Examination of the raw data revealed systematic extinctions of the type $0k0$ when $k = 2n + 1$ and $h0l$ when $h + l = 2n + 1$ which uniquely identified the space group as $P2_1/n$.

The intensity data were corrected as described earlier. Absorption corrections were not made due to sudden loss of the crystal; the maximum and minimum transmission factors were estimated at 0.67 and 0.40, respectively.

Equivalent data were averaged, yielding 3791 observed ($I_o > 3\sigma I_o$) reflections of which 1505 were considered independent, and subsequently retained for use in the structural solution and refinement.

Structural Solution and Refinement. The position of the bromine atom in 3 was obtained from an analysis of a standard sharpened three-dimensional Patterson map. The positions of the remaining nonhydrogen atoms were determined by successive structure factor[19] and electron density map calculations.[20]

The positions of the bromine, sulfur, and chlorine atoms in 4 were obtained from an analysis of a sharpened three-dimensional Patterson map by using superposition techniques.[21] The positions of the remaining nonhydrogen atoms were determined by successive structure factor and electron density map calculations.

The hydrogen positions were calculated with the C–H bond distance set to 1.05 Å. The isotropic thermal parameters for hydrogens were fixed at 4.0 Å^2.

The aromatic positional and anisotropic thermal parameters for the nonhydrogen atoms were refined initially by block-matrix and finally by full-matrix least-squares procedures,[19] minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma F^2$, to a conventional residual index of $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.045$ and a weighted residual index of $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.059$ for **3**. For **4**, $R = 0.071$ (0.058 for reflections limited to $2\theta \leq 45°$) and a weighted residual index of $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.080$ (0.070 for reflections limited to $2\theta \leq 45°$).

The final positional and thermal parameters for 3 are listed in Tables II and III, respectively, while bond lengths and bond angles are listed in Tables IV and V, respectively (see supplementary material). An ORTEP[22] drawing of the molecule is given in Figure 2. The least squares planes are given in Table VI.

The final positional and thermal parameters for 4 are listed in Tables VII and VIII, respectively, while bond lengths and bond angles are listed in Tables IX and X, respectively (see supplementary material). An ORTEP drawing of the molecule is given in Figure 3. The least-squares planes are given in Table XI.

Acknowledgment. Support (ISU) from Basic Energy Sciences, Materials Sciences, Department of Energy, is gratefully acknowledged. Support (BGSU) from the National Institute of Health (Grant NS 14883) is also acknowledged. The Bowling Green workers thank Dr. Murka Sindler-Kulyk and Professor J. C. Dalton for many helpful discussions. Mass spectra were run with the gracious assistance of Professor T. H. Kinstle.

Registry No. **3**, 85268-50-4; **4**, 85317-25-5; **5**, 85268-51-5; **6**, 85317-26-6; **7**, 78514-41-7; **8**, 85282-17-3; **9a**, 85268-52-6; **9b**, 85268-54-8; **10a**, 85268-55-9; **10b**, 85268-56-0; **11**, 85282-18-4; (*cis*)-**12**, 85268-57-1; (*trans*)-**12**, 85268-58-2; **13**, 85268-59-3; **14**, 85268-60-6; **15**, 85268-61-7; **16**, 85282-19-5; **17**, 85268-62-8; **18**, 78514-42-8; 2,3-dichlorobenzo[*b*]thiophene, 5323-97-7; vinyl bromide, 593-60-2; (*cis*)-1,2-dichloroethylene, 156-59-2; (*trans*)-1,2-dichloroethylene, 156-60-5; **9a** sulfone, 85268-53-7; 3-bromo-2-ethylbenzo[*b*]thiophene, 64860-32-8; 2-ethylbenzo[*b*]thiophene, 1196-81-2; 2-vinylbenzo[*b*]thiophene, 78646-50-1; 2-(α,β-dibromoethyl)benzo[*b*]thiophene, 85268-63-9; 3-vinylbenzo[*b*]thiophene, 6889-73-2; 3-(α,β-dibromoethyl)benzo[*b*]thiophene, 85268-64-0; ethylene, 74-85-1.

