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A Highly Delocalized Triplet Carbene, 5-Methylhexa-1,2,4-triene-1,3-diyl: Matrix IR Identification, Structure, and Reactions

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Abstract: The first representative of highly delocalized triplet carbenes bearing both vinyl and ethynyl groups at the formal carbene center, 5-methylhexa-1,2,4-triene-1,3-diyl, has been generated in a low-temperature Ar matrix upon UV photolysis of 5-ethynyl-3,3-dimethyl-3*H*-pyrazole and detected by FTIR spectroscopy. The transformation of 3*H*-pyrazole into the carbene proceeds in two stages via intermediate 3-diazo-5-methylhex-4-en-1-yne. According to DFT PBE/TZ2P calculations, 5-methylhexa-1,2,4-triene-1,3-diyl possesses an effective conjugation along the five-carbon chain and shows the same type of the bond length alternation as the $HC_{4m+1}H$-type polyacetylenic carbenes. The carbene readily reacts with molecular oxygen, producing carbonyl oxides, which undergo further transformations typical of this type of compound upon irradiation in the UV−visible region. Two major photolytic rearrangements of 5-methylhexa-1,2,4-triene-1,3-diyl represent reactions characteristic of vinyl carbenes and resulting in the formation of 1-ethynyl-3,3-dimethylcyclopropene and 3*E*-2-methylhexa-1,3-dien-5-yne. A minor reaction is that typical of ethynylcarbenes; this leads to the formation of singlet 2-(2-methylpropenyl)cyclopropenylidene. Fragments of singlet and triplet potential energy surfaces of the C_7H_8 system have been explored in DFT PBE/TZ2P calculations.

Introduction

Despite the long history of carbene chemistry, carbenes still remain among the most attractive organic intermediates, often challenging the modern understanding of the bonding.[1] During the last two decades, much attention has been paid to the investigation of conjugated carbenes such as vinyl- and ethynylcarbenes by different physicochemical methods and quantum-chemical calculations. This stems from both fundamental interest in an unusual electronic structure of such carbenes and their importance as the key intermediates in some chemical reactions.

Propynylidene (propargylene, HCCCH), the simplest ethynylcarbene, is an important intermediate in the formation of thin diamond-like carbon films,[2] combustion processes,[3,4] and astrochemistry.[5,6] Its congeners, polyacetylenic carbenes, HC_nH, $n =$ odd, are also of remarkable astrophysical interest.[7,8] Besides, they are considered as intermediates in some polymerization processes leading to polyacetylenes and are models of conjugated polyyne chains containing carbene centers as the defects responsible for the unique magnetic and optical properties of these chains.[9] A series of our works has been devoted to the investigation of ethynylcarbenes of new types and their applications in organic synthesis.[10−15]

The spatial and electronic structure of propargylene had been under discussion since its first observation in 1960,[16] and only recently was this discussion reconciled.[17,18] It has been shown that propargylene in its triplet ground state has C_2-symmetric W-shaped structure with large CCH and CCC angles (162° and

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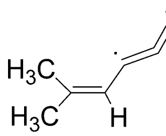
174° at CCSD(T)/cc-pVTZ level) and with the C−H bonds remarkably shifted from the plane of the carbon skeleton to opposite directions (dihedral HCCC angle is 143°).[18] The nonbonding electrons are symmetrically delocalized over the three carbon atoms, thus determining the diradical character of this species.[17,19] Although propargylene has both spatial and electronic structures differing from those of classical triplet carbenes, its reactivity is quite typical of the latter.[16] Similar conclusions regarding the electronic structure have been made for related triplet PhCCCH[9,20] and PhCCCPh,[20] although the latter species possesses a linear geometry, and, in both species, the phenyl groups participate in delocalization of the unpaired electrons.

According to quantum-chemical calculations, elongation of the propargylene chain by triple-bonded carbon−carbon fragments results in an interesting effect: the $HC_{4m+1}H$ species (m = nonnegative integer) are characterized by somewhat higher localization of nonbonding electrons on the central carbon atom and by elongated bonds between this and the adjacent atoms; that is, these species resemble carbenes more than diradicals, while the $HC_{4m+3}H$ species exhibit somewhat higher localization of nonbonding electrons on the carbon atoms neighboring to the central carbon atom and somewhat shortened bonds between these and the central atom; that is, they resemble cumulene and have more pronounced diradical character.[21,22] Experimental study of HC_5H (i.e., $HC_{4m+1}H$ with $m = 1$) and comparison of its spectroscopic and chemical properties with those known for HC_3H (i.e., $HC_{4m+3}H$ with $m = 0$) support this prediction.[23]

Vinylcarbenes play the key role in thermal[24,25] and photochemical[25] isomerization of cyclopropene and participate in some other reactions of synthetic value.[26] Similar to propargylene, parent propenylidene and its congeners with methyl and aryl substituents have electronic triplet ground state with one of the unpaired electrons being delocalized over the π system, similarly to that of allyl radical,[27−29] and with the second unpaired electron being localized in the σ orbital at the carbene center.[30−35] Such delocalization gives an unusual stability of methylvinylcarbene $Me(H_2C{=}CH)C$: to 1,2-H shift from the methyl group, which made it possible to observe this species in low-temperature matrices of noble gases,[34] whereas all attempts to observe methylcarbene under similar conditions failed.[36]

The following question naturally emerges from the above consideration: what would be an effect of the presence of both vinyl and ethynyl groups at the carbene center, and how would it affect the delocalization of nonbonding electrons and chemical properties of the carbene? Here, we report the first IR-spectroscopic observation of such ethynylvinylcarbene, 5-methylhexa-1,2,4-triene-1,3-diyl (**1**), research of its photochemical rearrangements and its interaction with oxygen, as well as DFT study of **1** and species located close to it on the potential energy surface. On the basis of the obtained data, we show that the carbene is characterized by a high degree of delocalization of the nonbonding electrons displaying the bond length alternation typical of the $HC_{4m+1}H$ species. At the same time, both terminal C atoms of the propargylenic fragment of the carbene reveal approximately equal reactivities toward oxygen, making this species similar to propargylene, HC_3H, rather than to pentadiynylidene, HC_5H. The presence of the formal vinyl group in the structure of **1** results in that its two major photolytic rearrangements correspond to those typical of vinyl carbenes and only the minor reaction is that characteristic of ethynylcarbenes.



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Results and Discussion

Generation and Identification of 5-Methylhexa-1,2,4-triene-1,3-diyl (1) and 1,4-Dideutero-5-methylhexa-1,2,4-triene-1,3-diyl (d_2-1). 3*H*-Pyrazoles are convenient photochemical precursors of vinylcarbenes.[30,32,37−40] Particularly, carbene **1** has been trapped by furan, vinyl ether, and cyclopentadiene upon photolysis of 5-ethynyl-3,3-dimethyl-3*H*-pyrazole (**2**) in solution.[41,42] Therefore, 3*H*-pyrazole **2** synthesized according to the published method[42] has been used as a photolytic precursor of **1** in the present study.

