2.45-2.26 (m, 2 H), 2.14 (pseudo t, 2 H, J = 9.0 Hz), 2.02 (d, 2 H, J = 21 Hz), 1.83-1.70 (m, 6 H), 1.60-0.96 (complex m), 0.95 (s, 6 H, Me-19,19'), 0.92 (d, 6 H, Me-21,21', J = 5.4 Hz), 0.87 (d, 12 H, Me-26,26', Me-27,27', J = 6.6 Hz), 0.74 (s, 6 H, Me-21,21').

Kinetics of syn-anti Rearrangement of 2 and 3. Kinetics are carried out as described above. The resulting data for **2** and **3** are given in Tables VI and VII, respectively, as supplementary material.

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Supplementary Material Available: Unprocessed kinetic data for the thermal rearrangements of *anti*-(*E*,*Z*)-**5** (Table V), *syn*-(*E*,*Z*)-**2** (Table VI), and *syn*-(*E*,*Z*)-**3** (Table VII) (4 pages). Ordering information is given on any current masthead page.

Central and Lateral Bicyclo[1.1.0]butane Bond Cleavage with Subsequent Wagner-Meerwein Rearrangements or Carbene Formation in the 185-nm Photolysis of Tricyclo[3.1.0.0^{2,6}]hexane, Tricyclo[4.1.0.0^{2,7}]heptane, and Tricyclo[5.1.0.0^{2,8}]octane

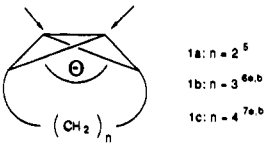
Waldemar Adam,* Christine Alt, Max Braun, Uwe Denninger, and Gerald Zang

Contribution from the Institut für Organische Chemie, Universität Würzburg, Am Hubland, D-8700 Würzburg, Germany. *Received December 11, 1990. Revised Manuscript Received February 4, 1991*

Abstract: The 185-nm photochemistry of tricyclo[3.1.0.0^{2,6}]hexane, tricyclo[4.1.0.0^{2,7}]heptane, [1,7-d_2]tricyclo[4.1.0.0^{2,7}]heptane, tricyclo[5.1.0.0^{2,8}]octane, and [1-d]tricyclo[5.1.0.0^{2,8}]octane was investigated. Tricyclo[5.1.0.0^{2,8}]octane yields bicyclo[4.2.0]oct-7-ene, tricyclo[4.1.0.0^{2,7}]heptane yields 85% bicyclo[3.2.0]hept-6-ene and 15% 3-methylenecyclohexene, and tricyclo[3.1.0.0^{2,6}]hexane yields 39% 3-methylenecyclopentene, 15% 1,3-cyclohexadiene, 26% *trans*-1,3,5-hexatriene, and 20% *cis*-1,3,5-hexatriene. From the deuterium-labeling studies, it is concluded that, in the case of the tricyclooctane, the central bicyclobutane bonds cleave in the primary step to give radical cationic or zwitterionic species that undergo a Wagner-Meerwein rearrangement. Also, in the case of tricycloheptane, this is the dominating pathway but lateral C-C bond cleavage with subsequent carbene and product formation takes place to the extent of ca. 15%. For tricyclohexane, this pathway becomes the major route. Our photomechanistic observations are in good agreement with earlier theoretical investigations on the relative energetic ordering of the bicyclobutane HOMOs, in that the product composition reflects this.

Photolysis of organic substrates at 185 nm in solution has become a well-established photochemical method in recent years.[1a-f] An important result is that the concept of orbital symmetry conservation[2] cannot be applied without some restrictions on the electrocyclic ring opening of alkyl-substituted cyclobutenes.[3a-c] It was shown that the diene products were not generated in the expected disrotatory manner.[3b,c] Besides π,π^* excited states, also radical cation like (π,3s) Rydberg states play an important role.[3a-c] Dunkin and Andrews[4] have developed an orbital symmetry concept in which preferential conrotatory ring opening of the cyclobutene radical cation in its ground state was predicted. The existence of such an additional intermediate could explain the observed lack of stereoselectivity.

Further information on ring-opening processes of small strained molecules, which only absorb $\lambda \leq 254$ nm radiation, should be accessible by studying the 185-nm photolysis of the bridged bicyclo[1.1.0]butanes **1a-c**. All of these compounds are literature known, and they can be deuterated or alkylated at the bridgehead



positions of the central carbon-carbon bond, thereby providing a stereolabel for mechanistic purposes. The following questions were of interest in regard to the 185-nm photochemistry of the bridged bicyclo[1.1.0]butanes **1a-c**:

Do such photolyses take a mechanistically uniform course for the different length (n = 2-4) of the connecting bridge in **1a-c**?

Does one observe changes in the ring-opening propensity of the central and lateral carbon-carbon bonds as a function of the dihedral angle θ?

Does one observe diradical chemistry or do radical cation like Rydberg states or zwitterions intervene that can be recognized by typical Wagner-Meerwein rearrangements or by trapping with

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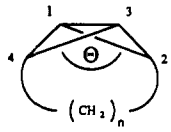
Table I. Bond Lengths, Dihedral Angles, Ionization Potentials and $^{13}C-^{1}H$ Coupling Constants of Bicyclo[1.1.0]butanes[a]

compound		Θ[deg]	C-1-C-3 [Å]	C-1-C-2 [Å]	$I_{v,j}$ [eV][b]	$^{1}J_{CH}$ [Hz]
		122 (9a)	1.497 (9a)	1.498 (9a)[c]	9.39 (9b) 11.3 (9b)	205 (9c)
	**1a**: $n = 2$	108	1.502	1.548[d]	9.43 (9d) 10.23 (9d)	212 (5)
	1b: $n = 3$	118	1.516	1.538[d]	8.72 (9d) 10.45 (9d)	200 (9c)
	1c: $n = 4$	126	1.533	1.531[d]	8.60 (9e) 10.45 (9e)	190 (9f)

[a] References in parenthesis. [b] Determined by photoelectron spectroscopy. [c] Dihedral angle and bond distances from electron deflection measurements. [d] Determined with the MNDO method (ref 9g); an Olivetti M 24 personal computer with arithmetic coprocessor (Intel 8087) was used.

external nucleophiles such as CF_3CH_2OH?[8]

Does an electrocyclic cycloreversion to the corresponding cis/trans dienes take place?

Although there exists much experimental and theoretical data on the bridged bicyclobutanes **1a–c** and the parent bicyclo[1.1.0]butane in regard to the dihedral angle θ, bond lengths, vertical ionization potentials, and $^{1}J_{CH}$ coupling constants of the bridgehead positions (for references, see Table I), their structural parameters have not been determined under comparable conditions. To fill this gap, it was thought to be necessary to perform MNDO calculations on these molecules, in the hope of permitting a more rational comparison of their photochemical behavior as a function of the dihedral angle θ.

In this paper, we present our results on the 185-nm photochemistry and MNDO calculations of the bicyclobutanes **1a–c** and their mechanistic implications. The salient conclusion of our investigations is that the photochemical behavior strongly depends on the length of the chain (n = 2–4) that links the methylene bridges in the bicyclo[1.1.0]butane unit of **1a–c**.

Results

Structural and Physical Parameters of Bicyclobutanes 1a–c. In Table I are listed the structural parameters of the bicyclobutanes **1a–c**, obtained by using the MNDO method, and earlier experimentally determined vertical ionization potentials and $^{1}J_{CH}$ coupling constants. For comparison, also the corresponding experimentally determined values of the parent bicyclo[1.1.0]butane are given.

Photolyses. 185-nm Photolysis of Tricyclo[3.1.0.0^{2,6}]hexane (1a). Irradiation of bicyclobutane **1a** in *n*-pentane at 185 nm gave at 42% conversion the four products methylenecyclopentene (**2a**), 1,3-cyclohexadiene (**3a**), and the hexatrienes *cis/trans*-**4a** in a 91% mass balance, as detected by capillary GC (Table II). The identification of the products entailed comparison of the capillary GC–FTIR spectra with those of the authentic substances and coinjection. The known[10] 3-methylenecyclopentene (**2a**) was prepared by vinylcyclopropane rearrangement from vinyl-substituted methylenecyclopropane. 1,3-Cyclohexadiene (**3a**) and *cis/trans*-1,3,5-hexatriene (*cis/trans*-**4a**) were commercially available compounds. For the structural assignment of the GC peaks in the chromatogram of the photolysate, the isomeric composition of the commercially available *trans/cis*-**4a** sample was first established by means of 200-MHz ^{1}H NMR to be 63:37. The same ratio was found in the capillary GC run of this sample, so the shorter retention time was attributed to the trans isomer **4a**.

254-nm and 185/254-nm Photolyses of 1,3-Cyclohexadiene (3a). Since the 254-nm photoreactivity of diene **3a** is well-known[11a,b] and about 70% of the output of the low-pressure mercury arc, used in our photolyses, was at 254 nm, control experiments were necessary to find out to what extent *cis*- and *trans*-**4a** were secondary products of diene **3a**. In one experiment, the unfiltered and, in another, the 185-nm filtered lamp outputs were used. In both cases, the *cis/trans*-1,3,5-hexatrienes (**4a**) were formed, and the results are given in Table II. The identification of the products was achieved by capillary GC–FTIR.

