) was added to the residue. The organic layer was separated, washed with water, dried over Na_2SO_4, and concentrated. The residue contained brown crystals. Vacuum sublimation of the crystals (3 mbar, bath temperature 80—100 °C) gave a light-yellow crystalline product (1.45 g, 75%) that was spectroscopically identified as pyrazole **1** (purity >95%).

^{1}H NMR, δ: 1.45 (s, 6 H, 2 CH_3); 7.01 (s, 1 H, =CH). ^{13}C NMR, δ: 20.3 (2 CH_3); 61.5 (C≡CCl); 73.1 (C≡CCl); 94.9 ($C(CH_3)_2$); 137.4 (CH=C); 148.3 (CH=C). Mass spectrum: found *m/z* 155.0376, 157.0346 $[M + H]^+$; calculated for $C_7H_8ClN_2^+$ 155.0371, 157.0341.

Synthesis of 1-chloro-1-(4-methylpent-3-en-1-ynyl)cyclopropanes 7a—f from pyrazole 1 (general procedure). A solution of pyrazole **1** (62 mg, 0.4 mmol) in a mixture of 4—6 mmol of the corresponding alkene (2,3-dimethylbut-2-ene, methylenecyclopentane, styrene, isopropenylbenzene, ethoxyethene, 1-methoxy-3-methylbut-2-ene) and benzene (0.5 mL) was photolyzed using unfiltered light of the DRSh-500 high-pressure mercury lamp in a quartz cuvette for 6—15 h until complete conversion of the starting pyrazole **1** (monitoring by NMR spectra). Then, the excess alkene and benzene was evaporated *in vacuo* and the dark mass that formed was dissolved in petroleum ether and passed through a silica gel layer. Subsequent evaporation of the solvent gave products **7**.

1-Chloro-2,2,3,3-tetramethyl-1-(4-methylpent-3-en-1-ynyl)-cyclopropane (7a) was synthesized from 2,3-dimethylbut-2-ene in 68% yield. ^{1}H NMR, δ: 1.21 (s, 6 H, 2 CH_3); 1.22 (s, 6 H, 2 CH_3); 1.81 (br.s, 3 H, CH_3); 1.90 (br.s, 3 H, CH_3); 5.35 (br.s, 1 H, =CH). ^{13}C NMR, δ: 18.9 (2 CH_3); 19.9 (2 CH_3); 21.2 (2 $C(CH_3)_2$); 24.9, 29.9 (=$C(CH_3)_2$); 50.6 (CCl); 83.6, 89.7 (C≡C); 105.1 (CH=); 148.7 (=$C(CH_3)_2$). Mass spectrum: found *m/z* 233.1068, 235.1042 $[M + Na]^+$; calculated for $C_{13}H_{19}ClNa^+$ 233.1067, 235.1039.

1-Chloro-1-(4-methylpent-3-en-1-ynyl)spiro[2.4]heptane (7b) was synthesized from methylenecyclopentane in 62% yield. ^{1}H NMR, δ: 1.19 (d, 1 H, CHH in *cyclo*-C_3, J = 5.7 Hz); 1.24 (d, 1 H, CHH in *cyclo*-C_3, J = 5.7 Hz); 1.41—1.59 (m, 2 H, *cyclo*-C_5); 1.60—1.72 (m, 4 H, *cyclo*-C_5); 1.73 (br.s, 3 H, CH_3); 1.81 (br.s, 3 H, CH_3); 1.90—2.11 (m, 2 H, *cyclo*-C_5); 5.23 (br.s, 1 H, =CH). ^{13}C NMR, δ: 21.2, 24.8, 26.8, 26.9, 32.1, 33.2, 34.4 (C(2), C(4), C(5), C(6), C(7), =$C(CH_3)_2$); 37.3 (C(3)); 41.1 (C(1)); 82.4, 90.8 (C≡C); 104.8 (CH=); 149.3 (=$C(CH_3)_2$). Mass spectrum: found *m/z* 231.0905, 233.0888 $[M + Na]^+$; calculated for $C_{13}H_{17}ClNa^+$ 231.0911, 233.0882.

[2-Chloro-2-(4-methylpent-3-en-1-ynyl)cyclopropyl]benzene (7c) was synthesized from styrene in 60% yield as a mixture of (1*R**,2*S**) and (1*R**,2*R**) stereoisomers in a 3.1 : 1 ratio. Mass spectrum: found *m/z* 231.0930, 233.0898 $[M + H]^+$; calculated for $C_{15}H_{16}Cl^+$ 231.0935, 233.0905.