Because the 3*H*-pyrazole **2** exhibits two UV bands[42] with maxima at 360 and 260 nm (Supporting Information), it was easily photolyzed in argon matrices by light within 230−550 nm, resulting in the formation of the same products, although in different ratios depending on the wavelength used. Predominant formation of a single product was observed only upon photolysis of **2** (and also its dideuterated derivative, **d_2-2**) at 320−390 nm for 10−15 min. This product shows a very strong absorption at 2051 cm^{-1} (or 2078 cm^{-1} for photolysis of **d_2-2**) characteristic of N−N stretching vibration in diazo compounds and has readily been identified as 3-diazo-5-methylhex-4-en-

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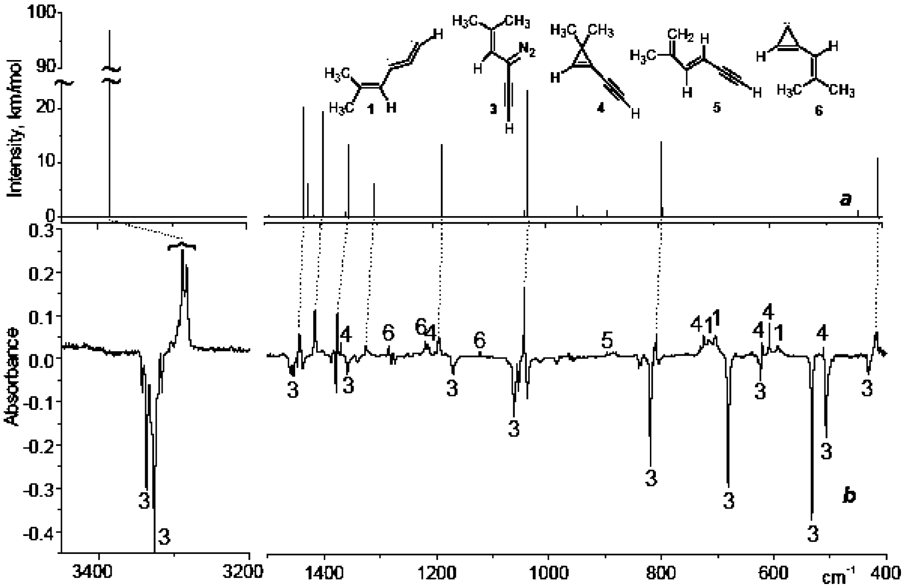
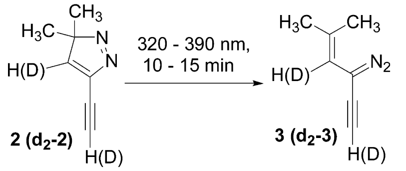


Figure 1. IR spectrum of 5-methylhexa-1,2,4-triene-1,3-diyl (**1**) calculated by means of DFT PBE/TZ2P (a); difference between the IR spectra obtained after photolysis of 3-diazo-5-methylhex-4-en-1-yne (**3**) at 313 nm for 55 min and before the photolysis; the bands with positive absorptions are enhanced upon the photolysis, while those with negative absorptions are diminished (b). The bands marked with 1 correspond to combination modes of 5-methylhexa-1,2,4-triene-1,3-diyl (**1**), and the bands marked with 3, 4, 5, and 6 belong to 3-diazo-5-methylhex-4-en-1-yne (**3**), 1-ethynyl-3,3-dimethylcyclopropene (**4**), 2-methylhexa-1,3-dien-5-yne (**5**), and 2-(2-methylpropenyl)cyclopropenylidene (**6**), respectively.

1-yne (**3**) mainly occurring in the matrix as the *s*-gauche-conformer (eq 1, Supporting Information).



(1)

The observation of this rearrangement is in agreement with the earlier conclusion that the initial step of phototransformations of 3*H*-pyrazoles is the formation of isomeric diazoalkenes[43−50] and that their best yield is achieved by irradiation at 300−400 nm, because these wavelengths result in their lower decomposition.[30,32,51,52] As shown below, the formation of the other products detected upon photolysis of **2** can be explained by further phototransformations of **3**.

The matrix IR spectra of both **2** and **3** isolated in the Ar matrices are somewhat complicated because of matrix splitting (Supporting Information). Nevertheless, except for this complication, the observed spectra of **2** and **3** and their dideuterated derivatives conform reasonably well to those predicted for these species at DFT PBE/TZ2P[53] level (Supporting Information), which belongs to generalized gradient approximation (GGA) methods well reproducing the vibration frequencies and their IR intensities.[54] From comparison of the experimental and theoretical IR spectra of **2** and **3**, one can conclude that PBE/TZ2P calculations generally overestimate the fundamental frequencies lying above 2000 cm^{-1} and slightly underestimate those lying below this point, qualitatively reproducing the corresponding IR intensities.

Upon photolysis of **3** at 313(±5) nm for ca. 1 h, it underwent ca. 90% (ca. 80% for **d$_2$-3**) decomposition, resulting in the formation of one major product (Figure 1), which, particularly, was characterized by a strong IR band at around 3290 cm^{-1} (2492 cm^{-1} in the case of **d$_2$-3**) corresponding to a stretching vibration of the C−H bond adjacent to the weakened C−C triple bond. In addition, a weak feature at 2208 cm^{-1} due to a vibration of the C(sp^2)−D bond has been assigned reliably to the same species in the spectra of the photolysis products of **d$_2$-3**. Besides, several bands have been observed in the regions 3000−2850 and 1450−1350 cm^{-1}, typical of methyl group vibrations. Their position and shape are practically unaffected by deuterium substitution. The pattern of the bands set in the region of 3000−2850 cm^{-1} resembles that of **2** and **3** in this region. Thus, the product contains a C═C−H fragment and a C≡C−H fragment with a weakened triple bond and rather retains both Me groups. The structure of ethynylvinylcarbene **1** conforms to these structural demands.

The general photodecomposition route of diazo compounds is elimination of dinitrogen to give carbenes. This reaction has been used for generation of different carbenes in low-temperature matrices[55] including ethynylcarbenes HC_3H,[17,18,56−58] HC_3Ph,[9] PhC_3Ph,[20,59] and HC_5H.[23] Thus, formation of **1** is highly expected in the course of photodecomposition of **3**.

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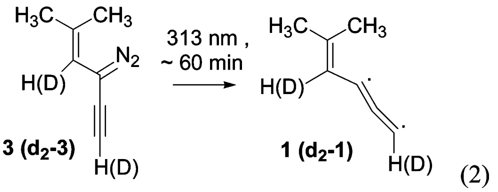
Table 1. Frequencies (cm^{-1}) of 5-Methylhexa-1,2,4-triene-1,3-diyl (**1**) and 1,4-Dideutero-5-methylhexa-1,2,4-triene-1,3-diyl (**d$_2$-1**) Observed in Ar Matrices and Corresponding Calculated (DFT PBE/TZ2P) Frequencies with Their IR Intensities (km mol^{-1}) and Assignment[a]