185-nm Photolysis of Tricyclo[4.1.0.0^{2,7}]heptane (1b). The synthesis of **1b** was carried out according to the literature procedure.[6b] Subsequent 185-nm photolysis yielded 3-methylenecyclohexene (**2b**) and bicyclo[3.2.0]hept-6-ene (**5b**). The quantitative results (determined by capillary GC) are given in Table II. In a preparative experiment, the bicycloheptene **5b** (major product) was isolated in 12% by preparative GC. The spectral data were in accordance with those of independently synthesized authentic material.[12] Also diene **2b** was prepared independently as described,[13] by employing the Wittig reaction on cyclohexen-3-one; coinjection on three different capillary GC columns confirmed its identity. A control experiment demonstrated that diene **2b** was not photoactive on 185-nm irradiation. Coinjection of the commercially available 1,3-cycloheptadiene (**3b**) with the photolysate solution of **1b** proved that **3b** was formed at best in quantities <0.5% (detection limit) during the irradiation of bicyclobutane **1b**. Therefore, a further control experiment was necessary to assess whether eventually generated diene **3b** could be efficiently transformed into bicycloheptene **5b** during the 185-nm photolysis of bicyclobutane **1b**. For this purpose, a solution of bicyclobutane **1b**, which contained 5 mol % of authentic diene **3b**, was irradiated for 40 min with the unfiltered output of the capillary lamp and essentially all (ca. 99%) of the originally present diene **3b** was consumed, as checked by capillary GC.

185-nm Photolysis of [1,7-d_2]Tricyclo[4.1.0.0^{2,7}]heptane (1b-d_2). The deuterated bicyclobutane **1b**-d_2 was prepared from **1b** by four deuteration cycles (cf. Experimental Section), which afforded a 50:50 mixture of **1b**-d_1 and **1b**-d_2, as established by 200-MHz ^{1}H NMR spectroscopy and GC–MS. By means of electronic integration of the ^{1}H NMR spectrum, it was determined that ca. 1.5 D atoms were located at the C-1 and the C-7. By mass spectrometry, the molecular ions m/e 96 (17), 95 (34), and 94 (15) were detected, of which the m/e 94 ion derived mainly from H-cleavage products of **1b**-d_2 and **1b**-d_1; this can be deduced from the mass fragments m/e 93 and 92 in the mass spectrum of the bicyclobutane **1b**. Therefore, the undeuterated bicyclobutane **1b** was not present in any significant quantity (>10%) and only **1b**-d_1 and **1b**-d_2 had to be considered in the deuterium tracer experiment. The 185-nm photolysis of the purified mixture of **1b**-d_1 and **1b**-d_2 yielded the corresponding mono- and dideuterated cyclobutenes **5b**-d_1 and **5b**-d_2. The quantitative product data for the deuterium-label distribution are given in Table II. ^{1}H NMR analysis

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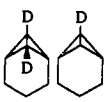
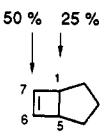
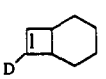
Table II. Product Studies of the Photolyses of the Bicyclobutanes **1a–c** and 1,3-Cyclohexadiene (**3a**)

entry	substrate	conditions	conv. [%]	mass balance [%]	product distribution [%] [a]
1	 **1a**	185 + 254 nm [b] n-pentane	42	91	 **2a** 39  **3a** 15  *trans*-**4a** 26  *cis*-**4a** 20
2	**3a**	185 + 254 nm [b] n-pentane	50	100	- - 43 57
3	**3a**	254 nm n-pentane	42	100	- - 31 69
4	 **1b**	185 + 254 nm [b] n-pentane	19	80	 **2b** 15  **5b** 85
5	 **1b-d_2** 50 **1b-d_1** 50	185 + 254 nm [b] n-pentane	72	30	[c]  50 % 25 % [d] **5b-d_2** and **5b-d_1** [c]
6	 **1c**	185 + 254 nm [b] n-pentane	33	64	 **5c** 75  10 others 13
7	 **1c-d_1**	185 + 254 nm [b] n-pentane			 **[7-D]-5c** 62  **[1-D]-5c** 38

[a] Determined by capillary GC and/or 200-MHz ^{1}H NMR spectroscopy. [b] 185 + 254 nm means that the unfiltered radiation of a low-pressure Hg lamp was used, which has 254 nm as main emission; bicyclobutanes **1a–c** do not react upon 254-nm irradiation. [c] **5b-d_2** and **5b-d_1** were isolated in 21%; the isolation of deuterated *exo*-methylenecyclohexene (**2b**) was not pursued. [d] These values represent the degree of deuteration of the particular position; thus, 67% of the available deuterium was bound to C-6 and C-7 and 33% to C-1 and C-5.

revealed that the degree of deuteration in the olefinic positions C-6 and C-7 was 50%, in the bridgehead positions C-1 and C-5 it was 25%, and no deuterium was in the remaining sites. In other words, 66.6% of the available deuterium was located at the olefinic and 33.3% at the bridgehead positions. No H/D exchange of bicycloheptene **5b** with the solvent took place during the photolysis because the deuterium mass balance was quantitative.

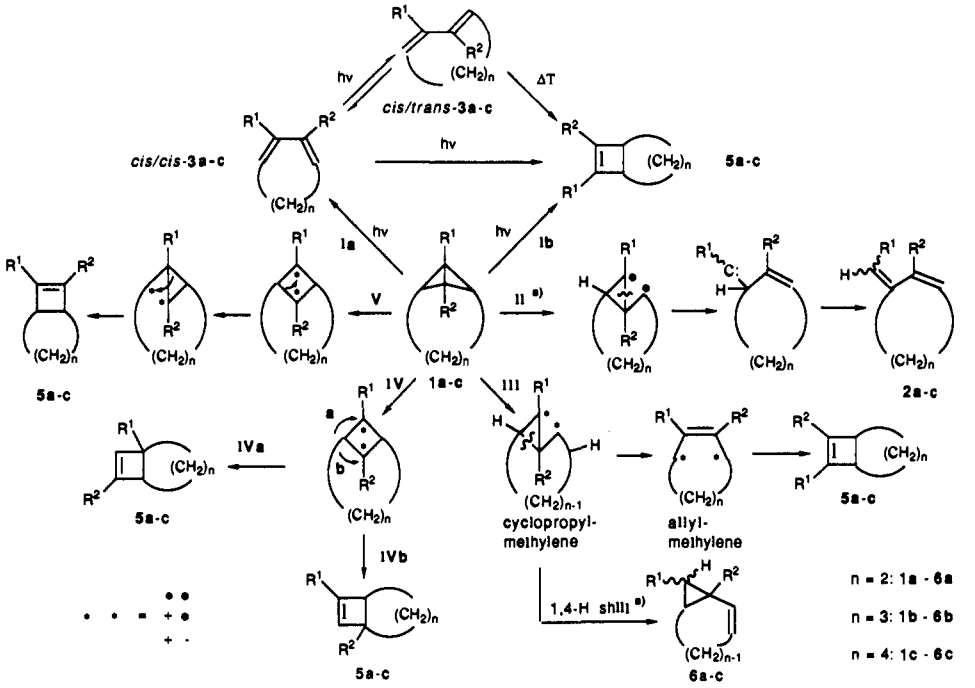
185-nm Photolysis of Tricyclo[5.1.0.0^{2,8}]octane (1c). Bicyclobutane **1c** was prepared in 70% from 1-bromotricyclo-[5.1.0,0^{2,8}]octane by the method of Düker.[7a] Gas chromatographically purified **1c** was then irradiated at 185 nm, and the quantitative product data are listed in Table II. Bicyclo-[4.2.0]oct-7-ene (**5c**) and cyclohexene were observed as 185-nm products of bicyclobutane **1c**. The cyclohexene, as reported,[14] is a well-known secondary product of bicyclooctene **5c** and was identified by coinjection in the capillary GC. In the preparative experiment, besides the bicyclooctene **5c**, also bicyclo[5.1.0]-oct-2-ene (**6c**) was isolated. Since bicyclobutane **1c** is known[7b] to rearrange readily on acid catalysis into bicyclooctene **6c** and since the latter was not observed in the analytical experiment, such a secondary route is a likely source for this product. Both bicyclooctenes **5c** and **6c** were identified by ^{1}H NMR and ^{13}C NMR. Furthermore, at least five other volatile products (ca. 13%) were detected by capillary GC. By means of preparative GC, ca. 2 mg of these unknown products were collected, but the 200-MHz ^{1}H NMR spectrum of this mixture was too complex to permit identification of any one of these products. However, the possible reaction products *cis/cis*-1,3-cyclooctadiene (*cis/cis*-**3c**), *cis/trans*-cyclooctadiene (*cis/trans*-**3c**), and 3-methylenecycloheptene (**2c**) were excluded by comparison with reported[15] spectral data. In a control experiment, it was shown that bicyclobutane **1c** was not photoactive upon 254-nm irradiation.

