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Direct Photolysis at 185 nm of Simple Alkynes. Intra- and Intermolecular Hydrogen Abstractions

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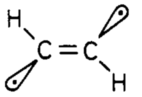
Abstract: The liquid-phase photolysis of simple alkynes is first examined with 185-nm light and the mechanism is discussed. The direct irradiation of 1- or 5-decyne in pentane gave the corresponding alkene, i.e., 1-decene ($\Phi = 0.14$) or *cis*- and *trans*-5-decenes ($\Phi = 0.10$ and 0.16, respectively); the photolysis of cyclononyne led to the formation of bicyclo[4.3.0]nona-1-ene ($\Phi = 0.25$) in addition to the reduction product, cyclononene ($\Phi = 0.16$). The photoreduction of the acetylenes is accounted for by successive intermolecular hydrogen abstractions from the solvent by an excited singlet alkyne and then by the vinyl radical produced in the first step. The formation of the bicyclononene is best interpreted in terms of the intramolecular hydrogen abstraction by the excited triple bond of cyclononyne via a six-membered transition state and the subsequent recombination of the resulting biradical.

Although the photochemistry of $C{=}C$ double bond had been the subject of much investigation in recent years,[1] relatively little is known about the photochemical behavior of $C\equiv C$ triple bond in the liquid phase. Photochemical addition,[2] dimerization,[3] and reduction[2a,d,4] of some *conjugated* acetylenes have been well documented. Photochemical study of simple acetylene without conjugated chromophers, on the other hand, has not been performed extensively,[5] partly due to the absence of an intense absorption band in the accessible UV regions.[6]

Spectroscopically, Ingold[7] has shown that the first excited singlet state of acetylene has the trans-bent structure illustrated below.



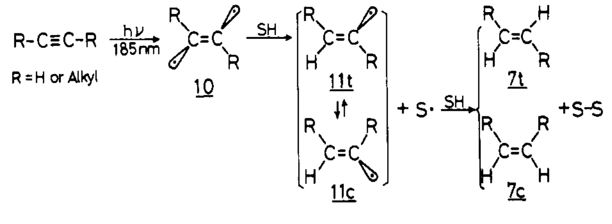
This species may be regarded as a "trans-vinyl biradical". However, little effort has been made to reveal the chemistry of the new biradical species, and the mechanism of photochemical transformation of conjugated acetylenes has not been discussed on the basis of the structure of the excited state.

We wish now to report a study on the direct photolysis at 185 nm of alkyl acetylenes to reveal the fundamental reactivity of the excited $C\equiv C$ triple bond or "trans-vinyl biradical". In this work, 1-decyne (**1**), 5-decyne (**2**), and cyclononyne (**3**) were photolyzed as examples of monoalkyl- and dialkylacetylenes and cyclic acetylene, respectively.

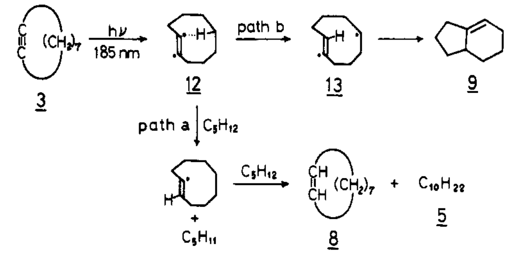
Results and Discussion

Direct photolysis of a pentane solution containing 0.01 M **1**, **2**, or **3** was carried out by using a 30-W mercury resonance lamp fitted with a Suprasil envelope. Products were separated on VPC and characterized by IR, ^{1}H and ^{13}C NMR, and mass spectra and, when the authentic specimens were available, by the retention time comparison on VPC. The products and the chemical and quantum yields in the initial stages of the photolysis are shown in Table I.

Scheme I



Scheme II



As can be seen from Table I, the major course of the reaction is the reduction of alkynes **1–3** to corresponding alkenes, **4**, **7**, and **8** in good yields. the photolyses also accompanied the formation of dimer **5** or **6** of the solvent radical generated by hydrogen abstraction from the solvent (SH). The first excited singlet of alkyne is known to be in the trans form (**10**)[7] and is believed to be a biradical in nature. Hence, the above result can be reasonably interpreted in terms of two-step intermolecular hydrogen abstractions by the excited singlet alkene **10**[8] and then by the vinyl radical **11** produced in the first step, as illustrated in Scheme I.