1[b] (exp.)	**1**[c] (calc.)	**d$_2$-1**[b] (exp.)	**d$_2$-1**[c] (calc.)	symmetry, assignment
3295 sh, 3290* s, 3284 s	3384 (97)	2501 vw, 2499 sh, 2492* s, 2478 vw	2543 (69)	a′, $\nu(C^1{-}H/D)$
2983 m, 2948 w, 2933 m, 2916 m, 2902 w, 2871 w, 2851 vw	3050 (9)	2987 m, 2954 w, 2933 sh, 2913 m, 2898 vw, 2868 m, 2848 vw	3050 (9)	a′, $\nu(C^6{-}H) + \nu(C^7{-}H)$
	3043 (22)		3043 (20)	a′, $\nu(C^6{-}H) + \nu(C^7{-}H)$
	2984 (18)		2984 (18)	a″, $\nu(C^6{-}H) + \nu(C^7{-}H)$
	2974 (16)		2974 (16)	a″, $\nu(C^6{-}H) + \nu(C^7{-}H)$
	2941 (53)		2942 (53)	a′, $\nu(C^6{-}H) + \nu(C^7{-}H)$
	2934 (31)		2934 (31)	a′, $\nu(C^6{-}H) + \nu(C^7{-}H)$
2735 vw, br		2733 vw, 2727 vw		
	3000 (18)	2208 vw	2208 (9)	a′, $\nu(C^4{-}H/D)$
1443 w	1429 (20)	1444 w	1429 (20)	a″, $\delta(H{-}C^6{-}H) + \delta(H{-}C^7{-}H)$
1416 m	1396 (20)	1405 w, 1402 s	1386 (24)	a′, $\nu(C^4{-}C^5) + \delta(H{-}C^6{-}H) + \delta(H{-}C^7{-}H)$
1379 sh	1354 (1)	1379 w	1354 (1)	a′, $\delta(H{-}C^6{-}H) + \delta(H{-}C^7{-}H)$
1377 m[d]	1350 (13)	1374 s	1345 (15)	a′, $\delta(H{-}C^6{-}H) + \delta(H{-}C^7{-}H)$
1325* w, 1322 sh br	1305 (6)		1250 (1)	a′, $\nu(C^5{-}C^6) + \nu(C^5{-}C^7) + \delta(C^5{-}C^4{-}H/D)$
1197* sh, 1195* w, 1193 sh	1183 (13)		953 (1)	a′, $\nu(C^5{-}C^6) + \nu(C^5{-}C^7) + \delta(C^5{-}C^4{-}H/D)$
1044 s	1031 (24)	1083 sh, 1082* m, 1078 m	1068 (33)	a′, $\delta(C^5{-}C^6{-}H) + \delta(C^5{-}C^7{-}H) + \delta(C^6{-}C^5{-}C^7) + \delta(C^5{-}C^4{-}H/D) + \nu(C^4{-}C^5) + \nu(C^1{-}C^2) + \nu(C^2{-}C^3)$
812 sh, 809* w	794 (14)	672 sh, 671* w, 670 sh	659 (6)	a″, $\delta(C^5{-}C^4{-}H/D)$
715 w br, 703 w br, 593 vw br				
419* w, 417 w	407 (11)		383 (7)	a″, $\delta(C^3{-}C^4{-}C^5) + \delta(C^1{-}C^2{-}C^3)$

[a] The numbering of carbon atoms is shown in Figure 2. The full list of calculated frequencies of **1** and **d$_2$-1** is presented in the Supporting Information. [b] s is strong, m is medium, w is weak, vw is very weak, sh is shoulder, br is broad; the asterisk marks bands decreasing upon annealing (up to 39 K) and, hence, related to molecules located in thermodynamically less favorable matrix sites. [c] frequency/cm^{-1} (intensity/km mol^{-1}). [d] Splits upon annealing into two bands at 1376 and 1375 cm^{-1}.

According to our DFT data and by analogy with ethynyl- and vinylcarbenes observed earlier, **1** is expected to have the electronic triplet ground state and, therefore, to react readily with molecular oxygen to form carbonyl O-oxides.[55] This is the case indeed, as it will be discussed below. Additionally, IR spectra of triplet **1** and **d$_2$-1** calculated at PBE/TZ2P level are in very good agreement with those observed in experiment (Figure 1 and Supporting Information), although experimental spectra are somewhat complicated by matrix splitting (Table 1). Thus, chemical reasoning, the positions of the observed bands, and their agreement with PBE/TZ2P-predicted frequencies suggest identification of the species formed upon 313 nm photolysis of **3** as 5-methylhexa-1,2,4-triene-1,3-diyl **1** (eq 2).



(2)

The IR spectrum of **1** reveals several analogies to spectra of ethynylcarbenes observed earlier. The $C^1{-}H(D)$ stretching vibration frequency of **1** (**d$_2$-1**) equal to 3290 (2492) cm^{-1} (Table 1) is located in the same region as frequencies of the same vibration mode of triplet propargylene (3265 cm^{-1} for HC_3H,[18] 3271 and 2469 cm^{-1} for HC_3D,[56,60] 2458 cm^{-1} for DC_3D[56,60]), pentadiynylidene (3292 cm^{-1} for HC_5H and 3294 and 2512 cm^{-1} for HC_5D)[23] and phenylpropargylene (3278 cm^{-1}),[9] as well as singlet chloropropargylene (3306 cm^{-1})[61] and shows similar deuterium shift. An intense band observed at 1044 (1082 and 1078) cm^{-1} for **1** (**d$_2$-1**) corresponds to a mode including "in-phase" vibration of the propargylenic fragment. This type of vibration is responsible for a band at 1045 cm^{-1} of HC_3D,[60] and for the strongest band of singlet HC_3Cl at 1055 cm^{-1}.[61] As PBE/TZ2P calculations predict, intense IR bending frequencies of the terminal C^2C^1H group are below 300 cm^{-1}, in accordance with an earlier observation for propargylene.[56] This region is out of range of our spectrometer. The band of **1** at 417 cm^{-1} has no counterpart in the spectrum of **d$_2$-1**. This is due to mixed bending vibrations of the propargylenic fragment and the attached vinyl group. Similar bending vibration of the propargylenic CCC fragment was identified in the spectrum of HC_3H at 402−403 cm^{-1}.[18,56,60] It shifts to 392 and to 384 cm^{-1} for HC_3D and DC_3D, respectively.[56,60] Vibration of this type has also been observed at around 475 cm^{-1} for HC_5H and HC_5D.[23]

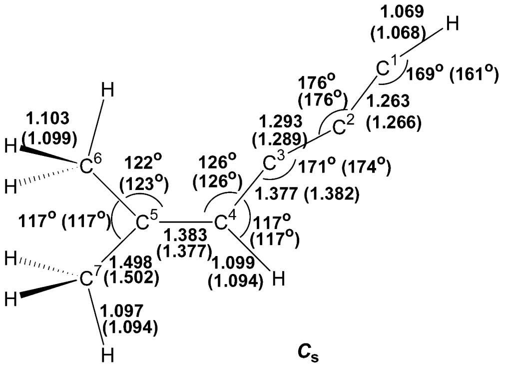


Figure 2. Structure of **1** according to DFT PBE/TZ2P (and B3LYP/6-31G(d) in parentheses) calculations.

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The analogies between the IR spectrum of **1** and the IR spectra of known vinylcarbenes[34,62−65] are also evident. The bands assigned to the C=C stretch (mixed with other vibrations) have been observed at 1431, 1455, and 1466 cm^{-1} for triplet pent-2-en-4-yn-1-ylidene (in Ar),[62] but-2-ene-1,3-diyl (in Xe),[34] and 2-(4-oxo-2,3,5,6-tetrafluorocyclohexa-2,5-dienylidene)ethylidene (in Ar).[63] The band of **1** (**d$_2$-1**) at 1416 (1402) cm^{-1} is located close to them and corresponds to a mixed vibration mainly consisting of the C=C stretch and Me group deformation. Deformation of the C=C−H fragment in **1** contributes to several vibrational bands (Table 1); analogous bands have been found in the IR spectra of 2-penten-4-yn-1-ylidene,[62] propene-1,3-diyl,[34] but-2-ene-1,3-diyl,[34] and 2-(4-oxo-2,3,5,6-tetrafluorocyclohexa-2,5-dienylidene)ethylidene.[63] Carbene **d$_2$-1** is characterized by a C^4−D stretching vibration at 2208 cm^{-1}. No band of this type has been reported before for any vinylcarbene, because no IR spectra of deuterated vinylcarbenes were recorded previously, while the bands of the corresponding C−H vibrations are weak and often hidden by other bands.

Carbene **1** was formed at quite early stages of decomposition of 3*H*-pyrazole **2** soon after the appearance of **3** at any wavelength used. This fact can be attributed to some decomposition of **3** during its formation, because fairly fast decay of **3** was observed upon irradiation at any wavelength within the 230−550 nm range, resulting in strong growth of the bands of **1**. Nevertheless, we cannot completely rule out the possibility of a minor pathway leading directly from **2** to **1**.