Supplementary Material Available: Tables II–XI containing final positional and thermal parameters, bond distances, bond angles, and least-squares planes for 3 and 4 (10 pages). Ordering information is given on any current masthead page.

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[19] Lapp, R. L.; Jacobson, R. A. U.S. Department of Energy Report IS-4708; Ames Laboratory, Iowa State University: Ames, IA, 1979.

[20] Powell, D. R., Jacobson, R. A. U.S. Department of Energy Report IS-4737; Ames Laboratory, Iowa State University: Ames, IA, 1980.

[21] Calculations were carried out on a VAX 11/780 computer. Positions of the heavier atoms were obtained by using the superposition program SUPR (Hubbard, C. R.; Babich, M. W.; Jacobson, R. A.). Structure factor calculations and least-squares refinements were done by using the block matrix/full matrix program ALLS (Lapp, R. L.; Jacobson, R. A.). Fourier series calculations were done by using the program FOUR (Powell, D. R.; Jacobson, R. A.), and for molecular drawings the program ORTEP (Johnson, C. K.) was used. Scattering factors, modified for the real and imaginary parts of anomalous dispersion, were taken from: "International Tables for X-ray Crystallography"; Vol. IV.

[22] Johnson, C. A. U.S. Atomic Energy Commission Report ORNL-3794 (Second Revision with Supplemental Instructions); Oak Ridge National Laboratory: Oak Ridge, TN, 1971.

Direct Photolysis of 1-Halo-1-hexynes. Lack of Ionic Behavior

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Direct photolyses at >200 nm of 1-bromo- and 1-iodo-1-hexynes were performed in polar and nonpolar solvents. Only radical-derived products were obtained even in polar solvents, contrary to the previously reported ionic photochemical behavior of alkyl and vinyl halides. The results are discussed from an energy point of view; the ionization potential of the initially formed organic radical well accounts for the obvious difference in photobehavior between alkynyl and alkyl or vinyl halides.

It had been generally believed that direct irradiation of organic halides leads to homolytic cleavage of the C–X bond and the subsequent formation of radical-derived products.[1] Recent investigations by Kropp et al.[2] and Taniguchi et al.[3] have, however, clearly shown that, upon irradiation in a polar solvent, alkyl and vinyl halides, particularly iodides, exhibit ionic behavior as well as radical behavior. The ionic behavior upon photolysis is reasonably understood by assuming initial homolytic cleavage of the

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[1] Major, J. R.; Simons, J. P. *Adv. Photochem.* **1964**, *2*, 137. Sammes, P. G. "Chemistry of the Carbon-Halogen Bond"; Patai, S., Ed.; Wiley: New York, 1973; Chapter 11.

[2] Kropp, P. J.; Jones, T. H.; Piondexter, G. S. *J. Am. Chem. Soc.* **1973**, *95*, 5420. Poindexter, G. S.; Kropp, P. J. *Ibid.* **1974**, *96*, 7142. McNeely, S. A.; Kropp, P. J. *Ibid.* **1976**, *98*, 4319. Kropp, P. J.; Poindexter, G. S.; Pienta, N. J.; Hamilton, D. C. *Ibid*, **1976**, *98*, 8135. Pienta, N. J.; Kropp, P. J. *Ibid.* **1978**, *100*, 655. Kropp, P. J.; Pienta, N. J.; Sawyer, J. A.; Polniaszek, R. P. *Tetrahedron* **1981**, *37*, 3229.

[3] Suzuki, T.; Sonoda, T.; Kobayashi, S.; Taniguchi, H. *J. Chem. Soc., Chem. Commun.* **1976**, 180. Kitamura, T.; Kobayashi, S.; Taniguchi, H. *Chem. Lett.* **1978**, 1223. Kitamura, T.; Kobayashi, S.; Taniguchi, H. *Tetrahedron Lett.* **1979**, 1619. Schnabel, W.; Naito, I.; Kitamura, T.; Kobayashi, S.; Taniguchi, H. *Tetrahedron* **1980**, *36*, 3229. Suzuki, T.; Kitamura, T.; Sonoda, T.; Kobayashi, S.; Taniguchi, H. *J. Org. Chem.* **1981**, *46*, 5324.