185-nm Photolysis of [1-d]Tricyclo[5.1.0.0^{2,8}]octane (1c-d_1). The deuterated bicyclobutane **1c-d_1** was prepared in a manner analgous to **1c**. The pure bicyclobutane **1c-d_1** was irradiated at 185 nm, and the deuterated bicyclooctene products **5c-d_1** were isolated and submitted to ^{1}H NMR analysis for determining the deuterium distribution. The results are given in Table II, which show that the [1-d]- and [7-d]bicyclo[4.2.0]oct-7-enes **5c** were formed in 62 and 38% yields, which corresponds to ca. 31% deuteration of

(14) Inoue, Y.; Sakae, M.; Hakushi, T. *Chem. Lett.* **1983**, 1495.

(15) We thank Prof. Dr. M. Christl for the spectra for comparison.

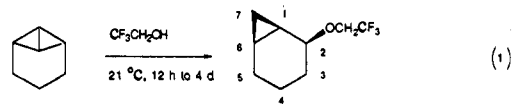
Scheme I. Possible Reaction Mechanisms in the 185-nm Photolysis of Bicyclobutanes **1a–c**



[a] When $R^1 \neq R^2$, a second isomer of **2a–c** and **6a–c** is possible in which the substituents are exchanged.

the olefinic positions C-7 and C-8 and ca. 19% at the bridgehead positions C-1 and C-6. The deuterium balance was again quantitative.

Reaction of Bicyclobutane 1b with 2,2,2-Trifluoroethanol. Originally it was planned to irradiate the bridged bicyclo[1.1.0]butanes **1a–c** in the presence of the nucleophilic solvent CF_3CH_2OH in order to trap possible radical cationic and/or zwitterionic intermediates. Unfortunately, the acidity of the fluorinated alcohol (pK_a = 11.3 and thus ca. 10^4 times more acidic than CH_3CH_2OH) was sufficient to cause effective acid-catalyzed solvolysis of bicyclobutane **1b** to the corresponding *cis*-bicyclo[4.1.0]hept-2-yl-2,2,2-trifluoroethyl ether (eq 1). The ^1H NMR



(1)

(400-MHz) spectrum shows that 2-H couples to both hydrogens in the 3-position and to 1-H with J = 5.7 Hz, which did not allow an assignment of the stereochemistry. Nevertheless, it is known[16] that bicyclobutane **1b** reacts with acetic acid and acidic methanol preferentially to the corresponding cis isomer (stereochemistry determined by secondary reactions of the resulting addition products); therefore, cis addition was assumed.

Discussion

Mechanistic Preview. On the basis of our results and previous published work, in Scheme I are presented five, reasonable but by no means the only ones possible, reaction pathways that rationalize the product distribution in the 185-nm photolysis of the bridged bicyclobutanes. Pathway I describes the concerted reaction course. Two alternatives are possible: On one hand (pathway Ia), the bicyclobutanes **1a–c** may open up to the corresponding cyclic *cis/cis*-1,3-dienes **3a–c**, which by secondary photolysis react further to the bicyclic cyclobutenes **5a–c**; alternatively the *cis/cis*-**3a–c** products are in a photochemical equilibrium with their *cis/trans*-**3a–c** isomers, which then close thermally to the cyclobutenes **5a–c**. On the other hand (pathway Ib), the bicyclobutanes **1a–c** are converted directly through a concerted process to the cyclobutenes **5a–c**.[17] Both pathways Ia,b predict that substituents at the central carbon–carbon bond of the bicyclobutanes **1a–c** appear only in the olefinic positions of the cyclobutenes **5a–c**.

Pathway II starts with lateral carbon–carbon bond cleavage in the bicyclobutanes **1a–c**; for sake of simplicity, we do not differentiate between unsymmetrically substituted cases. Subsequent opening of the central carbon–carbon bond leads to carbenes, which by means of a hydrogen 1,2-shift afford the exomethylenic cycloalkenes **2a–c**.[7b]

Pathway III was the favored mechanism in the Hg-sensitized photolysis of bicyclobutane **1b**.[18] As the primary step was proposed either homolysis of a lateral carbon–carbon bond to result in a cyclopropylmethylene 1,3-diradical (* * = • •; Scheme I) or heterolysis to a 1,3-dipole (* * = + −; Scheme I); furthermore, a cyclopropylmethylene radical cation (* * = + •; Scheme I) would also be appropriate. In a subsequent step, the corresponding allylmethylene species (diradicals, dipoles, and/or radical cations) could arise, which close to the cyclobutenes **5a–c**. Also here it is characteristic that the substituents finally emerge always in olefinic positions.

Pathway IV engages cleavage of the central carbon–carbon bond in the bicyclobutanes **1a–c**. Here also homolysis (1,3-diradicals) and heterolysis (1,3-dipoles and radical cations) are envisaged (Scheme I). Subsequent migration of the alkano bridge (alternative IVa,b in Scheme I) gives the cyclobutenes **5a–c** as products. Of all the mechanisms discussed so far, pathway IV is the only one that places a substituent in the bridgehead position. If R^1 and R^2 are different, one expects R^1 and R^2 to an equal extent in the olefinic and bridgehead positions, provided no substituent effect operates.

Finally, pathway V is proposed in analogy to the results obtained in the radical cation chemistry of derivatives of bicyclobutane **1b**.[19a–d] Substituents are only expected in the olefinic position of the photoproducts.

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The scene is now set to examine how compatible our experimental results of the 185-nm photochemistry of the bridged bicyclobutanes **1a–c** are with the proposed reaction mechanisms of pathways I–V in Scheme I. We begin with the case of bicyclobutane **1c** because its mechanistic features are clear-cut.

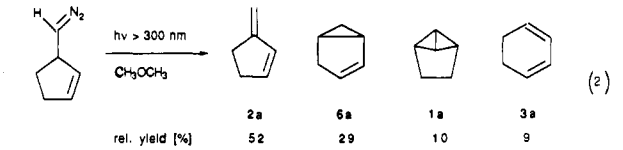
185-nm Photolysis of Bicyclobutanes 1c and 1c-d_1. The results in Table II for the deuterated **1c** (entry 7) show that deuterium is partially located at the bridgehead positions of the cyclobutene **5c** photoproducts. Only pathway IV in Scheme I reconciles bridgehead substitution, so this mechanism must be the main route for the 185-nm photolysis of this bicyclobutane. The unequal proportion of the [1-d]-**5c** and [7-d]-**5c** isomers, the latter dominating (Table II), might have its origin in a substantial secondary isotope effect or, alternatively, several parallel pathways apply in this photochemical transformation. The secondary isotope effect, however, cannot account for [7-d]-**5c** predominating over [1-d]-**5c** because for deuterium the product with higher p character should be favored.[20] In **1c-d_1**, the deuterium-bearing carbon atom has a hybridization state of $sp^{1.63}$, and during its conversion to [1-d]-**5c** (sp^3) and [7-d]-**5c** (sp^2) the former would be expected as the major product in view of its higher p character, which is contrary to the observed experimental facts (entry 7, Table II).[21] Similar discrepancies were reported for the 185-nm isomerization of 1-octene into *cis/trans*-2-octenes (k_H/k_D = 1.2–1.3)[22] and the silver ion catalyzed isomerization of 1-methyltricyclo-[4.1.0.$0^{2,7}$]heptane into 7-methylbicyclo[3.2.0]hept-6-ene (k_H/k_D = 1.74),[23] since for both examples inverse isotope effects should be expected.

Irrespective of whether a deuterium isotope effect operates in the **1c** → **5c** photochemical transformation, the distribution of the deuterium labeling clearly confirms that central carbon–carbon bond cleavage (pathway IV in Scheme I) dominates. The maximum extent to which pathways I, III, and V participate is reflected in the [1-d]-**5c** photoproduct, i.e., only ca. 23%, provided that the deuterium isotope effect is negligible. The possibility that the 1,3-dienes *cis/cis*- and *cis/trans*-**3c** are involved is unlikely because both photoproducts should have accumulated since the half-life for the thermal isomerization of *cis/trans*-**3c** is 34 min at 90 °C.[24]

In the absence of further experimental evidence, the connection between pathways III and IV (i.e., interconverting diyl species) can not be answered at this time.

As in pathway IV formally a Wagner–Meerwein rearrangement is involved, which is rare for 1,3-diradicals,[25a–c] zwitterionic or radical cationic intermediates appear to be favored; however, radical cations of bridged bicyclobutanes[19a–d] behave differently than the intermediates presently reported in the 185-nm photolysis. Nevertheless, our observations are in good agreement with photoelectron experiments,[26] which confirm selective removal of an electron from the central carbon–carbon bond of the bicyclo-[1.1.0]butane moiety. Thus, the bridged bicyclobutane **1c**, which possesses the highest dihedral angle θ of the series of bicyclobutanes **1a–c** examined here, is expected on 185-nm excitation to promote cation-type central carbon–carbon bond cleavage. On the basis of the bond length ratios and the dihedral angle θ in the bicyclobutane unit (cf. Table I), **1c** should show a photochemical behavior that is similar to that of bicyclo[1.1.0]butane. Although different ratios of cyclobutene and 1,3-butadiene were reported[3a,27] as products, the dominating primary step is central carbon–carbon bond cleavage, which is in accordance with the prediction.