The intensive formation of **1** from **3** continued until a relatively high concentration of **3** was retained (no more than ~90% conversion of **3**) in the matrix. Further irradiation of the matrices resulted both in further decomposition of **3** and in decomposition of **1** (and **d$_2$-1**). The effect of the light with $\lambda >$ 470 nm, 313 ± 5 nm, and 254 ± 5 nm on **1** was less pronounced than that of light within the 320−420 nm range. This explains why the irradiation at 313 nm turned out to be very profitable for generation of **1** from **3**: this light is quite effective to decompose **3** but not **1**. This indicates also that UV absorption of **1** responsible for its further transformations lies around 400 nm.

Structure of 5-Methylhexa-1,2,4-triene-1,3-diyl (1) According to Quantum-Chemical Calculations. DFT methods are well suitable for investigation of quite large systems like **1** and were repeatedly used for analysis of the nature of bonding in ethynyl- and vinylcarbenes.[20,21,34,62,63] The structure of **1** obtained at the PBE/TZ2P and B3LYP/6-31G(d)[66,67] levels is shown in Figure 2. It is characterized by the presence of the propargylenic W-shaped fragment, which is flat as opposed to propargylene itself.[18] Both of the C−C bonds have lengths intermediate between the typical double and triple bond lengths. The terminal C−C bond is shorter than the internal C−C bond. Such bond alternation resembles that in polyethynylcarbenes $HC_{4m+1}H$.[21] Hence, conjugation with a vinyl group leads to the same type of alternation as does conjugation with an additional ethynyl group. However, the effect of vinyl group is clearly weaker. By analogy with the $HC_{4m+1}H$ compounds, one can expect that the C^3 atom of **1** has a more pronounced carbenic character than the C^1 atom or the terminal carbon atoms in propargylene.[20,23]

The propargylenic fragment is attached to the formal vinyl fragment by a C^3−C^4 bond. The lengths of both the C^3−C^4 and the C^4−C^5 bonds correspond to that of a slightly elongated double bond, the C^4−C^5 bond being slightly longer (at PBE level) or slightly shorter (at B3LYP level) than the C^3−C^4 bond. Similar elongation of a formal vinyl C−C bond and shortening of a C−C bond connecting the vinyl group to the formal carbene center have been noticed for propene-1,3-diyl,[34] but-2-ene-1,3-diyl,[34] and 2-(4-oxo-2,3,5,6-tetrafluorocyclohexa-2,5-dienylidene)ethylidene.[63] This reflects the predominantly biradical character of vinylcarbenes. According to UB3LYP/6-31G calculations, the C−C bond length in the vinyl group is ca. 1.4% longer than the distance between the carbene center and the vinyl group for both propene-1,3-diyl and but-2-ene-1,3-diyl.[34] Even stronger alternation of the corresponding bonds has been found for 2-(4-oxo-2,3,5,6-tetrafluorocyclohexa-2,5-dienylidene)ethylidene (B3LYP/6-31G(d,p) calculations),[63] which can be interpreted as being due to the significant contribution of resonance structures with a nominally double bond between the carbene center and the vinyl group.[63] Thus, elongation of the vinyl C−C bond relative to the C−C bond connecting this group to the carbene center may serve as a measure of the degree of electronic delocalization in vinylcarbenes. If this is true, the vinyl group of carbene **1** participates in the electronic delocalization to a lesser extent, as such elongation is close to zero. This can be understood as being a result of competition between vinyl and ethynyl groups for the electronic delocalization in **1**.

To get better understanding of the electronic structure of **1**, its NBO analysis[68] has been performed for the structure obtained at the B3LYP/6-31G(d) level. The analysis has shown high occupancy of valence non-Lewis orbitals: 4.5% for α electrons and 2.7% for β electrons, thus indicating a highly delocalized structure. The C^4−C^5 π-bond is strongly depleted; viz., α electron occupancy is 0.96 and β electron occupancy is 0.84, while C^4−C^5 π^*-bond orbital is remarkably occupied (by 0.15). The π-electron system of the propargylenic fragment is mainly composed of two highly occupied (occupancy of 0.7−0.8) lone pair orbitals on each of the C1 and C3 atoms and two half-occupied (occupancy of 0.45) antibonding lone pair orbitals on the C2 atom for α electrons, and also of two π orbitals affixed to the C^1−C^2 pair of atoms for β electrons. In the whole, unpaired α electron density is localized predominantly on atoms C^1 (0.61), C^3 (0.47), and C^5 (0.18). Thus, NBO analysis confirms the conclusions made above.

From the above consideration, it follows that the structure of **1** is contributed by a series of resonance structures and cannot be easily depicted in the classical manner. This complicates the proper designation of compound **1**. Following the notation suggested by Maier et al. for vinylcarbenes,[34] we have named **1** as 5-methylhexa-1,2,4-triene-1,3-diyl, which seems to reflect its structure most adequately.

Reaction of 1 with Oxygen. Generation of **1** from **2** via **3** in 0.2−2% O_2-doped Ar matrices proceeded as in the pure Ar matrices. Reaction of **1** with O_2 was observed upon annealing of matrices at 30−35 K for several minutes. The bands of **1** strongly decreased, and a series of new bands appeared. Most prominent of them were those lying in the 900−1000 cm^{-1} range (Figure 3b) typical of the O−O stretching vibrations of carbonyl oxides, $R_2C{=}O^+{-}O^-$.[20,23,55,57,69−77] The presence of multiple

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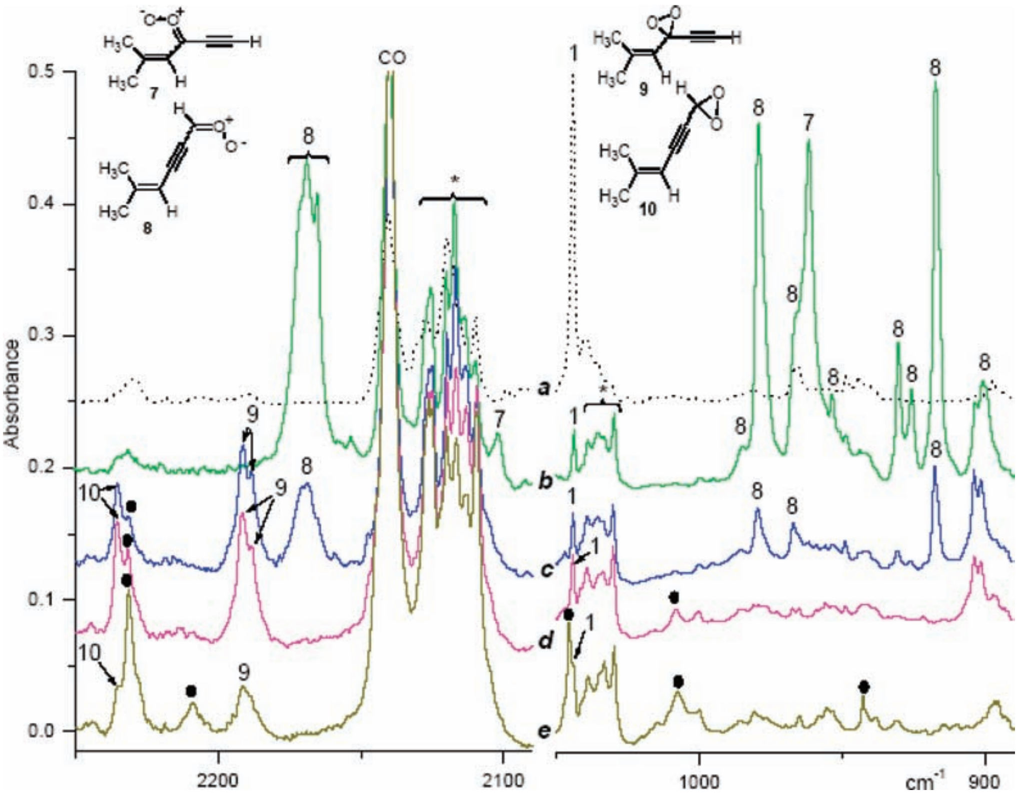