The photolysis of 5-decyne offers some intriguing features about the inversion of vinyl radical.[9] The vinyl radical formed in the first hydrogen abstraction step is interred to be in the trans form **11t** originally. A considerable amount of *cis*-5-decene, nevertheless, is yielded as a final product along with the trans isomer **7t** (Table I). Both the further trans → cis photoisomerization at 185 nm of **7t** formed initially and the fast inversion of the intermediate vinyl radical **11t** prior to the second hydrogen abstraction could account for the result. In order to test these possibilities, we photolyzed a pentane solution of 5-decyne (0.01

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(1) (a) Inoue, Y.; Takamuku, S.; Sakurai, H. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1635. (b) For recent reviews, see: Kropp, P. *J. Mol. Photochem.* **1978–1979**, *9*, 39. *Org. Photochem.* **1979**, *4*, 1.

(2) (a) Roberts, T. D.; Ardemagni, L.; Shechter, H. *J. Am. Chem. Soc.* **1969**, *91*, 6185. Roberts, T. D. *J. Chem. Soc. D* **1971**, 362. Wooldridge, T.; Roberts, T. D. *Tetrahedron Lett.* **1973**, 4007. (b) Kawanisi, M.; Matsunaga, K. *J. Chem. Soc., Chem. Commun.* **1972**, 313. (c) Schenck, G. O.; Steinmetz, R. *Naturwissenschaften* **1960**, *47*, 514. (d) Büchi, G.; Feairheller, S. H. *J. Org. Chem.* **1969**, *34*, 609. (e) Singh, P. *Ibid.* **1972**, *37*, 836. (f) Nishio, T.; Omote, Y. *Chem. Lett.* **1976**, 103.

(3) (a) Bdüchi, G.; Perry, C. W.; Robb, E. W. *J. Org. Chem.* **1962**, *27*, 4106. (b) Bryce-Smith, D.; Lodge, J. E. *J. Chem. Soc.* **1963**, 695.

(4) (a) Ben-Efrain, D. A. *Tetrahedron Lett.* **1967**, 957. (b) Wilson, J. W.; Stubblefield, V. S. *J. Am. Chem. Soc.* **1968**, *90*, 3423. (c) Zimmerman, H. E.; Pincock, J. A. *Ibid.* **1973**, *95*, 3246.

(5) (a) Fujita, K.; Yamamoto, K.; Shono, T. *Tetrahedron Lett.* **1973**, 3865. (b) Whitten, D. G.; Berngruber, W. *J. Am. Chem. Soc.* **1971**, *93*, 3204.

(6) Robin, M. B. "Higher Excited States of Polyatomic Molecules"; Academic Press: New York, 1975; Vol. 2, pp 106.

(7) Ingold, C. K. *J. Chem. Soc.* **1954**, 2991.

(8) The involvement of Rydberg excited state of alkyne is ruled out in the photolysis at 185 nm, since the Rydberg absorption bands arise at wavelengths shorter than 165 nm.[6] We prefer the π,π^* excited singlet state as the reactive species at the present time, although the possibility of triplet excited state is not completely excluded.

(9) (a) Neuman, R. C., Jr.; Holmes, G. D. *J. Org. Chem.* **1968**, *33*, 4317. (b) Kochi, J. K. "Free Radicals"; Wiley: New York, 1973; Vol. 1-2.

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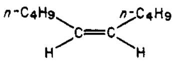
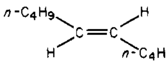
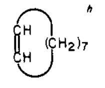
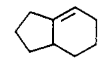
Table I. Direct Photolysis of Simple Alkynes 1-3 at 185 nm[a]

alkyne	solvent	% conversion ($\Phi_{-\text{alkyne}}$)[b]	product, % yield[c] (Φ)[d]		
n-$C_8H_{17}C{\equiv}CH$ (**1**)	pentane	6.6% (0.23)	n-$C_8H_{17}CH{=}CH_2$ (**4**), 62% (0.14)		$C_{10}H_{22}$[e] (**5**), 15% (0.034)
1	cyclohexane	5.4% (0.27)	**4**, 75% (0.20)		bicyclohexyl[f] (**6**), 39% (0.11)
n-$C_4H_9C{\equiv}C$-n-C_4H_9[g] (**2**)	pentane	11.3% (0.38)	 (**7c**), 26% (0.10)	 (**7t**), 41% (0.16)	**5**, 18% (0.068)
 (**3**)	pentane	11.5% (0.43)	 (**8**), 36% (0.16)[h]	 (**9**), 59% (0.25)	**5**, 8% (0.034)