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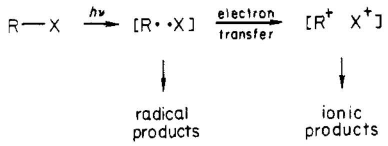
Scheme I[a]



[a] R =alkyl or vinyl.

Table I. Ultraviolet Properties of 1-Bromo-1-hexyne (1a) and 1-Iodo-1-hexyne (1b)

compd	solvent	λ_{max}, nm (ϵ, M^{-1} cm^{-1})	ϵ_{300},[a] M^{-1} cm^{-1}
1a	cyclohexane	219 (470)	≈0
	CH_3OH	214 (490)	≈0
1b	cyclohexane	254 (350), 210 (sh, 440)	51
	CH_2Cl_2	251 (410)	47
	CH_3OH	239 (400), 207 (sh, 640)	21

[a] Extinction coefficient at 300 nm.

C–X bond followed by electron transfer within the resulting radical pair in a solvent cage, as shown in Scheme I.[4] Thus the photochemistry of alkyl and vinyl halides provides a powerful method to generate a cation which is hard to prepare solvolytically. However, these results do not necessarily ensure the intervention of ionic intermediates in the photolyses of *all* organic halides, and therefore study of other organic halides is indispensable to ascertain the limitations and controlling factors of the homolysis–electron transfer process.

The solution-phase photochemistry of alkynyl halides has drawn less attention and has been concentrated mostly upon phenylethynyl halides; the products have been accounted for in terms of the conventional radical mechanism.[5] No studies to explore the potential ionic photochemical behavior of alkynyl halides have been carried out so far in spite of the tempting results with alkyl and vinyl halides.[2,3] Photolysis of alkynyl halides would also provide an attractive alternative route to 1-alkynyl cations, the solvolytic generation of which is not known.

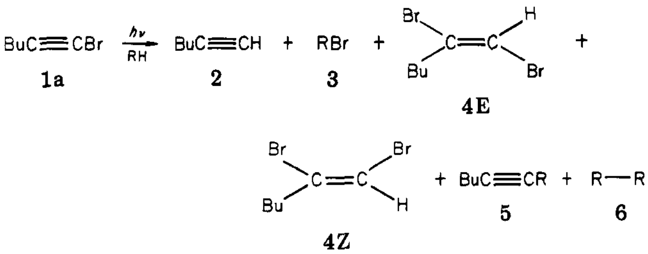
We now report results dealing with the direct photolyses of 1-bromo- and 1-iodo-1-hexynes in polar and nonpolar solvents. We also discuss the scope and limitation of the homolysis–electron transfer process and present energetic features which are useful for diagnosing the feasibility of the subsequent electron-transfer process.

Results and Discussion

Excited States. The ultraviolet spectra of 1-bromo-1-hexyne (**1a**) and 1-iodo-1-hexyne (**1b**) were measured in polar and nonpolar solvents. The absorption maxima and the molar extinction coefficients at the maxima and at 300 nm are shown in Table I.

As to iodohexyne **1b**, there is little ambiguity in assigning the first absorption band around 250 nm to an n,σ^* transition of the C–I bond. The assignment is supported by the position of the absorption maximum, its intensity, and the shape without fine structure, which are all analogous to those of alkyl iodides,[6] and also by the hyposochromic shift induced by the use of polar solvent. The shoulder at 210 nm observed in cyclohexane is attributable to a π,π^* rather than a π,R transition according to Robin.[7]

Scheme II[a]



[a] RH = pentane, cyclohexane, methanol, dichloromethane.

With bromohexyne **1a**, the situation is more complex. Compared with alkyl bromide in the same solvent,[8] the first absorption band for **1a** has moved to longer wavelength, and the intensity is also enhanced, in sharp contrast to the above observation on alkyl iodides and the iodohexyne **1b**. In bromohexyne **1a**, the π,π^* and n,σ^* transitions are inferred to be so close in energy[9] that interaction between the two states may occur; the bathochromic shift of the maximum and the enhanced extinction coefficient can be taken as evidence in support of overlapping or mixing of the two states. Thus the nature of the first excited state(s) of **1a** is somewhat intermediate, and both the C≡C and C—Br bonds have some antibonding character as in is the case of vinyl bromide.[10]