(1*R,2*S**)-7c.** ^{1}H NMR, δ: 1.54 (br.s, 3 H, =CCH_3); 1.74 (br.s, 3 H, =CCH_3); 1.83 (dd, 1 H, CHH in *cyclo*-C_3, J_1 = 6.4, J_2 = 8.1 Hz); 1.91 (dd, 1 H, CHH in *cyclo*-C_3, J_1 = 6.4 Hz, J_2 = 10.1 Hz); 2.89 (dd, 1 H, CHPh, J_1 = 8.1 Hz, J_2 = 10.1 Hz); 5.16 (br.s, 1 H, =CH); 7.24—7.41 (m, 5 H, Ph). ^{13}C NMR, δ: 20.7, 24.8 (=$C(CH_3)_2$); 25.4 (CH_2); 35.7 (CHPh); 45.4 (CCl); 84.2, 88.5 (C≡C); 104.4 (CH=); 127.1 (C(4), Ph); 128.2, 128.4 (C(2), C(3), C(5), C(6), Ph); 136.1 (C^1, Ph); 149.9 (=$C(CH_3)_2$).

(1*R,2*R**)-7c.** ^{1}H NMR, δ: 1.80 (dd, 1 H, CHH in *cyclo*-C_3, J_1 = 6.3 Hz, J_2 = 8.1 Hz); 1.87 (br.s, 3 H, =CCH_3); 1.88 (dd, 1 H, CHH in *cyclo*-C_3, J_1 = 6.3 Hz, J_2 = 9.8 Hz); 1.96 (br.s, 3 H, =CCH_3); 2.81 (dd, 1 H, CHPh, J_1 = 8.3 Hz, J_2 = 9.8 Hz); 5.35 (br.s, 1 H, =CH); 7.24—7.41 (m, 5 H, Ph). ^{13}C NMR, δ: 21.2, 24.9 (=$C(CH_3)_2$); 25.4 (CH_2); 34.1 (CHPh); 43.9 (CCl); 80.0, 92.5 (C≡C); 104.5 (CH=); 127.3 (C(4), Ph); 127.7, 128.2 (C(2), C(3), C(5), C(6), Ph); 135.2 (C(1), Ph); 150.1 (=$C(CH_3)_2$).

[2-Chloro-1-methyl-2-(4-methylpent-3-en-1-ynyl)cyclopropyl]benzene (7d) was synthesized from isopropenylbenzene in 76% yield as a mixture of (1*R**,2*R**)- and (1*R**,2*S**)-stereoisomers in a 2.5 : 1 ratio. Mass spectrum: found *m/z* 245.1099, 247.1074 $[M + H]^+$; calculated for $C_{16}H_{18}Cl^+$ 245.1092, 247.1063.

(1*R,2*R**)-7d.** ^{1}H NMR, δ: 1.40 (br.s, 3 H, =CCH_3); 1.48 (d, 1 H, CHH in *cyclo*-C_3, J = 6.1 Hz); 1.68 (br.s, 3 H, =CCH_3); 1.71 (s, 3 H, CH_3); 1.94 (d, 1 H, CHH in *cyclo*-C_3, J = 6.1 Hz); 5.07 (br.s, 1 H, =CH); 7.20—7.40 (m, 5 H, Ph). ^{13}C NMR, δ: 20.6, 24.6, 24.7 (=$C(CH_3)_2$, CH_3); 31.2 (CH_2); 35.7 ($C(CH_3)$Ph); 42.0 (CCl); 84.0, 90.7 (C≡C); 104.5 (CH=); 126.9 (C(4), Ph); 128.3, 128.5 (C(2), C(3), C(5), C(6), Ph); 142.2 (C(1), Ph); 149.3 (=$C(CH_3)_2$).

(1*R,2*S**)-7d.** ^{1}H NMR, δ: 1.54 (d, 1 H, CHH in *cyclo*-C_3, J = 6.1 Hz); 1.66 (s, 3 H, CH_3); 1.83 (br.s, 3 H, =CCH_3); 1.87 (d, 1 H, CHH in *cyclo*-C_3, J = 6.1 Hz); 1.97 (br.s, 3 H, =CCH_3); 5.39 (br.s, 1 H, =CH); 7.20—7.40 (m, 5 H, Ph). ^{13}C NMR, δ: 21.2, 24.9, 25.7 (=$C(CH_3)_2$, CH_3); 31.3 (CH_2); 35.8 ($C(CH_3)$Ph); 40.4 (CCl); 82.5, 90.2 (C≡C); 104.8 (CH=); 127.1 (C(4), Ph); 128.3, 129.2 (C(2), C(3), C(5), C(6), Ph); 141.5 (C(1), Ph); 149.7 (=$C(CH_3)_2$).