[a] Concentration of alkyne = 0.01 M; irradiation time = 5 min; see the text for experimental details. [b] Quantum yield of alkyne disappearance. [c] Yield based on consumed alkyne. [d] Quantum yield of the product. [e] A mixture of three branched decanes **5a-c**. [f] VPC analysis of the photolysis showed a significant formation (~35% yield) of cyclohexene as a disproportionation product of two cyclohexyl radicals, although quantitative analysis failed due to a pronounced tailing of the solvent peak on VPC. [g] Unidentified product (10% yield) was also detected on VPC. [h] Cyclononene 8 was analyzed as a cis, trans mixture, because of the incomplete separation on VPC.

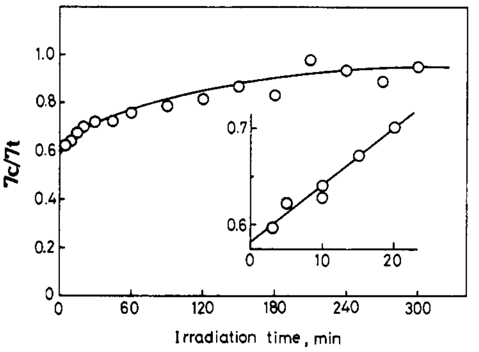


Figure 1. The *cis*- to *trans*-5-decene ratio as a function of irradiation time upon direct photolysis of 5-decyne in pentane. The insert gives the ratios at the initial stages of the photolysis, showing the extrapolated **7c**/**7t** ratio at zero conversion.

M) for up to 5 h, and we plotted the *cis*- to *trans*-5-decene ratio **7c**/**7t** as a function of irradiation period in Figure 1. As expected, the ratio gradually increased up to 0.95 with extending irradiation period, due to the further photoisomerization of the initial product **7t**. However, important is that, even at the least conversion, a significant amount of *cis*-5-decene is produced. Thus, the nonzero value of **7c**/**7t** ratio at zero conversion, i.e., $(\mathbf{7c}/\mathbf{7t})_{t\to0} = 0.58$,[10] is obtained by extrapolating the ratios at $t \le 20$ min to $t = 0$ (see the insert in Figure 1). This result is rationalized only by permitting the inversion of the vinyl radical **11t** to **11c**. It is obvious, therefore, that the second hydrogen abstraction process can not sufficiently compete with the vinyl inversion, although it is still somewhat equivocal whether or not the equilibrium is fully established between **11c** and **11t**.

In the direct photolysis of cyclononyne **3**, the simultaneous formation of cyclononene **8** and bicyclononene **9** is of special interest. The above-mentioned two-step intermolecular hydrogen abstraction mechanism (path a in Scheme II) only explains the formation of the reduction product, i.e., cyclononene **8**. The formation of bicyclononene **9**, on the other hand, is best interpreted in terms of *intramolecular* hydrogen abstraction by the excited alkyne **12** via a six-membered transition state[11] (path b) and the subsequent recombination of the resulting biradical **13**, as illustrated in Scheme II. This may be the first example of competitive inter- and intramolecular hydrogen abstractions by an excited C≡C triple bond and would be compared with the similar inter- and intramolecular behaviors of an excited C=O bond well established in the carbonyl photochemistry[12] and also with an intramolecular hydrogen transfer of vibrationally activated triplet alkenes generated by mercury photosensitization in the vapor phase.[13] However, since we did not observe any cyclic C_{10} products other than **4** or **7** upon direct irradiation of **1** or **2**, the intramolecular hydrogen abstraction (path b) appears to be characteristic of the cyclic acetylene, or at least unfavorable for acyclic alkynes.

We may conclude that an excited C≡C triple bond abstracts two hydrogens stepwise from the solvent to give an alkene as a reduction product and, when a hydrogen atom readily accessible to the excited triple bond is available without significant conformational changes, also suffers intramolecular hydrogen abstraction as a competing reaction process. It is noteworthy that, contrary to the spreaded and believed tendency of acetylenes to undergo polymerization upon irradiation, these inter- and intramolecular processes are highly efficient to give high yields of more than 60%. The reported photoreductions of conjugated acetylenes upon direct irradiation at longer wavelengths[2a,d,4] are now reasonably understood within the framework of the present mechanism.