1-Bromo-1-hexyne (1a). Direct photolyses of **1a** (0.05 M) were performed in a variety of solvents. The products obtained were 1-hexyne (**2**), (*E*)- and (*Z*)-1,2-dibromo-1-hexene (**4E** and **4Z**), and the solvent-incorporated products **3**, **5**, and **6** (Scheme II). However, neither 1-chloro-1-hexyne nor 1-methoxy-1-hexyne, which might be formed in a reaction of 1-hexynyl cation, if formed, with dichloromethane or methanol, could be detected in significant yield (>1%) on VPC. The product yields based on consumed **1a**, along with conversion rates, are shown as a function of irradiation time in Table II. As clearly shown upon photolysis in cyclohexane, good total recoveries of both hexynyl and bromine moieties were achieved in most solvents. Upon prolonged irradiation, the yields of **2** and **3** were increased to some extent at the expense of **4**, suggesting further photochemical decomposition of **4**.[11] However, the plots of molar yields vs. irradiation time gave nearly linear relationships at the early stages of photolyses, indicating that all products are the primary photoproducts.

Of these products, **2**, **3**, **5**, and **6** are undoubtedly accounted for by initial C–Br photocleavage and subsequent radical reactions of the resulting 1-hexynyl and bromine radicals with the solvent. On the other hand, another

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(4) However, Cristol et al. have shown that, in certain cases, the ion pair is produced directly and in competition with radical-pair formation: Cristol, S. J.; Daussin, R. D. *J. Am. Chem. Soc.* **1980**, *102*, 2866 and the references cited therein.

(5) Kharasch, N.; Göthlich, L. *Angew. Chem.* **1962**, *74*, 651. Cambell, I. D.; Eglinton, G. *J. Chem. Soc. C* **1968**, 2120. Martelli, G.; Spagnolo, P.; Tiecco, M. *Chem. Commun.* **1969**, 282. There are some reports on the vapor-phase photolysis of haloalkynes: Tarr, A. M.; Strausz, O. P.; Gunning, H. E. *Trans. Faraday Soc.* **1965**, *61*, 1946; **1966**, *62*, 1221. Evans, K.; Scheps, R.; Rice, S. A.; Heller, D. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 856.

(6) *n*-Propyl iodide has λ_{max} at 256 nm (ϵ 499 M^{-1} cm^{-1}) in cyclohexane and at 253 nm (ϵ 494) in methanol (our results).

(7) Robin, M. B. "Higher Excited States of Polyatomic Molecules"; Academic Press: New York, 1975; Vol. 2, p 116.

(8) *n*-Propyl bromide has λ_{max} at 208 nm (ϵ 228) in cyclohexane and at 207 nm (ϵ 223) in methanol (our results).

(9) Substitution of halogen for acetylenic hydrogen generally results in a bathocromic shift of the π,π^* absorption due to interaction between the lone-pair electrons on the halogen atom with the acetylenic π orbitals. For a detailed discussion, see: Wagnière, G. H. "Chemistry of the Carbon-Halogen Bond"; Patai, S., Ed; Wiley: New York, 1973; p 31 and the references cited therein.

(10) Calvert, J. G.; Pitts, J. N. "Photochemistry"; Wiley: New York, 1965; p 523.

(11) In a separate experiment under similar photochemical conditions, irradiation of **4E** synthesized independently gave small amount of **2** and **3** in addition to the major isomerization product **4Z** (see Table VII).

Table II. Photolyses of 1-Bromo-1-hexyne (1a)[a]

solvent (RH)	irradn time, min	% conv	yield,[b] % 2	3	4E	4Z	5	6	R
pentane	10	21	c	9	8.8	34	c	3.9	C_5H_{11}
	20	40	c	12	9.2	30	c	4.2	
cyclohexane	5	13	39	14	8.4	39	14	6.6	C_6H_{11}
	10	24	41	18	9.2	34	13	6.8	
	20	49	46	22	8.6	31	11	4.9	
	30	63	44	25	8.9	29	9	5.5	
	50	90	52	24	8.9	27	6	4.0	
CH_3OH	10	22	44	c	5.4	31	c	c	CH_2OH
	20	43	40	c	4.8	21	c	c	
CH_2Cl_2	10	20	c	c	1.4	20	c	1.5	$CHCl_2$
	20	39	>16[d]	c	2.0	22	c	3.4	