Figure 3. IR spectra of products of the reaction of carbene **1** with O_2. (a) The spectrum obtained after irradiation (λ = 320−390 nm for 7 min, then λ = 313 nm for 100 min) of **2** isolated in 1.5% O_2-doped Ar matrix. (b) Spectrum of the same matrix after annealing at 34 K for ca. 5 min. (c) Spectrum of the same matrix after additional irradiation at $\lambda > 580$ nm for 25 min. (d) Spectrum of the same matrix after supplementary irradiation at $\lambda > 420$ nm for 25 min. (e) Spectrum of the same matrix after irradiation at $\lambda > 300$ nm for 20 min. Bands marked with numbers 1, 7−10 belong to species **1**, **7**−**10**, bands marked with black circles belong to products of further transformations of **9** and **10**, and other unidentified bands are marked with asterisks.

bands in this range unambiguously implies the formation of several carbonyl oxides.

As it is characteristic for carbonyl oxides,[70] all of these bands decreased (Figure 3c) and then disappeared upon irradiation with visible light (with $\lambda > 580$ nm for ca. 1 h). However, the decrease of the bands was nonsynchronous. Decay of the intense band at 961 cm^{-1} was remarkably faster than that of the bands of similar intensity at 917 and 979 cm^{-1} and simultaneous with decay of the bands at 3309 ($\nu(\equiv C-H)$), 2102 ($\nu(C\equiv C)$), and 1619 cm^{-1} ($\nu(C=C)$), as well as of several bands in the bending region of Me groups between 1450 and 1350 cm^{-1} and in the $\delta(C\equiv C-H)$ region around 650 cm^{-1}. This set of the bands associated with the band at 961 cm^{-1} clearly corresponds to 5-methylhex-4-en-1-yn-3-one O-oxide (**7**) arisen from O_2 attack on C^3 of **1** (Scheme 1).

As for the two other intense bands in the O−O stretching region, the band at 917 cm^{-1} decreased somewhat slower than the band at 979 cm^{-1}. The sets of bands associated with these two bands have been determined less definitely, as the difference in rates of their decay was quite little. Nevertheless, it has been concluded that both sets include strong bands in the $\nu(C\equiv C)$ region at around 2170 cm^{-1} and do not include bands in the $\delta(C\equiv C-H)$ region. This suggests assignment of these sets to different conformers of 5-methylhex-4-en-2-ynal O-oxide (**8**) (Scheme 1).

It is known that DFT GGA methods reproduce vibration frequencies of carbonyl oxides quite well.[20,23,77] Therefore, to support the above identification, IR spectra of different conformers of **7** and **8** as well as their $^{18}O_2$- and D_2-isotopomers have been calculated at the PBE/TZ2P level. It has been found that the calculations reasonably reproduce all of the features of IR spectra observed experimentally for systems **1** + O_2, **1** + $^{16}O_2/^{18}O_2$ (1:4), and $\mathbf{d_2}$**-1** + O_2, assuming that all four conformers of **7** and **8** (Scheme 1) are simultaneously present in the matrix (Supporting Information). Particularly, they predict that different conformers of **8** differ considerably as regards the position of the O−O vibrations, while frequencies of this vibration for different conformers of **7** are close to each other. On the basis of the results of the calculations, an assignment of the observed frequencies to fundamental modes of different conformers of **7** and **8** has been proposed (Supporting Information).

The simultaneous presence of different conformers of carbonyl oxides is explained by the large energy gain upon formation of both **7** (ca. 40 kcal/mol at PBE/TZ2P level including ZPE correction) and **8** (ca. 45 kcal/mol), a known[57,70,78]

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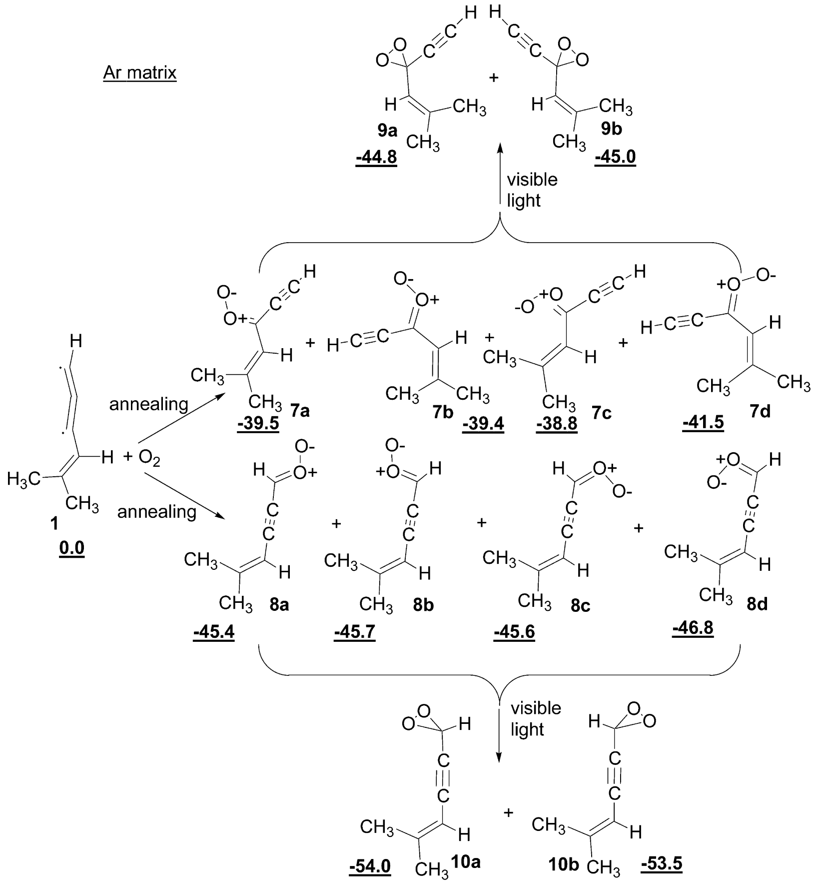
Scheme 1[a]



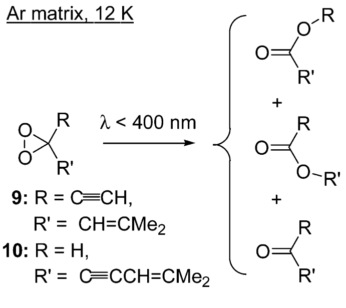
[a] Underlined numbers below each structure are PBE//TZ2P energies (in kcal/mol) with ZPE correction relative to **1** + O_2.

high energy barrier to the O—O group inversion (39.9 and 40.5 kcal/mol to the inversion in **7d** and **8d** at PBE/TZ2P level including ZPE correction), and a remarkable barrier to rotation around the C—C bond adjacent to the O_2 group (7.8 and 4.4 kcal/mol for **7d** and **8d**, respectively), leading to stabilization of all of the conformers in the matrices in the nonequilibrium concentration.