Experimental Section

Materials. Commercially available 1- and 5-decynes (>99% pure) from Tokyo Kasei Co. were used after fractional distillation. Cyclononyne (98.7% pure) was synthesized from azeloin via cyclonona-1,2-dione and its ditosylhydrazone derivative in a similar method reported by Meier and Menzel.[14] The solvent pentane was stirred over sulfuric acid until the acid layer no longer turned yellow, washed with water, dried over potassium carbonate, and fractionally distilled.

Analysis. VPC analyses of the reaction products from the direct photolyses of **1-3** were carried out over a 3-m column of 20% β,β'-oxydipropionitrile and a 1.5-m column of 15% Carbowax-20M, on which all products, except for the cis-trans isomers of cyclononene, could be separated from each other under these conditions. The FID responses of the compounds were calibrated. Decane, dodecane, or tetradecane was employed as an internal standard.

Direct Photolysis at 185 nm. A pentane solution containing 0.01 M alkynes **1-3** and a small amount of internal standard was

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(10) This value is in accord with *cis*- to *trans*-3-heptene ratio of ~0.5 reported in the photolysis of *trans*-4-iodo-3-heptene in pentane,[9a] where a vinyl radical similar to ours is believed to be an intermediate, although the subsequent formation of a vinyl cation has recently been indicated by: McNeely; Kropp *J. Am. Chem. Soc.* **1976**, *98*, 4319.

(11) A HGS model of the excited cyclononyne in a trans form also supports this transannular interaction between one of the p lobes of the excited triple bond and the hydrogen attached to the carbon at the center of methylene chain of cyclononyne.

(12) Calvert, J. G.; Pitts, J. N., Jr. "Photochemistry"; Wiley: New York, 1966; pp 377, 533.

(13) Inoue, Y.; Takamuku, S.; Sakurai, H. *Can. J. Chem.* **1976**, *54*, 3117 and references cited therein.

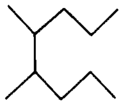
(14) Meier, H.; Menzel, I. *Synthesis* **1971**, 215.

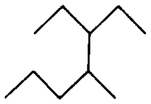
charged in an immersion well reactor (50 mL), flushed with nitrogen gas for 15 min at −10 °C, and then irradiated at room temperature. The light source was a 30-W low-pressure mercury lamp made of Suprasil. Since the alkynes **1**–**3** are transparent at 254 nm, the effective resonance line of mercury is the radiation at 185 nm. Usually, an alkyne concentration of 0.01 M was employed, since alkynes have extinction coefficients of >1000 L/(mol·cm) at 185 nm,[6] and the light path of our apparatus is 5 mm. In a limited experiment on 1-decyne (**1**), pentane solutions at higher concentrations of 0.02 and 0.04 M were irradiated along with a regular 0.01 M solution under similar conditions. Only negligible differences within the experimental error (±5%) were observed in the product yield between these three runs, suggesting that the incident light at 185 nm was completely absorbed even at 0.01 M concentration.

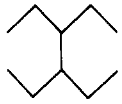
The quantum yields were determined by cyclooctene actinometer, where the quantum yield for the cis–trans photoisomerization of cyclooctene at 185 nm was taken as 0.33.[15]

Preparative scale photolyses were carried out at a higher concentration (0.05 M) in a large immersion well reactor (200 mL) fitted with a low-pressure mercury lamp and a magnetic stirrer. The irradiation was continued for 8–10 h with periodical analysis on VPC and washing of the lamp surface after every 2 h of irradiation. On removal of pentane from the photolized solution, yellow oil was obtained and was separated by VPC to give pure products.