1-Chloro-2-ethoxy-1-(4-methylpent-3-en-1-ynyl)cyclopropane (7e) was synthesized from ethoxyethene in 42% yield as a mixture of (1*R**,2*S**)- and (1*S**,2*S**)-stereoisomers in a 2.1 : 1 ratio. Mass spectrum: found *m/z* 199.0887, 201.0856 $[M + H]^+$; calculated for $C_{11}H_{16}ClO^+$ 199.0884, 201.0855; found *m/z* 221.0707, 223.0670 $[M + Na]^+$; calculated for $C_{11}H_{15}ClNaO^+$ 221.0704, 223.0675.

(1*R,2*S**)-7e.** ^{1}H NMR, δ: 1.26 (t, 3 H, OCH_2CH_3, J = 7.0 Hz); 1.55 (d, 2 H, CH_2 in *cyclo*-C_3, J = 6.2 Hz); 1.82 (br.s, 3 H, =CCH_3); 1.90 (br.s, 3 H, =CCH_3); 3.63 (dd, CHOEt, J_1 = 6.2 Hz, J_2 = 6.2 Hz); 3.74 (dq, 1 H, OCHH, J_1 = 9.3 Hz, J_2 = 7.0 Hz); 3.89 (dq, 1 H, OCHH, J_1 = 9.3 Hz, J_2 = 7.0 Hz); 5.31 (br.s, 1 H, =CH). ^{13}C NMR, δ: 15.0 (OCH_2CH_3); 21.1 (CH_2 in *cyclo*-C_3); 24.9, 27.3 (=$C(CH_3)_2$); 34.0 (CCl); 65.3, 66.9 ($CHOCH_2CH_3$, $CHOCH_2CH_3$); 82.9, 87.9 (C≡C); 104.7 (CH=); 149.9 (=$C(CH_3)_2$).

(1*S,2*S**)-7e.** ^{1}H NMR, δ: 1.29 (t, 3 H, OCH_2CH_3, J = 7.0 Hz); 1.41 (dd, 1 H, CHH in *cyclo*-C_3, J_1 = 7.4 Hz, J_2 = 5.2 Hz); 1.54 (dd, 1 H, CHH in *cyclo*-C_3, J_1 = 7.5 Hz, J_2 = 7.4 Hz); 1.80 (br.s, 3 H, =CCH_3); 1.88 (br.s, 3 H, =CCH_3); 3.45 (dd, CHOEt, J_1 = 7.5 Hz, J_2 = 5.2 Hz); 3.59—3.72 (m, 1 H,

OCHH); 3.77 (dq, 1 H, OCHH, J_1 = 9.3 Hz, J_2 = 7.0 Hz); 5.18 (br.s, 1 H, =CH). ^{13}C NMR, δ: 14.9 (OCH_2CH_3); 21.2 (CH_2 in *cyclo*-C_3); 24.9, 26.3 (=C(CH_3)$_2$); 34.7 (CCl); 63.0, 67.2 ($CHOCH_2CH_3$, $CHOCH_2CH_3$); 80.7, 90.8 (C≡C); 104.4 (CH=); 150.2 (=C(CH_3)$_2$).

1-Chloro-3-methoxymethyl-2,2-dimethyl-1-(4-methylpent-3-en-1-ynyl)cyclopropane (7f) was synthesized from 1-methoxy-3-methylbut-2-ene in 64% yield as a mixture of (1*R**,3*S**)- and (1*R**,3*R**)-stereoisomers in a 1.2 : 1 ratio. Mass spectrum: found *m/z* 227.1204, 229.1180 $[M + H]^+$; calculated for $C_{13}H_{20}ClO^+$ 227.1197, 229.1168; found *m/z* 244.1471, 246.1443 $[M + NH_4]^+$; calculated for $C_{13}H_{23}ClNO^+$ 244.1463, 246.1434.

(1*R, 3*S**)-7f.** ^{1}H NMR, δ: 1.23 (s, 3 H, CH_3); 1.24 (s, 3 H, CH_3); 1.35 (dd, 1 H, $CHCH_2OCH_3$, J_1 = 6.9 Hz, J_2 = 6.5 Hz); 1.83 (br.s, 3 H, =CCH_3); 1.91 (br.s, 3 H, =CCH_3); 3.39 (s, 3 H, OCH_3); 3.54 (dd, 1 H, $CHCHHOCH_3$, J_1 = 11.0 Hz, J_2 = 6.5 Hz); 3.60 (dd, 1 H, $CHCHHOCH_3$, J_1 = 11.0 Hz, J_2 = 6.9 Hz); 5.34 (br.s, 1 H, =CH). ^{13}C NMR, δ: 17.8 (CH_3); 21.1 (CH_3); 24.0, 25.1 (=C(CH_3)$_2$); 28.9 (C(CH_3)$_2$ in *cyclo*-C_3); 38.5 ($CHCH_2OCH_3$); 44.7 (CCl); 58.5 (OCH_3); 69.5 (CH_2OCH_3); 81.9, 90.7 (C≡C); 104.8 (CH=); 149.7 (=C(CH_3)$_2$).