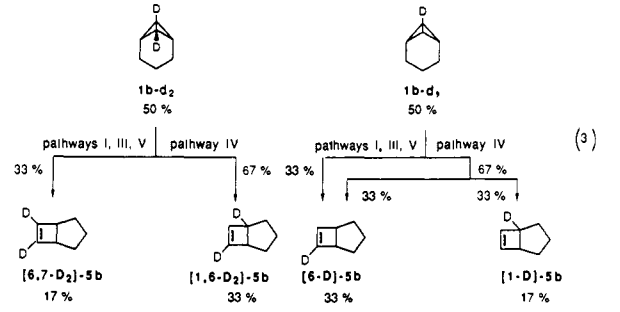
185-nm Photolysis of Bicyclobutanes 1b and 1b-d_2. Although in the 185-nm photolysis of the bicyclobutane **1b** again a cyclobutene **5** is formed as the major product (entry 4 in Table II), one finds as much as 15% 3-methylenecyclohexene (**2b**). A change in the reaction mechanism is indicated, in that the latter product arises presumably from the carbene mechanism in pathway II (Scheme I). Although this particular carbene is not known, the analogous lower homologue, generated in the long-wavelength photolysis (>300 nm) of the corresponding diazoalkane (eq 2),



(2)

was shown to give indeed 3-*exo*-methylenecyclopentene (**2a**) as the major product (hydrogen 1,2-shift), besides bicyclobutanes **1a**, 1,3-diene **3a**, and vinylcyclopropane **6a**, chemistry that substantiates the carbene route in pathway II for the 185-nm photoreaction **1b** → **2b**.[28]

The mechanistic analysis of the deuterium-labeling experiment for this case was cumbersome because only a 50:50 mixture of bicyclobutanes **1b-d_1** and **1b-d_2** was available for its 185-nm photolysis; nevertheless, the results are conclusive. From the fact that, in the bridgehead position of the cyclobutene product **5b**, the degree of deuteration was as much as 25% (entry 5, Table II), it is evident that pathway IV (Scheme I) again plays a central role. The alternative pathways I, III, and IV would provide 75% deuteration in the olefinic and none in the bridgehead positions, which is contrary to the experimentally determined degree of deuteration of 50:25 (entry 5, Table II) for these positions. Unquestionably, in the 185-nm photolysis of the deuterated bicyclobutanes **1b**, the formation of the cyclobutene product **5b** derives from a competition of pathway IV (deuterium located at both the olefinic and bridgehead positions) and pathways I, III, and V (deuterium located exclusively at the olefinic sites). Assuming a negligible deuterium isotope effect (besides it could only operate in the monodeuterated bicyclobutane **1b-d_1** and at that only for pathway IV), to reconcile the experimentally observed distribution of the deuterium label of 67:33 [cf. footnote *d*) in Table II] between the olefinic and bridgehead positions in the cyclobutenes **5b-d_1** and **5b-d_2**, the proportion of the sum of pathways I, III, and V to pathway IV should be approximately 33:67 (cf. the detailed analysis in eq 3). Again, of the various



(3)

possible intermediates, i.e., diradicals (* * = • •) in Scheme I), zwitterions (* * = + −) and radical cations (* * = + •), the latter two types are preferred in view of the fact that the **1b** → **5b** transformation represents a rearrangement of the Wagner–Meerwein-type. Such rearrangements are rare for 1,3-diradicals.[25a–c] Furthermore, since not even traces of the 1,3-diene *cis/cis*-**3b** were observed, pathway Ia (Scheme I) is unlikely.

In view of the fact that also 15% 3-methylenecyclohexene (**2b**) was formed in the 185-nm photolysis of bicyclobutane **1b**, a

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photoproduct that requires lateral carbon–carbon bond cleavage through pathway II in Scheme I, the extent of central carbon–carbon bond cleavage in bicyclobutane **1b** is 57% in the primary step, i.e., (1.00 - 0.15)(0.67)(100) = 57%. Thus, also for this bicyclobutane substrate, central carbon–carbon bond scission dominates, since the lateral carbon–carbon bond is cleaved to the extent of 43%. For comparison, in the thermolysis of bicyclobutane **1b**-d_2, only cyclobutene **5b**-d_2 was found,[29] for which the deuterium distribution speaks for a purely concerted mechanism; moreover, also the Hg-sensitized photolysis of bicyclobutane **1b** shows a distinct behavior.[18] The observed bicyclo[4.1.0]hept-2-ene (**6b**) is the result of a hydrogen 1,4-shift of the cyclopropylmethylene species in pathway III (Scheme I); the other three products, namely, the 1,3-diene *cis*/*cis*-**3b**, the cyclobutene **5b**, and bicyclo[3.2.0]hept-2-ene, are presumably generated from the allylmethylene species (pathway III).

185-nm Photolysis of Bicyclobutane 1a. The tendency toward preferred lateral carbon–carbon bond cleavage on decreasing the dihedral angle (cf. Table I) is unambiguously confirmed in the 185-nm photolysis of bicyclobutane **1a**. The major product (entry 1, Table II) is 3-methylenecyclopentene (**2a**), presumably generated via the carbene intermediate in pathway II (Scheme I), while the hexatrienes *cis*-**4a** and *trans*-**4a** are chiefly secondary products of the photolysis of the 1,3-diene **3a** (entries 2 and 3 in Table II). In principle, the reverse order is possible (not shown in Scheme I), in that, at first, central bond cleavage takes place with subsequent fragmentation of the lateral bond to afford the carbene. Such a mechanistic possibility does not change our conclusion that products **3a** and **4a** (together 61%) require lateral carbon–carbon bond cleavage. This possible pathway is at best of minor importance because a 1,3-diyl species of **1a** with a broken central bond would, besides fragmentation into the carbene, be expected to undergo some rearrangement into **5a**. The latter is sufficiently stable (half-life is 46 h at 102.5 °C)[30] under the experimental conditions and should have been detected by gas chromatography; however, not even traces were observed.

It seems that, for the *trans*-**4a** triene, there is an additional route of subordinate importance, because control experiments (entries 2 and 3 in Table II) with 1,3-cyclohexadiene (**3a**) showed that the triene *cis*-**4a** should be expected as the major secondary product in the 185-nm photolysis.

Summary

On the basis of our experimental results, we can answer the questions that were asked at the beginning:

The 185-nm photolyses of the bicyclobutanes **1a–c** do not take a mechanistically uniform course for the different length (n = 2–4) of the connecting bridge. The product distribution can be rationalized in terms of varying participation of pathways I–V in Scheme I.

There is a clear-cut dependence of the ring-opening propensity of the central and lateral carbon–carbon bonds as a function of the dihedral angle θ (cf. Table I). In the case of bicyclobutane **1c** (θ = 126°; highest dihedral angle in the series), the central bond cleaves preferentially in the primary step. The other extreme is bicyclobutane **1a** with the lowest dihedral angle (θ = 108°). Here one observes exclusively lateral bond cleavage in the primary step. The ratio of central and lateral bond lengths is only another manifestation of the varying dihedral angle. The same holds true for the energy of the two highest occupied MOs, which was determined by PES (cf, Table I). In bicyclobutane **1c** (highest HOMO energy in the series, HOMO was assigned to the central bond[26]), removal of an electron from the central bond on excitation is the most probable primary step. In the bicyclobutane **1a**, the energy of the second highest MO (assigned to the lateral bond[26]) approaches that of the HOMO; consequently one observes cleavage of the lateral bond. The photochemical behavior of bicyclobutane **1b** lies between these two extremes.

It is very probable that radical cation like Rydberg states or zwitterions are responsible for the Wagner–Meerwein rearrangement to afford the products **5** (pathway IV in Scheme I). Trapping by CF_3CH_2OH was not possible because the alcohol is too acidic and adds to the bicyclobutanes in the dark.

Electrocyclic cycloreversion was found in the case of bicyclobutane **1a**, for which considerable amounts of 1,3-cyclohexadiene (**3a**) and its secondary products were found (entry 1, Table II). On the basis of the present results, it is not clear whether this process occurs concerted or stepwise.

Experimental Section

General Aspects. Photolysis. All photolyses were conducted in degassed spectrograde *n*-pentane, which was purified as reported.[31]

Photolysis Equipment. The 185-nm photolyses in a 5-mL scale were carried out with the capillary lamp Nr.4 (Gräntzel Co., Karlsruhe). The thermostated cuvette holder was mounted on an optical bench with defined geometry. During the photolyses under a N_2 atmosphere in a closed Suprasil quartz cuvette, the solution was continuously stirred magnetically to avoid the formation of a polymer film on the inner surface of the cuvette. With use of a Vycor M 235 cut-off filter, the capillary lamp was also used for 254-nm photolyses on an analytical scale. Preparative 185-nm photolyses were performed with an HNS 10W/U_{oz} lamp (Osram Co.); the lamp was placed into a double-walled evacuated tube out of Suprasil quartz and operated under a N_2 atmosphere. The photolysis solutions were externally cooled with ice–water and irradiated under vigorous stirring under N_2 flow. The spectral energy distribution of the lamps is given by the following: capillary lamp Nr.4 Gräntzel, λ (nm)(%), 184.9 (7.9–9.7), 253.7 (66.0), 296.8 (1.0), 312/313 (2.7), 365/366 (2.4), 404.7/407.8 (4.5), 435.8 (7.3), 546.1 (6.5), 577/579 (1.8); HNS 10W/U_{oz}, Osram, λ (nm)(%), 184.9 (12), 253.7 (78.5), 296.8 (0.5), 302.3 (0.3), 312/313 (2.7), 365/366 (2.1), 404.7/407.8 (1.6), 435.8 (3.7), 546.1 (1.6), 577/579 (0.3).