Identification of Products. The major products, **4**, **6**, **7**, and **8**, except **9**, were identified by direct comparison of IR, ^{1}H and ^{13}C NMR, and mass spectra and the retention time of two or three different VPC columns with the authentic specimens. Compound **5** isolated by VPC had a retention time different from that of decane and showed the following spectra: mass spectrum (70 eV), *m/e* (M$^+$) 142 ($C_{10}H_{22}$); IR (neat) 2960, 2925, 1460, 1125 cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si standard) δ 1.27 (br s, 10 H), 0.93 (br s, 12 H). These spectroscopic features indicate branched decanes with four methyl groups in a molecule. The ^{13}C NMR spectrum in $CDCl_3$ showed ~15 peaks of various intensities in the region of δ 12–48 from Me_4Si. Four intense peaks of them are reasonably attributable to four methyl (δ 15.7) four methylene (δ 22.0, 37.6), and two methine carbons (δ 38.5) of 4,5-dimethyloctane (**5a**), the dimer of 2-pentyl radical. The other weaker peaks were also attributed to 3-ethyl-4-methylheptane (**5b**) and 3,4-diethylhexane (**5c**) by applying the chemical shift parameters of Lindeman and Adams.[16] The approximate ratio of these isomeric decanes was evaluated from the peak intensities of ^{13}C NMR spectrum as **5a**/**5b**/**5c** = 5:3:1. This suggests the preferencial formation of 2-pentyl radical over 3-pentyl one in accord with the reported results in radical chemistry.[9b]


5a


5b


5c

Product **9** isolated by VPC showed the following spectra: mass spectrum (70 eV), *m/e* (M$^+$) 122 (C_9H_{14}); IR (neat) 3010 (>C=C—H), 1680 (>C=C<), 1450, 1435, 930, 890, 850, 780 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.3 (br s, 1 H), 0.9–2.2 (m, 13 H). The skeleton of **9** was confirmed by VPC comparison of authentic *cis*-bicyclo[4.3.0]nonane[17] with the hydrogenated product of **9** over 5% Pd on charcoal. Therefore, the product **9** is inferred to be either bicyclo[4.3.0]nona-1-ene or -9-aene. The ^{13}C NMR spectrum of **9** in $CDCl_3$ provided definitive evidence. By comparison with the ^{13}C NMR spectra of 2,3-dimethylcyclohexene and of 1,2-dimethylcyclopentane as model compounds for **9**, each carbon of **9** was assigned as follows: δ 143.5 (C-1), 118.0 (C-2), 42.2 (C-6), 34.7 (C-7), 31.3 (C-5), 30.3 (C-9), 26.4 (C-3), 24.4 (C-8), and 23.8 (C-4).

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(15) Although the quantum yield for cis–trans photoisomerization of cyclooctene at 185 nm was reported to be unity [Srinivasan, R.; Brown, K. H. *J. Am. Chem. Soc.* **1978**, *100*, 2589], recently, in a private communication, Srinivasan has corrected the value to be 0.33 and this result will be published soon by Schuchmann, Sonntag, and Srinivasan.

(16) Lindeman, L. P.; Adams, J. Q. *Anal. Chem.* **1971**, *43*, 1245.

(17) Inoue, Y.; Takamuku, S.; Sakurai, H. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1147.

Tricyclo[5.3.0.0^{1,6}]decan-5-one and Tricyclo[5.4.0.0^{1,6}]undecan-5-one. Synthesis and Selective Transformation to Spiro and Fused Bicyclic Systems

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Abstract: The title compounds (**10** and **11**) were prepared by copper-catalyzed intramolecular cycloaddition of cyclopentenyl (**8**) and cyclohexenyl (**9**) diazo ketones. Reduction of **10** and **11** with lithium in ammonia gave spiro compounds **12** and **14** while exposure to HCl gave chloro ketones **13** and **15**. In contrast, acid-catalyzed methanolysis of **10** and **11** afforded fused bicyclic structures **16** and **17**. Solvolysis of endo and exo alcohols **24**–**27** in methanol produced cis fused ethers **28** and **29**, which slowly underwent isomerization to the trans structures **30** and **31**. A mechanism involving opening of a cyclopropylcarbinyl cation, either via a bicyclobutonium ion or by a stepwise pathway which entails a subsequent 1,2-alkyl shift, would be consistent with these results.

Cyclic structures which incorporate conjoined rings can be regarded as members of a progression which begins[2] with spiro cyclic systems (connected rings with one shared carbon) and extends through fused (two shared carbons) to bridged frames, incorporating three or more common atoms. Although a large number of methods of broad applicability exist for the construction of fused and bridged ring skeletons, relatively few general strategies are available for the elaboration of spirocyclic structures. Recently, considerable effort has been made to repair this deficiency, and some developments along these lines have been reviewed.[3]

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(1) National Institutes of Health Research Career Development Awardee, 1976–1981.

(2) In a formal sense, the family of catenanes (conjoined rings with no shared atoms) would be the first member of this series.

(3) A. P. Krapcho, *Synthesis*, 77 (1978), and references cited.

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