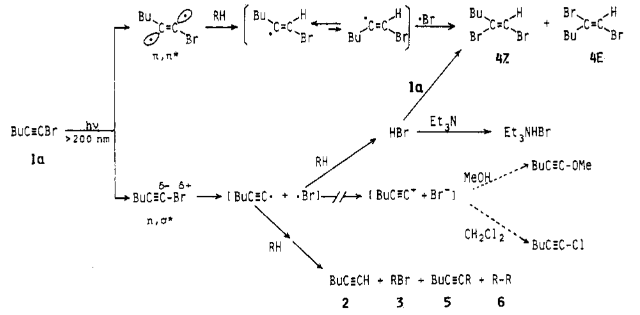
[a] All irradiations were performed under comparable conditions; the concentration of **1a** is equal to 0.05 M. [b] Product yield based on consumed **1a**. [c] Yield not determined. [d] Minimum value is shown due to overlap of solvent peak on VPC.

Table III. Photolyses of 1-Bromo-1-hexyne (1a) in the Presence of Triethylamine in Cyclohexane[a]

Et_3N/1a[b]	yield,[c] mM 2	3	4E	4Z	5	6
0	2.7	1.0	0.50	2.3	0.35	0.45
0.1[d]	2.7	0.9	0.29	1.3	0.35	0.45
0.2	2.4	0.7	0.28	1.0	0.25	0.30
1.0	1.7	0.2	0.25	0.3	0.15	0.10

[a] Irradiations were performed for 5 min in a merry-go-round apparatus; conversion <10%. [b] Molar ratio of triethylamine to **1a**, where the concentration of **1a** is equal to 0.05 M. [c] Product yield in millimolar concentration. Photolyses in the presence of the amine gave a significant amount of Et_3NHBr as a white precipitate. [d] In a separate experiment of thermal addition of hydrogen bromide to **1a** in the dark at room temperature, it was shown that hydrogen bromide was completely trapped by the amine above this concentration (see Table VIII).

Scheme III



Scheme IV

$$\underset{\mathbf{1b}}{\text{BuC}{\equiv}\text{CI}} \xrightarrow[\text{RH}]{h\nu} \underset{\mathbf{2}}{\text{BuC}{\equiv}\text{CH}} + \underset{\mathbf{7}}{\text{RI}} + \underset{\mathbf{8}}{\text{BuCI}{=}\text{CHI}} + I_2$$

mechanism should be operative in the formation of **4**. There may be three possibilities: (1) initial addition of bromine radical to **1a** followed by hydrogen abstraction from the solvent by the resulting vinyl radical, (2) thermal and/or ionic addition to **1a** of hydrogen bromide produced through hydrogen abstraction by bromine radical, and (3) initial hydrogen abstraction by an excited C≡C bond and the subsequent addition of bromine radical. The first possibility is readily ruled out, since any trace of 1,1,2-tribromo-1-hexene, which should be produced in a further addition of a second bromine radical to the dibromovinyl radical formed in the first step, could not be detected. For the same reason, the radical addition of hydrogen bromide (case 2) may also be eliminated, although enough hydrogen bromide would be readily formed from bromine radical under these conditions.

However, the ionic addition mechanism (case 2) merits further consideration. Photolyses of **1a** (0.05 M) in cyclohexane were performed in the absence and presence of triethylamine under the equivalent conditions in a merry-go-round apparatus. As can be seen from Table III, triethylamine in a concentration as low as 0.005 M, just one-tenth the concentration of **1a**, showed discriminating effects upon product yields; the yields of **2**, **3**, **5**, and **6** were virtually unaffected by the addition of triethylamine, whereas **4E** and **4Z** suffered a drastic decrease in their yields.[12] Important is the fact that, in a separate experiment on thermal addition of hydrogen bromide to **1a** under similar but dark conditions, hydrogen bromide was completely trapped by triethylamine above this concentration. It is concluded therefore that, although about half of the **4** produced photochemically is attributable to secondary HBr addition to **1a**,[13] the remaining **4** must arise via another path.