Gas Chromatography. Preparative gas chromatographic separations were performed on a Carlo Erba Model 4200 gas chromatograph (FID). Analytical separations and quantitative analyses were carried out with a Carlo Erba Strumentazione 4100 (FID), a Fractovap 2900 series Capillary-Column-GC, or a HRGC 5160 Mega-Series. As electronic integrators, a Shimadzu C-R1B Chromatopac, a Carlo Erba Mega 2 or a Spectra-Physics System I Computing system were used. GC–MS analyses were performed either in the Institute of Pharmacy and Food Chemistry by Dr. C. Kahre (Finnigan MAT 44 Quadrupol mass spectrometer with SS 200 data evaluation system coupled to a Varian Aerograph 1440) or in the Institute of Organic Chemistry by Dr. G. Lange (8200 Finnigan MAT mass spectrometer and a Varian 3700 gas chromatograph).

Spectroscopy. Infrared spectra were recorded on a Perkin-Elmer Infrared Ratio Recording Spectrometer 1420. Capillary GC–FTIR analyses were performed by Dr. Kahre (Nicolet 20 SXB in connection with a DANI 6500 gas chromatograph). ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker AC 200 or WM 400 spectrometer by using Me_4Si or $CDCl_3$ as reference. UV spectra were recorded on a Hitachi U-3200 Spectrometer.

Conversion, Yield, and Mass Balance. Error Limits. The conversion was determined by gas chromatography according to eq 4a, where A_t is the peak area after the reaction time t, A_0 is the peak area before the reaction, S is substrate, and IS is internal standard. Relative yields were

$$\% \text{ conversion} = [1 - [A_t(S)/A_t(IS)]/[A_0(S)/A_0(IS)]]100 \quad (4a)$$

determined by gas chromatography or NMR spectroscopy. Peak areas of the gas chromatograms or peak areas of characteristic NMR signals normalized to one proton were used (eq 4b), where $A(P)$ is the peak area of a product and $\sum A(P)$ is the sum of the peak areas of all products.

$$\text{relative yield } (\%) = [A(P)/\textstyle\sum A(P)]100 \quad (4b)$$

The mass balance (MB) was determined by gas chromatography by applying eq 4c. Gas chromatographically determined yields are within an error of ca. 2%, and yields determined by NMR spectroscopy are within an error of ca. 5%.

$$\% \text{ MB} = [\textstyle\sum A_t(P)/A_t(IS)]/[A_0(S)/A_0(IS) - A_t(S)/A_t(IS)]100 \quad (4c)$$

Starting Materials and Authentic Compounds for Comparison. Tricyclo[3.1.0.0^{2,6}]hexane (1a) was synthesized as reported by Christl.[5] For

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photolysis purposes, the product was further purified by preparative GC by using two different columns (1.5-m, 10% Apiezon L on Volaspher A2 column, N_2 flow of 1.5 kp/cm^2, oven, injector, and detector temperatures of 80, 150, and 150 °C, R_t(**1a**) = 4.5 min (contaminated with benzene); 1.5-m, 10% CW 20 M on Volaspher A2 column, N_2 flow of 1.7 kp/cm^2, oven, injector, and detector temperatures of 95, 150, and 150 °C, R_t(**1a**) = 3.5 min): IR ($CDCl_3$) 3050, 2950, 2910, 2870, 1600, 1470, 1390, 1298, 1270, 1240, 1175, 1090, 847 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.24 (br s, 4 H, 3-H, 4-H), (m_c, 2 H, 1-H, 6-H), 2.05 (m_c, 2 H, 2-H, 5-H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 2.0 (d, C-1, C-6), 25.7 (t, C-3, C-4), 33.8 (d, C-2, C-5).

3-Methylenecyclopentene (2a),[10] A sample of 1.50 g (18.7 mmol) of (vinylmethylene)cyclopropane in 10 mL of *n*-pentane was stirred for 3 days in a laboratory autoclave at 80 °C. Fischer "Spaltrohr" distillation with a reflux ratio of 20:1 yielded at 72–77 °C (760 Torr) (lit.[10] 43 °C (217 Torr)) 1.50 g (100%) of 3-methylenecyclopentene (**2a**), which was further purified by preparative GC (1.5-m, 10% SE 30 on Chromosorb WHP column, N_2 flow of 1.5 kp/cm^2, oven, injector, and detector temperatures of 50, 100, and 150 °C, R_t(**2a**) = 11.0 min). Traces of acid were rigorously excluded to avoid rearrangement to 2-methylcyclopentadiene: Capillary GC–FTIR 3095, 3078, 3064, 2953, 2939, 2925, 2911, 2862, 1638, 1448, 1007, 940, 865, 814, 767, 655 cm^{-1}; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 1.9–2.3 (m, 4 H, 4-H, 5-H), 4.2–4.5 (m, 2 H, methylene-H), 5.5–5.9 (m, 2 H, 1-H, 2-H).

Tricyclo[4.1.0.0^{2,7}]heptane (1b) was prepared according to the literature.[6b] For photolysis purposes, the product was further purified by preparative GC (1.5-m, 10% Apiezon L on Volaspher A2 column, N_2 flow of 1.5 kp/cm^2, oven, injector, and detector temperatures of 100 °C for 14 min, raised at 30 °C/min to 180 °C and kept there for 5 min, 160 °C, and 160 °C, R_t(**1b**) = 10.0 min): IR ($CDCl_3$) 3090, 3000, 2930, 2860, 1460, 1445, 1335, 1260, 1145, 1110, 1060, 985, 820 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.30 (br s, 6 H, 3-H, 4-H, 5-H), 1.48 (m_c, 2 H, 1-H, 7-H), 2.37 (m_c, 2 H, 2-H, 6-H); GC–MS (70 eV) *m/e* 94 (41, M$^+$), 93 (12), 92 (3), 91 (20), 80 (7), 79 (100), 78 (7), 77 (42), 66 (16), 65 (9), 53 (7), 51 (6), 41 (7), 40 (9), 39 (20), 27 (10). Capillary GC conditions: 30-m, SE 30 column, He gas flow of 0.35 kp/cm^2, oven, injector, and interface temperatures of 50, 150, and 175 °C, R_t(**1b**) = 11.2 min.

[1,7-d$_2$]Tricyclo[4.1.0.0^{2,7}]heptane (1b-*d*$_2$).[6b] All steps in which alkyllithium reagents were used were performed under a N_2 atmosphere. From 32.0 mL of a 2.50 M solution of *n*-BuLi in *n*-hexane, the solvent was distilled off. Subsequently the residue was taken up in 80 mL of dry Et_2O. At 0 °C, 9.00 g (77.4 mmol) of TMEDA and then 3.64 g (38.7 mmol) of **1b** were added. After 5 min of stirring at 0 °C, a colorless precipitate had formed; stirring was continued for 1 h at 21 °C and the mixture hydrolyzed with an excess of D_2O. LiOD was filtered off and the ether layer washed free of TMEDA with 5 × 30 mL of H_2O and then dried over Na_2CO_3. The partially deuterated tricyclic hydrocarbon was dropped into 5.01 g (77.4 mmol) of hexane-free *n*-BuLi, and under strong heat evolution again a colorless compound precipitated. The suspension was stirred for 30 min and hydrolyzed with an excess of D_2O, LiOD removed by filtration, and the ether layer dried. This procedure was repeated two times, and subsequent fractional distillation yielded at 100–112 °C (760 Torr) (lit.[6b] 111–112 °C (760 Torr)) 2.40 g (64%) of deuterated tricyclic hydrocarbon **1b-*d*$_2$**, which was further purified by preparative GC (1.5-m, 10% Apiezon L on Volaspher A2 column, N_2 flow of 1.6 kp/cm^2, oven, injector, and detector temperatures of 80, 150, and 150 °C, R_t(**1b-*d*$_2$**) = 8.5 min): IR (CCl_4) 3100, 3000, 2930, 2860, 2655, 1460, 1443, 1410, 1162, 1135, 1055, 910, 717, 687, 650 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.30 (br s, 6 H, 3-H, 4-H, 5-H), 1.48 (m_c, 0.50 H, nondeuterated positions 1 and 7), 2.37 (m_c, 2 H, 2-H, 6-H); GC–MS (70 eV) *m/e* 96 (17, M$^+$), 95 (34), 94 (15), 93 (11), 92 (20), 91 (16), 85 (10), 81 (28), 80 (100), 79 (66), 78 (36), 77 (37), 68 (7), 67 (20), 66 (84), 65 (11), 57 (12), 56 (15), 55 (6), 54 (11), 53 (11), 52 (6), 51 (10), 50 (6), 43 (14), 42 (6), 41 (21), 40 (32), 39 (33), 29 (17), 27 (18). For capillary GC conditions, cf. GC–MS of **1b**.