Calculations predict that intensities of O—O vibrations of the conformers of **8** are approximately twice as large as those of different conformers of **7**. However, the two major bands of the O—O vibrations (at 917 and 979 cm^{-1}) of **8** are as intense as the corresponding band of **7** (at 961 cm^{-1}). Hence, both carbonyl oxides are formed in comparable concentrations, and both of the reaction centers of carbene **1** are approximately equally reactive toward oxygen in agreement with the unpaired electron density distribution found in NBO analysis. This observation greatly distinguishes carbene **1** from pentadiynylidene, which possesses similar bond alternation, but reacts with oxygen at its central carbon atom only.[23] Thus, carbenic character of the central atom of pentadiynylidene is much more pronounced than that of the C^3 atom of **1**.

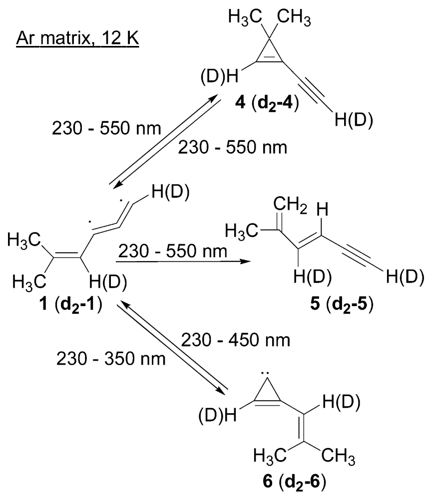
Decomposition of **7** and **8** upon visible light irradiation was accompanied by the appearance and increase of a series of new bands, which could be divided into two groups: one appeared in parallel with the fast decrease of the bands of **7**, and the other appeared in parallel with the slower decrease of the bands of **8** (Figure 3c,d). Both groups of the bands decay slowly upon irradiation with light below 400 nm, thus revealing photochemical behavior typical of dioxiranes.[9,20,23,55,70,74,75,77] The positions of the observed bands are in good agreement with the frequencies of the fundamental vibrations predicted by the PBE/TZ2P method for dioxiranes **9** and **10** (Scheme 1) and their $^{18}O_2$ and D_2 isotopomers under the assumption that both conformers are present for each species (Supporting Information). Thus, carbonyl O-oxides **7** and **8** transform into dioxiranes **9** and **10**, respectively, on irradiation with visible light in accordance with the known photochemical behavior of this class of species.[9,20,23,55,70,74,75,77]

Scheme 2



Decomposition of **9** and **10** upon irradiation with $\lambda < 400$ nm (Figure 3e) resulted in the formation of CO, CO_2, and a series of products, revealing themselves by a series of bands that appear or grow simultaneously with decrease of the dioxirane bands. According to the available data on the decomposition of dioxiranes in low-temperature matrices,[9,20,23,55,70,74,75,77] one may expect the formation of a set of products shown in Scheme 2. Indeed, several strong bands developed in the ν(C=O) vibration region indicate the usual decomposition routes for **9** and **10**. Because of the large number of the expected

Scheme 3



products, which additionally can exist in the matrices as several conformers, we did not attempt to assign the observed bands.

Phototransformations of 5-Methylhexa-1,2,4-triene-1,3-diyl (1). The pathways of photorearrangements of **1** (**d$_2$-1**), which will be discussed below, are summarized in Scheme 3.

The generation of **3** from **2** was accompanied by formation of some minor product, which was observed only after the appearance of **1**. Decomposition of **3** also resulted in the growth of the bands of this product, although this was markedly slower than the growth of bands of **1**. When the conversion of **3** arrived at a degree where the bands of **1** no longer increased or even somewhat decreased, the bands of this species continued to grow. When the matrix was exposed to the light at 340−540 nm causing strong decomposition of **1**, especially fast increase of the bands of this species occurred, including the case when no diazo compound **3** was present in the matrix and **1** was the only product, whose bands decreased. Thus, clearly, this species mainly is a product of phototransformation of **1**, which proceeds to some extent at any wavelength used for the production of **3** and **1**.

The set of characteristic frequencies found for this species and its d$_2$-counterpart (Supporting Information) corresponds to the structure of 1-ethynyl-3,3-dimethylcyclopropene (**4**). These frequencies correlate well with the corresponding fundamental frequencies of the series of cyclopropenes[34,55,62−65,79] obtained in low-temperature matrices and with the respective frequencies of the first stable 1-ethynylcyclopropene, 3,3-dimethyl-1-phenyl-2-phenylethynylcyclopropene.[80] It is worth noting that no ethynylcyclopropene has been observed by matrix spectroscopy before. The PBE/TZ2P calculated IR spectra of **4** and **d$_2$-4** are in a good agreement with those observed in the experiments (Supporting Information).

It has been suggested[43] that the formation of cyclopropenes in the photolysis of vinyldiazomethanes may occur directly from the excited state of the diazo compounds without intermediate formation of the corresponding vinylcarbenes. Available data lead to the conclusion that such a process could only be minor for diazo compound **3** under the conditions used.

The formation of **4** from **1** is highly expected because the vinylcarbene−cyclopropene rearrangement is the predominant reaction pathway for both thermally and photochemically generated vinylcarbenes.[24,25] This process requires overcoming a very low potential barrier of several kcal/mol;[24,81,82] however, no thermal conversion of **1** to **4** was detected upon annealing of the matrices. Several cyclopropenes have been observed in low-temperature Ar matrices as products of photochemical vinylcarbene−cyclopropene rearrangements,[55,62−65,79] and vice versa cyclopropene and 1-methylcyclopropene have been used to generate the simplest vinyl- and vinylmethylcarbenes.[34] Like our case, no thermal rearrangement of vinylcarbenes to cyclopropenes has been noticed in these studies. The only effect of annealing (up to 40 K) on the bands of **4** consisted of removal of site splitting, including the cases where matrices were doped with oxygen. Therefore, cyclopropene **4** is stable up to at least 40 K and is insensitive to oxygen at these temperatures.

We were unable to convert **1** to **4** completely, as the decrease of the bands of **1** (and **d$_2$-1**) almost stopped after ca. 1 h of photolysis with unfiltered light, and simultaneously the bands of **4** (and **d$_2$-4**) started to decrease, while the bands of only one product, called hereafter product **5**, increased. This implies the existence of reverse transformation of **4** into **1** and agrees with the common ability of cyclopropenes to rearrange into isomeric vinylcarbenes upon photolysis or thermolysis.[24,25]

Species **5** appeared in the matrices at later stages of the rearrangement of **2** into **3**, but only after the appearance of species **1** and **4**. Its bands slowly grew upon decomposition of **3**. However, their strong growth was observed only when a strong decrease of **1** took place. The decrease of the bands of **4** after cessation of the decrease of the bands of **1** was also accompanied by the increase of the bands of **5**. Thus, the product **5** is formed from **1** and also from **4**, although most probably via **1**.

Species **5** is characterized by the presence of a terminal alkyne fragment responsible for the C−H stretching and C≡C−H bending vibration bands (at 3330 and 3316 cm^{-1}, 638, 603, and 600 cm^{-1} for **5**, and at 2594, 481, and 471 cm^{-1} for **d$_2$-5**), and of a terminal methylene double-bonded fragment responsible for an intense doublet of wagging vibration bands around 895 cm^{-1}, whose position is almost insensitive to the deuterium substitution. The latter fact is evidence for the origination of the methylene group from a methyl group. The best candidate for **5** is 2-methylhexa-1,3-dien-5-yne formed from **1** upon 1,4 H shift, well-known for vinylcarbenes.[24,25,83] Comparison of PBE/TZ2P calculated and experimental spectra indicates that, in accordance with the stereochemistry of this reaction, all of the observed bands of **5** (and **d$_2$-5**) can be assigned to fundamental modes of 3*E*-2-methylhexa-1,3-dien-5-yne (Supporting Information) represented by two conformers. However, the *s-trans*-conformer predominates over the *s*-gauche conformer, although only the latter must be formed in this reaction. The energy necessary for such an extensive conformational reorganization of **5** could be gained from the 1,4 H shift whose heat is ca. 30 kcal/mol according to PBE/TZ2P calculations, and also can be supplied by irradiation as the result of its energy excess.