The third mechanism, i.e., initial hydrogen abstraction followed by recombination with bromine radical,[14] is rationalized as an additional channel to dibromohexenes **4**, since our recent study on the photochemistry of simple alkynes[15] revealed that hydrogen abstraction is a general and principal decay process of a π,π^* excited C≡C bond. The probable overlapping or mixing of the π,π^* and n,σ^* transitions described above and the stereochemistry of the product **4**, **4Z** being predominant, also support this mechanism. It is concluded therefore that upon direct irradiation the bromohexyne **1a** suffers simultaneous C–Br bond-cleavage and hydrogen-abstraction reactions. Scheme III explains the sequence leading to the products. However, since no cation-derived products were found in significant yields even in polar solvents, electron transfer within the radical pair resulting from the C–Br cleavage seems energetically unfavorable in this system.

1-Iodo-1-hexyne (1b). In the photolyses of alkyl and vinyl halides[2] a significant difference in photochemical

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[12] Light absorption by triethylamine is responsible for the general decrease of all products upon further addition of triethylamine up to the equimolar amount, since the amine has a strong absorption band around 210 nm ($\epsilon \sim 6000$ M^{-1} cm^{-1}).

[13] The present Z/E ratios of **4** suggest involvement of an ionic rather than radical intermediate, though the addition of hydrogen bromide to 1-bromo-1-alkyne may occur via radical and/or ionic mechanisms: Simamura, O. *Top. Stereochem.* **1969**, *4*, 1.

[14] Absence of 1-bromo-1-hexene as a reduction product may be atributable to fast recombination of the initially formed vinyl radical with abundant bromine radical or to the low ability of the bromovinyl radical to abstract hydrogen.

[15] Inoue, Y.; Ueda, Y.; Hakushi, T. *J. Am. Chem. Soc.* **1981**, *103*, 1806; and the unpublished results.

Table IV. Photolyses of 1-Iodo-1-hexyne (1b)[a]

solvent (RH)	irradn time, min	% conv	yield,[b] %				R
			2	7	8	I_2	
cyclohexane	10	43	48	24	2.1	*c*	C_6H_{11}
	20	72	32	13	2.1	*c*	
	15[d]	16	65	37	~0	14[e]	
	45[d]	45	55	29	~0	*c*	
CH_3OH	10	17	60	*c*	1.6	*c*	CH_2OH
	20	26	66	*c*	1.5	*c*	
CH_3OH + Zn[f]	10	29	69	*c*	1.6	~0	
	20	59	66	*c*	1.6	~0	
CH_2Cl_2[g]	10	14	>42[h]	16	9.0	*c*	$CHCl_2$
	20	26	>40[h]	13	5.7	*c*	
CH_2Cl_2[g] (-78 °C)	10[i]	6	>62[h]	*c*	*c*	*c*	
	50[i]	29	76	*c*	10	*c*	
$(CH_2OH)_2$[j]	10[k]	15	>70[h]	*c*	*c*	*c*	$CHOHCH_2OH$
	60[k]	88	76	*c*	0.2	*c*	

[a] Irradiations were run at room temperature at a distance of 4 cm from the lamp in a merry-go-round apparatus, unless otherwise noted. The concentration of **1b** is equal to 0.05 M. [b] Yield based on consumed **1b**. [c] Yield not determined. [d] Irradiation through a Pyrex filter with the same light source. [e] Measured from the characteristic absorption of I_2 at 523 nm (ϵ 924). [f] Zinc powder (0.48 M) was added as a suspension. No other volatile products were detected in significant yield (>1%). [g] VPC analysis showed the formation of 1-chloro-1-hexyne but in ~0.8% yield at room temperature and in 1.5% yield at -78 °C. [h] Minimum values are shown due to overlap of solvent peak on VPC. [i] Irradiations at -78 °C were performed in a dry ice-methanol bath through a transparent quartz Dewar vessel. [j] The reaction mixture was poured into 3% aqueous sodium thiosulfate solution and extracted with ether prior to VPC analysis. Any other volatile products could not be detected on VPC in significant yield (>1%). [k] Since conversions were very small under the usual photochemical conditions employed, irradiations were run at a distance of 1 cm from the light source.

behavior between the iodides and bromides was observed; in general, the iodides are prone to give more ionic and less radical products than the corresponding bromides. In this context, iodohexyne **1b** is expected to undergo prompt electron transfer within the initially formed radical pair.