3-Methylenecyclohexene (2b) was synthesized as reported in the literature.[13] For complete purification, preparative GC was employed (1.5-m, 10% SE 30 on Chromosorb WHP column, N_2 flow of 1.5 kg/cm^2, oven, injector, and detector temperatures of 100, 160, and 160 °C, R_t(**2b**) = 7.0 min): IR ($CDCl_3$) 3085, 3035, 2940, 2870, 2835, 1635, 1600, 1450, 1435, 1415, 1340, 1250, 1140, 1060, 980, 860 cm^{-1}; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 1.3–2.4 (m, 6 H, 4-H, 5-H, 6-H), 4.5 (br s, 2 H, 7-H), 5.4–5.8 (m, 1 H, 1-H), 5.8–6.2 (m, 1 H, 2-H).

Bicyclo[3.2.0]hept-6-ene (5b) was prepared as earlier described.[12] After purification by preparative GC, a purity of >99% was obtained (1.5-m, 10% Apiezon L on Volaspher A2 column, N_2 flow of 1.8 kp/cm^2, oven, injector, and detector temperatures of 80, 150, 150 °C, R_t(**5b**) = 5.5 min): IR (CCl_4) 3125, 3040, 2940, 2870, 2855, 1460, 1440, 1322, 1300, 1257, 1150, 1102, 1087, 1053, 935, 895, 843 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.05–1.28 (m, 2 H, 3-H), 1.45–1,89 (m, 4 H, 2-H, 4-H), 3.15 (pseudo d, 2 H, 1-H, 5-H), 5.83 (pseudo t, 2 H, 6-H, 7-H); GC–MS (70 eV) *m/e* 94 (11, M$^+$), 93 (14), 91 (15), 80 (6), 79 (100), 77 (31), 67 (7), 66 (19), 65 (9), 41 (6), 40 (7), 39 (18), 27 (7). Capillary GC conditions: 30-m, SE 30 column, He gas flow of 0.35 kp/cm^2, oven, injector, and interface temperatures of 50, 170, 175 °C, R_t(**5b**) = 14.8 min.

Tricyclo[5.1.0.0^{2,8}]octane (1c).[7a,b] All steps in which alkyllithium reagents were used were performed under a N_2 atmosphere. From 6.40 mL of a 2.50 M solution of *n*-BuLi in *n*-hexane, the solvent was distilled off at 20 °C (0.01 Torr). The residue was taken up in 10 mL of dry Et_2O and slowly dropped to a solution of 3.00 g (16.0 mmol) of 1-bromotricyclo[5.1.0.0^{2,8}]octane in 10 mL of Et_2O that was precooled to −78 °C. Subsequently the temperature was raised to 20 °C, the solution was stirred for 3 h, which resulted in a fine, colorless precipitate, and 500 mg (27.8 mmol) of H_2O was added at 0 °C. The voluminous precipitate that consisted of LiOH was removed by filtration, and the solvent was evaporated at 20 °C (20 Torr). Subsequently the mixture of 1-bromobutane and tricyclo[5.1.0.0^{2,8}]octane (**1c**) was distilled off at 50 °C (20 Torr) from nonvolatile impurities, and **1c** was further purified by preparative GC (1.5-m, 10% Apiezon L an Volaspher A2 column, N_2 flow of 1.8 kp/cm^2, oven, injector, and detector temperature of 140, 180, and 180 °C, R_t(**1c**) = 5.0 min, R_t(1-bromobutane) = 6.5 min). There was obtained 1.21 g (70%; lit.[7a] 83%) of a colorless liquid: IR ($CDCl_3$) 3080, 2960, 2920, 2850, 1452, 1445, 1395, 1280, 1220, 1197, 1150, 1118, 1010 cm^{-1}; UV (*n*-pentane) λ (ε) 218 nm (182), 254 (13); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.21 (t, $J_{1,2} = J_{1,7} = J_{8,2} = J_{8,7} = 3.8$ Hz, 2 H, 1-H, 8-H), 1.26–1.34 (m, 4 H, 4-H, 5-H), 1.64–1.75 (m, 4 H, 3-H, 6-H), 2.75–2.85 (m, 2 H, 2-H, 7-H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 10.4 (d, C-1, C-8), 26.8 (t, C-4, C-5), 31.6 (t, C-3, C-6), 53.3 (d, C-2, C-7); GC–MS (70 eV) *m/e* 108 (39, M$^+$), 93 (69), 91 (34), 80 (58), 79 (100), 78 (16), 77 (44), 67 (50), 66 (18), 65 (17), 54 (17), 53 (16), 52 (6), 51 (13), 50 (5), 44 (18), 43 (5), 41 (43), 39 (41), 34 (10). Capillary GC conditions: 30-m, SE 30 column, He gas flow of 0.35 kp/cm^2, oven, injector, and interface temperatures of 80, 180, and 175 °C, R_t(**1c**) = 16.4 min.

[1-d]Tricyclo[5.1.0.0^{2,8}]octane (1c-*d*$_1$) was synthesized in analogy to **1c**; however, the lithium salt of octavalane **1c** was hydrolyzed with D_2O. By starting with 685 mg (10.7 mmol) of *n*-BuLi, 2.00 g (10.7 mmol) of 1-bromotricyclo[5.1.0.0^{2,8}]octane, and 520 mg (26.0 mmol) of D_2O there was obtained after preparative GC 840 mg (72%) of **1c-*d*$_1$**: IR (CCl_4) 3080, 2960, 2920, 2845, 2700, 2300, 1450, 1443, 1393, 1291, 1227, 1218, 1190, 1165, 1110, 1093, 985, 970, 940, 835, 717, 700, 640 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.15–1.25 (m, 1 H, 8-H), 1.25–1.33 (m, 4 H, 4-H, 5-H), 1.63–1.74 (m, 4 H, 3-H, 6-H), 2.75–2.83 (m, 2 H, 2-H, 7-H); GC–MS (70 eV) *m/e* 109 (42, M$^+$), 108 (8), 95 (5), 94 (65), 93 (32), 92 (25), 91 (17), 81 (48), 80 (100), 79 (55), 78 (30), 77 (29), 68 (43), 67 (38), 66 (20), 65 (12), 55 (11), 54 (16), 53 (12), 52 (12), 51 (12), 44 (23), 42 (21), 41 (29), 39 (40). For capillary GC conditions, cf. **1c**.

Photolysis Experiments. 185-nm Photolysis of Tricyclo[3.2.0.0^{2,6}]-hexane (1a). A sample of 20.0 mg (0.250 mmol) of **1a** in 5.00 mL of *n*-pentane was irradiated with the capillary lamp Nr.4 for 90 min at 15 °C. The conversion, as determined by gas chromatography, was 42% and the mass balance 91%. The identification of the products is described below. The retention times are capillary GC values (30-m, SE 30 column, N_2 flow of 0.35 kp/cm^2, oven, injector, and detector temperatures of 20, 150, and 150 °C).

Data for *trans*-1,3,5-Hexatriene (*trans*-4a): R_t = 7.62 min; relative yield of 26%; GC–FTIR 3104, 3090, 3022, 3010, 1813, 1620, 1441, 1280, 1005, 905 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.11–5.28 (m, 4 H, 1-H, 1′-H, 6-H, 6′-H), 6.14–6.47 (m, 4 H, 2-H, 3-H, 4-H, 5-H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 117.7 (t, C-1, C-6), 133.7, 136.8 (d, C-2/C-5 or C-3/C-4). Coinjection and comparison of the GC–FTIR spectrum[32a] with the commercially available comparison compound established the identity of this photo-product. In the commercially available sample a trans:cis ratio of 63:37 was determined by capillary GC and 200 MHz ^{1}H NMR spectroscopy. The assignment of the trienes was made by comparison with the literature known ^{1}H NMR data.[32b]

Data for Tricyclo[3.2.0.0^{2,6}]hexane (1a): R_t = 7.80 min.

Data for *cis*-1,3,5-Hexatriene (*cis*-4a): R_t = 7.99 min; relative yield of 20%; GC–FTIR 3106, 3088, 3036, 1812, 1613, 1445, 987, 908, 811, 660 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.09 (m_c, 2 H, 1′-H, 6′-H), 5.22 (m_c, 2 H, 1-H, 6-H), 6.01 (m_c, 2 H, 3-H, 4-H), 6.82 (m_c, 2 H, 2-H, 5-H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 118.4 (t, C-1, C-6), 130.4, 132.0 (d, C-2/C-5 or C-3/C-4). Coinjection and comparison of the GC–FTIR

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spectrum[32a] with the commercially available compound established the identity of this photoproduct. The same comments hold as for *trans*-**4a**.

Data for 1,3-Cyclohexadiene (3a): R_t = 8.50 min; relative yield of 15%; GC–FTIR 3058, 2951, 2916, 2897, 2884, 2839, 1714, 1432, 745, 669, 680 cm^{-1}. Coinjection and comparison of the GC–FTIR spectrum[32c] with the commercially available compound established the identity of this photoproduct.

Data for 3-Methylenecyclopentene (2a): R_t = 8.59 min; relative yield of 39%. Coinjection and comparison of the GC–FTIR spectrum with independently synthesized (see above) material established the identity of this photoproduct.