(1*R, 3*R**)-7f.** ^{1}H NMR, δ: 1.35 (s, 3 H, CH_3); 1.40 (s, 3 H, CH_3); 1.48 (dd, 1 H, $CHCH_2OCH_3$, J_1 = 7.1 Hz, J_2 = 6.9 Hz); 1.82 (br.s, 3 H, =CCH_3); 1.89 (br.s, 3 H, =CCH_3); 3.40 (s, 3 H, OCH_3); 3.46 (dd, 1 H, $CHCHHOCH_3$, J_1 = 10.8 Hz, J_2 = 7.1 Hz); 3.63 (dd, 1 H, $CHCHHOCH_3$, J_1 = 10.8 Hz, J_2 = 6.9 Hz); 5.31 (br.s, 1 H, =CH). ^{13}C NMR, δ: 16.7 (CH_3); 21.1 (CH_3); 24.7, 24.8 (=C(CH_3)$_2$); 27.7 (C(CH_3)$_2$ in *cyclo*-C_3); 36.3 ($CHCH_2OCH_3$); 44.9 (CCl); 58.5 (OCH_3); 68.9 (CH_2OCH_3); 84.4, 87.7 (C≡C); 104.8 (CH=); 149.3 (=C(CH_3)$_2$).

[2-Chloro-3,3-dimethyl-2-(4-methylpent-3-en-1-ynyl)cyclopropyl]methanol (7h). A solution of pyrazole **1** (77 mg, 0.5 mmol) in a mixture of 3-methylbut-2-enol (430 mg, 5 mmol) and benzene (0.3 mL) was photolyzed with unfiltered light of the DRSh-500 high-pressure mercury lamp in a quartz cuvette over a period of 11 h. Then, volatile substances were evaporated *in vacuo* and subsequent vacuum microdistillation of the dark residue (2 mbar, bath temperature 130—140 °C) gave a viscous fluid (59 mg, 56%) identified as compound **7h** (mixture of stereoisomers in a 1.15 : 1 ratio). Mass spectrum: found *m/z* 213.1046, 215.1026 $[M + H]^+$; calculated for $C_{12}H_{18}ClO^+$ 213.1041, 215.1022; found *m/z* 230.1311, 232.1280 $[M + NH_4]^+$; calculated for $C_{12}H_{21}ClNO^+$ 230.1306, 232.1276.

(1*R,2*S**)-7h.** ^{1}H NMR, δ: 1.22 (s, 3 H, CH_3); 1.24 (s, 3 H, CH_3); 1.38 (dd, 1 H, $CHCH_2OH$, J_1 = 6.6 Hz, J_2 = 7.8 Hz); 1.80 (br.s, 3 H, =CCH_3); 1.87 (br.s, 3 H, =CCH_3); 2.24 (br.s, 1 H, OH); 3.71 (dd, 1 H, $CHCHHOH$, J_1 = 11.8 Hz, J_2 = 6.6 Hz); 3.78 (dd, 1 H, $CHCHHOH$, J_1 = 11.8 Hz, J_2 = 7.8 Hz); 5.29 (br.s, 1 H, =CH). ^{13}C NMR, δ: 17.9 (CH_3); 21.1 (CH_3); 24.0, 25.3 (=C(CH_3)$_2$); 29.7 (C(CH_3)$_2$ in *cyclo*-C_3); 41.2 ($CHCH_2OH$); 44.5 (CCl); 60.4 (CH_2OH); 84.3, 87.6 (C≡C); 104.6 (CH=); 149.4 (=C(CH_3)$_2$).

(1*R,2*R**)-7h.** ^{1}H NMR, δ: 1.32 (s, 3 H, CH_3); 1.37 (s, 3 H, CH_3); 1.52 (dd, 1 H, $CHCH_2OH$, J_1 = 6.9 Hz, J_2 = 8.08 Hz); 1.79 (br.s, 3 H, =CCH_3); 1.86 (br.s, 3 H, =CCH_3); 2.24 (br.s, 1 H, OH); 3.74—3.81 (m, 2 H, $CHCH_2OH$); 5.30 (br.s, 1 H, =CH). ^{13}C NMR, δ: 16.7 (CH_3); 21.1 (CH_3); 24.8, 24.9 (=C(CH_3)$_2$); 28.5 (C(CH_3)$_2$ in *cyclo*-C_3); 38.9 ($CHCH_2OH$); 45.1 (CCl); 59.2 (CH_2OH); 82.1, 90.7 (C≡C); 104.7 (CH=); 149.9 (=C(CH_3)$_2$).

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