Direct irradiations of **1b** were performed in polar and nonpolar solvents to give 1-hexyne (**2**) and the solvent-derived **7**, along with smaller amounts of 1,2-diiodo-1-hexene (**8**) and iodine (Scheme IV) as shown in Table IV. The results are negative as to electron transfer; these major products are all radical-derived, and no cation-derived products are detected in significant yields in the photolyses in polar solvents. Careful VPC analysis, however, showed that a trace amount (~0.8% yield) of 1-chloro-1-hexyne was produced upon photolysis in dichloromethane. The effect of temperature upon product yields was examined, since higher ion yields were reported in the photolyses of alkyl and vinyl halides at lower temperature.[2] The photolysis of iodohexyne **1b** was performed in dichloromethane at -78 °C but produced only a slightly improved, but still negligible, yield (1.5%) of 1-chloro-1-hexyne (Table IV). The same negative result was obtained even in ethylene glycol, although the apparent conversion was diminished due to efficient geminate recombination of the initial radical pair in the solvent cage of viscous ethylene glycol. The use of zinc powder as an iodine scavenger in the photolysis in methanol gave analogous results except for increased conversion rates due to obstraction of recombination of the initial radical pair.

Lack of Ionic Behavior. As has been shown above, little ionic behavior could be found in the photolyses of 1-bromo- and even 1-iodo-1-hexynes; attempts to generate 1-hexynyl cation through the homolysis–electron transfer sequence resulted in total failure. This was not anticipated from the successful formation of alkyl and vinyl cations in the photolyses of the corresponding halides in polar solvents.[2]

Energy considerations for the electron-transfer process not only unravel this puzzling knot but also provides a diagnostic criterion for the feasibility of ion-pair formation. The present process may be formulated as a sequence of electron transfers within a radical pair followed by solvation of the resulting ion pair (see Scheme V). The first electron-transfer process requires energy equal to IP - EA, where IP and EA refer to the ionization potential of the organic radical R· and the electron affinity of the halogen radical X·, respectively. Usually this process is highly endothermic and does not proceed unless stabilization through solvation is accomplished in the second step; only the system in which the solvation energy (E_s) is greater than IP - EA gives ion pairs. When two systems with identical X· but different R· are compared as is the case here, the ionization potential of R· is the only factor controlling the feasibility of electron transfer and is therefore the criterion to be employed.

Scheme V

$$R\cdot + X\cdot \xrightarrow[\text{transfer}]{\text{electron}} R^+ + X^- \xrightarrow{\text{solvation}} R^+_{\text{solv}} + X^-_{\text{solv}}$$

Table V. Ionization Potentials of Ethyl, Vinyl, and Ethynyl Radicals

radical ⟶ cation	IP[a]
$CH_3CH_2\cdot \longrightarrow CH_3CH_2^+$	193[b]
$CH_2{=}CH\cdot \longrightarrow CH_2{=}CH^+$	218[c]
$CH{\equiv}C\cdot \longrightarrow CH{\equiv}C^+$	267[d]

[a] Vertical ionization potential in kilocalories/mole determined by electron impact. [b] Williams, J. M.; Hamill, W. H. *J. Chem. Phys.* **1968**, *49*, 4467. Lossing, F. P.; Semeluk, G. P. *Can. J. Chem.* **1970**, *48*, 955. The photoelectron spectrum gives an analogous IP of 196 kcal/mol; see footnote *b* in Table VI. [c] Harrison, A. G.; Lossing, F. P. *J. Am. Chem. Soc.* **1960**, *82*, 519. [d] Wyatt, J. R.; Stafford, F. E. *J. Phys. Chem.* **1972**, *76*, 1913. A somewhat higher IP of 276 kcal/mol is derived from the heats of formation of ethynyl cation and radical: Okabe, H.; Dibeler, V. H. *J. Chem. Phys.* **1973**, *59*, 2430. Dibeler, V. H.; Walker, J. A.; McCulloh, K. E. *Ibid.* **1973**, *59*, 2264.