254- and (185 + 254)-nm Photolyses of 1,3-Cyclohexadiene (3a).[11a,b] A sample of 12.4 mg (0.155 mmol) of 1,3-cyclohexadiene (**3a**) in 5.00 mL of *n*-pentane was irradiated with the capillary lamp Nr.4 for 90 min at 15 °C, of which the 185-nm portion of the lamp was eliminated by means of a Vycor M 235 filter. At a conversion of 42% and mass balance of 100%—as determined by capillary GC—there were obtained 31% *trans*- and 69% *cis*-1,3,5-hexatriene (**4a**). The identification was carried out as in the photolysis of tricyclohexane **1a**. In a further experiment, unfiltered light was employed and with the same concentration of **3a** a conversion of 50% was achieved, which led to a mixture of 43% *trans*- and 57% *cis*-1,3,5-hexatriene (**4a**).

185-nm Photolysis of Tricyclo[4.1.0.0^{2,7}]heptane (1b). A sample of 406 mg (4.31 mmol) of **1b** in 195 mL of *n*-pentane was irradiated for 4.5 h in the preparative photolysis apparatus. The most volatile components were first distilled off at 20 °C (19 Torr) and then the less volatile ones at 60 °C (19 Torr) and collected in a cold trap at −78 °C. From the distillate, most of the solvent *n*-pentane was distilled off on a 30-cm Vigreux column until a final volume of about 2 mL was obtained. By preparative GC (1.5-m, 10% Apiezon L on Volaspher A2 column, N_2 flow of 1.8 kp/cm^2, oven, injector, and detector temperatures of 100, 130, and 150 °C, R_t(**5b**) = 7.5 min, R_t(**1b**) = 10.0 min), there were isolated 50 mg (12%) of bicyclic olefin **5b** and 70 mg of starting material **1b**. IR and ^{1}H NMR spectra were identical with those of the independently synthesized authentic compound.

In another experiment, 14.9 mg (0.158 mmol) of **1b** in 5.00 mL of *n*-pentane was irradiated for 20 min with the capillary lamp Nr.4. At 19% conversion, there were detected by GC **5b** as the major product (85% relative yield) and **2b** as the minor product (15% relative yield). The mass balance was 80%. The identity of the side product **2b** was confirmed by coinjection of the photolysate with independently synthesized authentic material on three capillary GC columns (50-m OV 101, 40-m OV 101, 30-m SE 30). *cis,cis*-1,3-Cycloheptadiene (**3b**) could not be detected even in traces as the photolysis product (coinjection with commercially available authentic material on a 50-m OV 101 column, N_2 flow of 0.50 kp/cm^2, oven, injector, and detector temperatures of 70, 150, and 150 °C, R_t(**5b**) = 7.62 min, R_t(**2b**) = 8.70 min, R_t(**1b**) = 8.82 min, R_t(**3b**) = 9.98 min).

Joint Photolysis of Tricyclo[4.1.0.0^{2,7}]heptane (1b) and *cis,cis*-1,3-Cycloheptadiene (3b) at 185 nm. A sample of 11.3 mg (0.120 mmol) of tricyclo[4.1.0.0^{2,7}]heptane (**1b**) and ca. 0.6 mg (ca. 0.006 mmol) of *cis,cis*-1,3-cycloheptadiene (**3b**) in 5.00 mL of *n*-pentane was irradiated with unfiltered light of the capillary lamp Nr.4, and the reaction progress was monitored by gas chromatography. After 40 min of irradiation time, there could only be detected ca. 1% of the originally present diene **3b**.

185-nm Photolysis of 3-Methylenecyclohexene (2b). A sample of 15.1 mg (0.160 mmol) of **2b** in 5.00 mL of *n*-pentane was irradiated for 66 min with the unfiltered light of the capillary lamp Nr.4. No significant decrease (≥1%) of the starting material was observed by capillary GC.

185-nm Photolysis of [1-d]- and [1,7-d$_2$]Tricyclo[4.1.0.0^{2,7}]heptane (1b-d_1 and 1b-d_2). A sample of 162 mg (1.70 mmol) of [1-d]- and 164 mg (1.70 mmol) of [1,7-d$_2$]tricyclo[4.1.0.0^{2,7}]heptane (**1b-$d_{1,2}$**) in 290 mL of *n*-pentane was irradiated at 0 °C for 6 h in the preparative photolysis apparatus. The solvent was removed by distillation on a 30-cm Vigreux column until a ca. 2-mL final volume was reached, and from this residue 70 mg (21%) of deuterated bicyclic compound **5b-$d_{1,2}$** and 90 mg (28%) of starting material **1b-$d_{1,2}$** were isolated by preparative GC (1.5-m, 10% Apiezon L on Volaspher A2 column, N_2 flow of 1.7 kp/cm^2, oven, injector, and detector temperatures of 80, 150, and 150 °C, R_t(**5b-$d_{1,2}$**) = 5.5 min, R_t(**1b-$d_{1,2}$**) = 7.5 min): IR (CCl_4) 3080, 3035, 2940, 2870, 2855, 2295, 2265, 2200, 2180, 1457, 1441, 1323, 1292, 1240, 1130, 1102, 1080, 910, 892, 867, 842, 657, 633 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.04–1.26 (m, 2 H, 3-H), 1.43–1.87 (m, 4 H, 2-H, 4-H), 3.13 (pseudo d, 1.5 H, 1 H, 5-H), 5.84 (br s, 1.0 H, 6-H, 7-H); GC–MS (70 eV) *m/e* 96 (6, [d$_2$]M$^+$), 95 (17, [d$_2$]M$^+$ − 1 and [d$_1$]M$^+$), 94 (13), 93 (6), 92 (12), 81 (33), 80 (100), 79 (39), 78 (25), 77 (14), 68 (10), 67 (22), 66 (12), 54 (5), 53 (6), 51 (5), 41 (7), 40 (12), 39 (16), 27 (8). For capillary GC conditions, cf. preparation of **5b**.

185-nm Photolysis of Tricyclo[5.1.0.0^{2,8}]octane (1c). A sample of 275 mg (2.54 mmol) of **1c** in 300 mL of *n*-pentane was irradiated for 3 h at 0 °C in the preparative photolysis apparatus. The solvent was removed by distillation on a 30-cm Vigreux column until a final volume of ca. 2 mL was reached. From this residue, the following products were isolated by preparative GC (1.5-m, 10% Apiezon L on Volaspher A2 column, N_2 flow of 1.8 kp/cm^2, oven, injector, and detector temperatures of 130, 180, and 180 °C).

Unknown Products. A fraction with R_t = 2.75 min was collected, ca. 2 mg (ca. 13% relative yield), that consisted of at least five components (detected by capillary GC: 50-m, OV 101 column, N_2 flow of 0.35 kp/cm^2, oven, injector, and detector temperatures of 60, 175, and 175 °C) with R_t = 11.0, 11.8, 11.9, 12.1, and 13.8 min; the ^{1}H NMR spectrum of this fraction was too complex to be interpreted.

For the subsequent products, first the preparative GC R_t value and second, in parenthesis, the corresponding capillary GC R_t value are given.

Data for Cyclohexene: R_t = − (7.67) min; relative yield of ca. 10%. Coinjection with the commercially available authentic material established the identity of this photoproduct.

Data for Bicyclo[4.2.0]oct-7-ene (5c): R_t = 4.5 (15.3) min; isolated yield of ca. 40 mg, relative yield of ca. 75%; IR ($CDCl_3$) 3040, 2940, 2860, 1600, 1450, 1355, 1310, 1290, 1262, 1140, 1065 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz)[33] δ 1.30–1.75 (m, 8 H, 2-H, 3-H, 4-H, 5-H), 2.83 (m$_c$, 2 H, 1-H, 6-H), 6.10 (s, 2 H, 7-H, 8-H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 18.8 (t, C-3, C-4), 24.9 (t, C-2, C-5), 41.5 (d, C-1, C-6), 140.5 (d, C-7, C-8); GC–MS (70 eV) *m/e* 108 (6, M$^+$), 93 (52), 91 (18), 80 (58), 79 (100), 78 (10), 77 (30), 67 (55), 66 (17), 65 (12), 54 (14), 53 (9), 52 (6), 51 (9), 44 (8), 41 (29), 39 (33). Capillary GC conditions; 30-m, SE 30 column, He gas flow of 0.35 kp/cm^2, oven, injector, and interface temperature of 80, 180, and 175 °C, R_t(**5c**) = 13.9 min.

Data for Tricyclo[5.1.0.0^{2,8}]octane (1c): R_t = 6.1 (19.3) min; isolated yield of ca. 45 mg; collected together with **6c**.

Data for Bicyclo[5.1.0]oct-2-ene (6c): R_t = 6.1 (19.8) min; isolated yield of ca. 45 mg, since compound **6c** was not a photolysis product, but was generated by traces of acid, it was not considered in the relative yield; ^{1}H NMR ($CDCl_3$, 200 MHz)[34a,b] δ 0.08 (dt, $J_{8\text{-}syn,1,7}$ = 5.6 (t), $J_{8\text{-}syn,8\text{-}anti}$ = 3.8 Hz (d), 1 H, 8-*syn*-H), 0.74 (pseudosextet, 1 H, 8-*anti*-H), 1.00–1.75 (m, 4 H, 5-H, 6-H), 1.92–2.34 (m, 4 H, 1-H, 4-H, 7-H), 5.36 (dddd, $J_{2,1}$ = 11.0 Hz, $J_{2,3}$ = 6.5 Hz, $J_{2,4}$ = 4.3 and 1.3 Hz, 1 H, 2-H), 5.72 (m$_c$, 1 H, 3-H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 13.8 (t, C-8), 15.6 (d, C-1 or C-7), 18.4 (d, C-1 or C-7), 24.1, 29.2, 30.0 (t, C-4, C-5, C-6), 127.9, 129.7 (d, C-2, C-3).