The formation of **5** and **d$_2$-5** was also observed upon pyrolysis of **2** and **d$_2$-2** in a quartz reactor at 10^{-3} Torr and at 750−900 K. Hexadienyne **5** was the major product in a fairly complex

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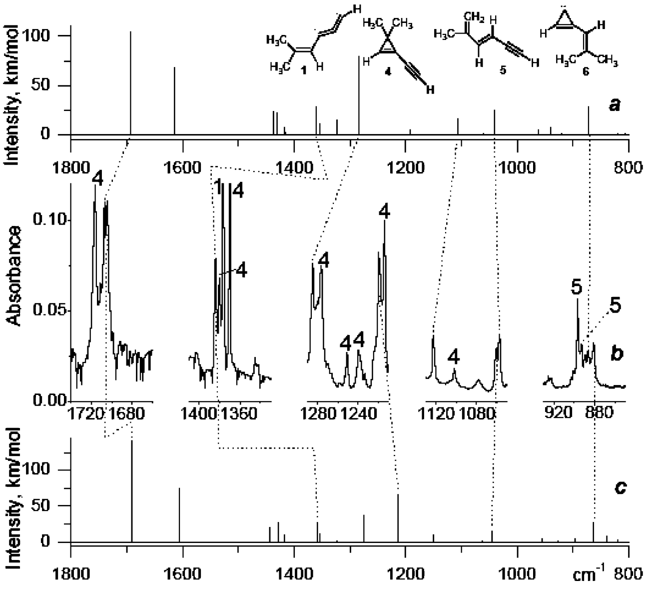

Figure 4. DFT PBE/TZ2P calculated IR spectrum of 2-*s*-*cis*-2-(2-methylpropenyl)cyclopropenylidene **6** (a); selected fragments of matrix IR spectrum containing bands of 2-(2-methylpropenyl)cyclopropenylidene **6** (b); and DFT PBE/TZ2P calculated IR spectrum of 2-*s*-*trans*-2-(2-methylpropenyl)cyclopropenylidene **6** (c). The bands marked with 1, 4, and 5 belong to **1**, **4**, and **5**, respectively.

mixture of products and was represented by the *s-trans* conformer only, because this conformer is remarkably more stable (by 3 kcal/mol according to PBE/TZ2P calculations). The mechanism of formation of **5** upon thermolysis is expected to be similar to that operating upon photolysis.[24] Nevertheless, neither **1** nor **4** have been observed in these experiments. Obviously, they underwent further transformations before being stabilized in the matrices.

In the paper of Franck-Neumann and co-workers,[42] which has served as a background of the present study, it has been reported that in the preparative photolysis of **2** in solution a complex mixture of nonisolable products was obtained. According to NMR and IR data, the mixture contained species comprising isobutylenic fragment and ethynyl group.[42] On the basis of our findings, we surmise that 2-methylhexa-1,3-dien-5-yne **5** was the major component of that mixture, being a compound of high photolytic stability but rather inclined to thermal polymerization.

Besides the bands of **4** and **5**, two additional sets of relatively weak bands were observed simultaneously in experiments when matrices containing large amounts of **1** had been irradiated at $\lambda < 350$ nm. They included the bands at 1707, 1384, 1285, 1122, 1057, and 886 cm^{-1} and at 1705, 1220, 1061, and 881 cm^{-1} (Figure 4b). Relative intensities of the bands varied between these sets only slightly. Taking into account the fact that six of these bands form pairs by one band from each set (1707 and 1705, 1061 and 1057, 886, and 881 cm^{-1}), one may suggest that all of the bands most likely correspond to two conformers of the same product, called product **6**.

The higher was the concentration of carbene **1** in the matrix, the more intense were the bands of **6** observed after subsequent photolysis. However, prolonged photolysis with light within 230−450 nm resulted in a slow decrease of the bands of **6**, if most of carbene **1** was already consumed. The only species whose bands increased was dienyne **5**. Thus, carbene **1** is the obvious precursor of product **6**, while **6** represents only a minor product of photolytic transformations of **1**. Phototransformation of **6** results in the formation of **5**, very likely via **1**.

No significant changes were noticed in the spectrum of **6** upon annealing up to 39 K as far as it could be concluded taking into account weakness of these bands and overlap of most of them with the bands of other products. Thus, product **6** is stable in Ar matrix at least up to 39 K, and its conformational transformations are hampered (actually, like those of dienyne **5** and 2,3-dimethylbuta-1,3-diene[84]). No effect of oxygen doping on the annealing behavior of **6** has been noticed, which indicates that **6** is not a triplet species.

Because the set of frequencies of **6** (**d$_2$-6**) contains no bands assignable to vibrations of ethynyl group and the only characteristic frequencies lie in the stretching region of double C=C bonds of cyclopropenes, viz., around 1700 cm^{-1}, close to the corresponding frequency of **4**, 2-(2-methylpropenyl)cyclopropenylidene has been proposed as a possible structure for **6**. Analogous rearrangements of triplet propargylene,[18,56,58,60,85] diphenylpropargylene,[20] and singlet cloro-, dichloro-,[61] and difluoropropargylene[86] into the corresponding singlet cyclopropenylidenes upon photolysis at around 300 nm and their back rearrangements upon photolysis at somewhat shorter wavelengths have been reported earlier.

The PBE/TZ2P calculated IR spectra of two conformers of singlet 2-(2-methylpropenyl)cyclopropenylidene and its d$_2$-counterpart reproduce the experimentally observed spectra of **6** (and **d$_2$-6**) quite well (Figure 4, Supporting Information), assuming that both conformers are present in the matrix in comparable amounts. Thus, we have identified the minor product of photolytic transformations of **1** as cyclopropenylidene **6**.

In addition to the bands assigned to compounds **1** and **3**−**6**, several other weak bands were observed in different experiments. Because of their weakness, any correlations among them were utterly difficult, and their nature was left unknown. Most of these bands appeared when conversion of **2** was complete and **3** had decomposed to a large extent. Thus, the products responsible for these weak bands arise from minor phototransformations of the species **1** and **3**−**6**, most probably of the species **1** and **4**−**6**.

As shown above, two major pathways of phototransformations of **1** are determined by the presence of the vinyl group in the carbene, while only one minor pathway is due to the presence of the propargylenic fragment. Thus, the presence of the vinyl group in the structure of **1** is a crucial factor in its photochemical behavior, while according to the structural consideration made above, both formal vinyl and formal ethynyl groups efficiently participate in the electron delocalization. No specific reaction has been found, which is related to the quite unusual conjugation chain of this carbene.

Potential Energy Surface of the System C$_7$H$_8$. Scheme 4 shows all reported pathways of photochemical[43,55] and thermal[24,25] rearrangements of vinylcarbenes and photochemical rearrangements[18] of ethynylcarbenes as applied to carbene **1**, and thereby outlines reactions that could be in principle expected of **1** upon matrix photolysis. The PBE/TZ2P calculations of the depicted products and their IR spectra have been carried out (Supporting Information). Comparison of the calculated IR spectra with the experimentally observed spectra excludes the formation of

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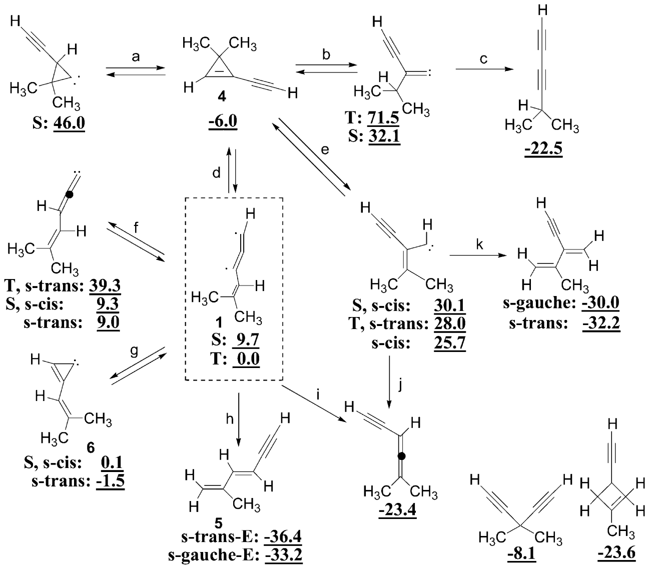
Scheme 4[a]



[a] PBE//TZ2P calculated relative energies (relative to triplet **1**, including ZPE correction, in kcal/mol) are shown near each structure for several conformers in the ground and, for valence unsaturated species, in the lowest excited electronic states.

noticeable amounts of all of these products, except species **4**−**6**, in the matrices.

The fact that we did not observe 2-ethynyl-3-methylbut-2-ene-1,3-diyl upon photolysis of cyclopropene **4** (reaction e) points to much easier cleavage of the more substituted bond to give carbene **1** (reaction d). Earlier, the regioselectivity of the photochemical cleavage of σ-bonds in cyclopropenes was discussed only shortly,[87] and no general views were elaborated. The rearrangement of cyclopropenes via intermediate formation of vinylidenes (paths b,c) is a common pathway of thermal isomerization of these species. This type of isomerization has also been observed for parent cyclopropene upon photolysis in Ar matrix,[34] but not for 1-methylcyclopropene[34] or other cyclopropenes. Transformation of cyclopropenes into corresponding cyclopropylidines requires the presence of a mobile group attached to the double bond,[25] which is not the case here; therefore, such rearrangement (reaction a) is hardly expected for **4**. Surprisingly, we did not observe the formation of 5-methylhexa-3,4-dien-1-yne (allene, reaction i) easily detectable by IR spectroscopy, although propene-1,3-diyl, but-2-ene-1,3-diyl,[34] and pent-2-en-4-yne-1,3-diyl[62] readily produced corresponding allenes upon photolysis. Similarly, no formation of vinylidenecarbene (reaction f) has been observed. This species is expected to be easily detectable by its intense bands around 1950 cm^{-1}. The corresponding vinylidenecarbenes were detected as products of photolysis of matrix isolated triplet propargylene,[18,56,58,60,85] singlet cloro-,[61] dichloro-,[61] and difluoropropargylene,[86] but not triplet diphenylpropargylene.[20]

The relative energies of the species obtained at PBE/TZ2P level are also shown in Scheme 4. These values give a qualitative picture of the potential energy surface of the C_7H_8 system. It is interesting to note that all experimentally observed species lie in energy below or near the carbene **1**, and despite permanent delivery of energy into the system by irradiation, the system loses the energy and goes stepwise to its global minimum.

Summary

The first representative of highly delocalized triplet carbenes bearing both formal vinyl and ethynyl groups at the carbene center, 5-methylhexa-1,2,4-triene-1,3-diyl, has been observed in low-temperature Ar matrices. According to the DFT calculation, it is characterized by an effective conjugation along the five-carbon chain exhibiting the same type of alternation in the bond lengths as in the $HC_{4m+1}H$-type compounds. The carbene readily reacts with oxygen, with both of the terminal carbon atoms of the propargylenic fragment showing approximately equal reactivity. The subsequent principal photolytic rearrangements of the carbene include two major reactions that are typical of vinyl carbenes and lead to the corresponding cyclopropene and 1,3-dien-5-yne and one minor reaction characteristic of ethynylcarbenes and resulting in the formation of vinylcyclopropenylidene.

Experimental Section

The setup for the matrix isolation experiments included a vacuum cryostat with a KBr window for IR measurements and a CaF_2 window for irradiation of matrices, equipped with two separate lines for independent supply of a matrix gas (Ar or Ar + O_2) and a precursor, and a mirror copper plate inside. Cooling of the plate to ca. 12 K was achieved using a CSW-208R Displex closed-cycle refrigeration system (APD Cryogenics, Inc.). The temperature of the plate was measured by a DT-470 silicon diode fixed at the Cu plate and was preset by a Lake Shore model 330-11 temperature controller (Lake Shore Cryotronics, Inc.). The Cryostat was evacuated by a diffusion pump to the residual pressure of ca. 10^{-6} Torr. Deposition of the matrices was carried out at 12 K. The typical time of deposition of the matrices was 3 h at a rate of 8 mmol/h. Mixtures of Ar and O_2 ($^{18}O_2$) of known composition were prepared by a standard manometric procedure for several hours before the experiment, thus allowing sufficient mixing of the components. Typical pressure in the precursor flow was about 10^{-4} Torr. Dilution of the precursor by the matrix gas was in the range of 1:700−1:3000 (molar ratio). In the pyrolysis experiments, the precursor flow was directed through a quartz reactor heated to the desired temperature by a resistance heater. The temperature was measured with a chromel-alumel thermocouple. Photolysis of the matrices was carried out by means of a DRSh-500 high pressure Hg arc lamp (500 W) equipped with a water filter and suitable cutoff (50% transmission at the wavelength specified in the text) or LOT-Oriel narrow band interference (half bandwidths of ca. 10 nm) filters. IR spectra were recorded with a Bruker IFS 113v FTIR spectrometer (detector DTGS/KBr) in the range of 400−4000 cm^{-1} with standard resolution 0.5 cm^{-1} by scheme of reflection.

5-Ethynyl-3,3-dimethyl-3*H*-pyrazole was prepared according to the procedure of Franck-Neumann et al.;[42] 3,3-dimethyl-4-deutero-5-deuteroethynyl-3*H*-pyrazole was prepared by analogy, using C_4D_2 containing 90% deuterium (Joint stock company "Saint-Petersburg "Izotop", RF). The purity of the samples was controlled by GLC analysis, and their identities were proved by recording NMR ($CDCl_3$ solution, Bruker AC-200P), MS (electron impact, 70 eV, Finnigan MAT Incos 50), IR (KBr pellets, Bruker IFS 113v FTIR spectrometer), and UV (hexane, T_{room}, 8453 spectrometer, Agilent Technologies) spectra. $^{18}O_2$ of 80.3% isotopic purity was received from JSC Spb Izotop (RF).

DFT calculations were performed by the PBE method[88] with the PRIRODA program[53] using the TZ2P basis set.[53] They included geometry optimizations and computations of relative energies and harmonic vibration frequencies. Frequency calculations were carried out to determine the nature of stationary points, to obtain zero point energy corrections and theoretical IR spectra. Unscaled frequencies

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were used. The structure of **1** was also obtained by the B3LYP[66] method using the 6-31G(d) basis set[67] with the Gaussian 03, revision C.02, software package,[89] and its NBO analysis was carried out with NBO program, Version 3.1,[90] included in the Gaussian 03 software package.

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Supporting Information Available: DFT PBE/TZ2P calculated structures for all of the considered species in graphical and digital (Cartesian coordinates) forms, complete lists of calculated fundamental frequencies and their IR intensities for species **2**−**10** and several other relevant species, more complete experimental IR spectra for species **1**−**10** and their isotopomers, comparison of experimental and calculated IR spectra, and complete literature citation for ref 89. This material is available free of charge via the Internet at http://pubs.acs.org.

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