In another experiment, 13.5 mg (0.125 mmol) of **1c** in 5.00 mL of *n*-pentane was irradiated at 20 °C with the capillary lamp Nr.4. After 30 min, the relative yields as described above were obtained at a conversion of 33% and a mass balance of 64%.

185-nm Photolysis of [1-d]Tricyclo[5.1.0.0^{2,8}]octane (1c-d_1). A sample of 320 mg (2.93 mmol) of **1c-d_1** in 300 mL of *n*-pentane was irradiated at 20 °C for 3.5 h in the preparative photolysis apparatus. The *n*-pentane was removed by distillation on a 30-cm Vigreux column until a final volume of ca. 2 mL was obtained, and from the residue 40 mg (13%) of [1-d]- and [7-d]bicyclo[4.2.0]oct-7-ene (**5c-d_1**) was isolated by preparative GC (for conditions, cf. photolysis of **1c**): IR (CCl_4) 3040, 2937, 2900, 2860, 2280, 2178, 2140, 1460, 1450, 910, 652, 638 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.30–1.75 (m, 8 H, 2-H, 3-H, 4-H, 5-H), 2.83 (pst, 1.61 H, 1-H, 6-H), 6.10 (s, 1.39 H, 7-H, 8-H); GC–MS (70 eV) *m/e* 109 (6, [1-d]- and [7-d]M$^+$), 108 (3), 94 (46), 93 (19), 92 (15), 91 (8), 81 (46), 80 (100), 79 (47), 78 (26), 77 (20), 68 (41), 67 (39), 66 (18), 65 (6), 55 (9), 54 (14), 53 (10), 52 (9), 51 (8), 44 (10), 42 (14), 41 (19), 39 (37). Capillary GC conditions: 30-m, SE 30 column, He gas flow of 0.35 kp/cm^2, oven, injector, and interface temperatures of 80, 180, and 175 °C, R_t(**5c-d_1**) = 14.6 min.

Reaction of Tricyclo[4.1.0.0^{2,7}]heptane (1b) with 2,2,2-Trifluoroethanol. A sample of 22.5 mg (0.239 mmol) of **1b** was dissolved in 2.00 mL of CF_3CH_2OH and stirred for 12 h at 21 °C. Preparative GC (1.5-m, 10% SE 30 on Chromosob WHP column, N_2 flow of 1.6 kp/cm^2, oven, injector, and detector temperatures of 160, 170, and 170 °C, R_t = 10.0 min) of the reaction mixture yielded 29.0 mg (62%) of *cis*-bicyclo[4.1.0]hept-2-yl 2,2,2-trifluoroethyl ether as a colorless liquid (n_D^{22} = 1.4112).

In another experiment, 500 mg (5.31 mmol) of **1b** and 532 mg (5.31 mmol) of CF_3CH_2OH were mixed, which at first gave two layers that became one after 10 min of stirring at 21 °C. After 4 days, the reaction was complete according to ^{1}H NMR monitoring and only the trifluoroethyl ether product was observed: IR (film) 3080, 3020, 2935, 2860, 1465, 1450, 1425, 1405, 1385, 1370, 1340, 1280, 1155, 1120, 1080, 1025, 975, 910, 890, 845, 825, 738, 685, 670, 655 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.42 (q, $J_{7\text{-}syn,7\text{-}anti} = J_{7\text{-}syn,1} = J_{7\text{-}syn,6} \approx 5$ Hz, 1 H, 7-*syn*-H), 0.63

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(ddd, $J_{7\text{-}anti,7\text{-}syn} \approx 5$ Hz, $J_{7\text{-}anti,1} = J_{7\text{-}anti,6} \approx 8.8$ Hz, 1 H, 7-anti-H), 1.11-1.29 (m, 4 H, 4-H, 5-H), 1.32-1.42 (m, 1 H, 6-H), 1.50-1.59 (m, 2 H, 3-H), 1.77-1.85 (m, 1 H, 1-H), 3.92 (m_c, 2 H, 8-H), 4.07 (q, $J_{2,1} = J_{2,3} = 5.7$ Hz, 1 H, 2-H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 6.95 (t, C-7), 12.5, 13.3 (d, C-1, C-6), 19.0, 23.1, 27.7 (t, C-3, C-4, C-5), 65.1 (m_c, C-8), 75.5 (d, C-2), 124.5 (q, C-9); MS (70 eV) m/e 194 (16, M^+), 179 (21), 166 (56), 165 (42), 152 (37), 140 (41), 139 (64), 95 (51), 94 (62), 93 (12), 91 (10), 83 (25), 81 (31), 80 (11), 79 (100), 77 (20), 69 (13), 68 (40), 67 (72), 66 (25), 65 (13), 59 (19), 57 (15), 55 (56), 54 (29), 53 (36), 43 (13), 42 (29), 41 (88), 40 (12), 39 (54), 29 (19), 28 (29), 27 (31). Anal. Calcd for $C_9H_{13}F_3O$ (194.1): C, 55.68; H, 6.75. Found: C, 55.92; H, 6.93.

Preparation and Chemistry of $PhI^+C{\equiv}CI^+Ph{\cdot}2^-OTf$, Bis[phenyl[[(trifluoromethyl)sulfonyl]oxy]iodo]acetylene, a Novel Difunctional Acetylene, Bis(iodonium) Species and a Stable C_2-Transfer Agent†

Peter J. Stang* and Viktor V. Zhdankin

Contribution from the Department of Chemistry, The University of Utah, Salt Lake City, Utah 84112, *Received December 27, 1990. Revised Manuscript Received February 19, 1991*

Abstract: The title compound **2** is readily prepared as a stable microcrystalline solid from bis(tri-*n*-butylstannyl)acetylene and PhICN·OTf. It was fully characterized by multinuclear NMR, IR, and elemental analysis. As expected, the electron-deficient acetylene **2** reacts with a number of nucleophiles (e.g., Ph_3P, PhSNa, and PhOLi) providing a variety of bifunctionalized acetylenes **5**, **6**, **7**, and **9**. It also undergoes cycloaddition reactions with cyclopentadiene, furan, and other 1,3-dienes to afford useful bis(iodonium)norbornadiene-type adducts **12-14**.

As a consequence of their ready availability and the considerable versatility of their transformations, acetylenes play a key role in organic chemistry.[1] They easily add electrophiles resulting in functionalized olefins, undergo cycloadditions, possess novel photochemistry, and undergo numerous other interesting and useful transformations and rearrangements.[1,2] Most recently acetylenes and their homopolymers have attracted attention in the field of new materials; especially as potential organic conductors[3] and nonlinear optical materials.[4]

Although numerous functionalized alkynes are accessible, little is known about difunctional acetylenes, XC≡CX and XC≡CY, with the functional groups directly attached to the triple bond. Recently, we[5] and others[6,7] have demonstrated that alkynyl(phenyl)iodonium salts **1**, the latest members of the family of multicoordinate iodine species,[8] serve as premier progenitors for a variety of monofunctional acetylenes, RC≡CX, and other useful transformations.

$$\underset{\mathbf{1}}{RC{\equiv}CI^+Ph{\cdot}X^-} \qquad \underset{\mathbf{2}}{PhI^+C{\equiv}CI^+Ph{\cdot}2CF_3SO_3^-}$$

In this paper we wish to report the ready preparation, characterization, and chemistry of the title compound **2**, a novel, versatile, difunctional acetylene and a unique, stable C_2 species.[9,10]

Results and Discussion

Preparation and Characterization of 2. Alkynyliodonium salts **1** are generally prepared by one of the following common procedures: (a) reaction of terminal alkynes with [hydroxy(tosyloxy)iodo]benzene (Koser's reagent),[11] (b) reaction of (trimethylsilyl)acetylenes with $PhIO/BF_3$–etherate,[12] (c) reaction of alkynes with iodobenzene fluoroborates, fluorophosphates, or fluoroantimonates,[13] or (d) reaction of (trimethylsilyl)acetylenes with $PhIO/Tf_2O$ (Zefirov's reagent).[14] In our experience none of these methods worked for the preparation of the diiodonium acetylene **2**. Specifically, reactions of bis(trimethylsilyl)acetylene with any of the above iodine(III) reagents gave either only the monoiodonium salts under mild conditions or tar under forcing

† Dedicated to Professor Ernest L. Eliel on the occasion of his 70th birthday.

(1) For reviews, see: *The Chemistry of the Carbon-Carbon Triple Bond*; Patai, S., Ed.; Wiley-Interscience: London, 1978; Parts 1 and 2. *Methoden der Organischen Chemie, Houben-Weyl*, 4th ed.; Georg Thieme Verlag: Stuttgart, 1977; Vol. 5/2a. Viehe, H. G. *Chemistry of Acetylenes*; Marcel Dekker: New York, 1969. Brandsma, L.; Verkruijsse, H. D. *Synthesis of Acetylenes, Allenes and Cumulenes*; Elsevier: Amsterdam, 1981. Brandsma, L. *Preparative Acetylenic Chemistry*; Elsevier: Amsterdam, 1971.

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