For the purpose of simplification, ethyl, vinyl, and ethynyl radicals are adopted as models for their higher analogues. The ionization potentials of these radicals obtained in the gas-phase electron-impact study are listed in Table V. As can be seen from this table, ethyl and vinyl radicals can be ionized by energies near 200 kcal/mol, while ethynyl requires as much as 267 kcal/mol, 49–74 kcal/mol more

Table VI. Ionization Potentials of Some Radicals

radical	IP[a]	radical	IP[a]
$CH_3\cdot$	227[b]		194[c]
$(CH_3)_2CH\cdot$	177[b]		
$(CH_3)_3C\cdot$	160[b]		
	177[c]		202[d]
		Ph·	212[e]
	161[c]	$CH_3\dot{C}O$	186[f]

[a] Vertical ionization potential in kilocalories/mole. [b] Houle, F. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 4067. Chupka, W. A.; Lifshitz, C. *J. Chem. Phys.* **1968**, *48*, 1109. Footnote *b* in Table V. [c] Lossing, F. P.; Traeger, J. C. *J. Am. Chem. Soc.* **1975**, *97*, 1579. [d] Estimated by adding the IP difference (25 kcal/mol) between ethyl and vinyl radicals (Table V) to the IP of the cyclopentyl radical. [e] Fischer, I. P.; Palmer, T. F.; Lossing, F. P. *J. Am. Chem. Soc.* **1964**, *86*, 2741. [f] Reed, R. I. *Trans. Faraday Soc.* **1958**, *54*, 478.

than required by the former two.[16] This difference between ethynyl and ethyl or vinyl radicals may be responsible for the lack of ionic behavior in the photolyses of 1-halo-1-hexynes even in the polar solvents. Ab initio calculations also suggest that formation of 1-alkynyl cations is improbable; among valence isomeric C_3H_3 cations, 1-propynyl cation is higher in energy by 110–115 kcal/mol than cyclopropenyl and higher by 80–95 kcal/mol than propargyl cation.[17]

The ionization potential may also be useful for evaluating the feasibility of ion-pair formation from any given radical pair. We can now predict whether or not a radical pair, for example, generated photochemically, can undergo electron transfer in a polar solvent to give the corresponding ion pair, even though such an experimental attempt has not been made. Some radicals of interest and their gas-phase ionization potentials are shown in Table VI. From these data and the observation of Kropp et al.[2] that even primary alkyl or terminal vinyl iodides exhibit ionic photobehavior in polar solvents, we may deduce that radicals of IP ≤ 200 kcal/mol can undergo electron transfer to the counter iodine, or bromine, radical, giving rise to the corresponding ion pairs. It is therefore expected that the photolysis of 5-iodo-1,3-cyclopentadiene leads to prompt formation of the antiaromatic cyclopentadienyl cation, although solvolysis of the iodide has been reported to be extremely slow.[18] The IP consideration also indicates that methyl iodide does not exhibit ionic photochemical behavior since the IP of methyl radical is considerably above the threshold, while any other alkyl, as well as allyl, iodides may yield ion-derived photoproducts. Judging from the IP of the phenyl radical, it is quite likely that aryl halides, particularly those with electron-donating group, should exhibit ionic photochemical behavior in polar solvents,[19] although the photochemistry or aryl halides has been exclusively interpreted by a radical mechanism.[1,10] More interesting is acyl halide case. The acetyl radical, for example, has an IP as low as 186 kcal/mol, which is well below the threshold. Hence, the photochemistry of acyl halides may provide a direct access to "photo-Friedel–Crafts acylation" in the absence of Lewis acid catalysts.

We may conclude that, in sharp contrast to the facile ion-pair formation in photolyses of alkyl and vinyl halides, the photolyses of 1-halo-1-alkynes give only radical-derived but no ion-derived products even in polar solvents. This is most probably due to the much higher ionization potential of the initially formed alkynyl radical than that of alkyl or vinyl radical. The ionization potentials of radicals are also useful as a diagnostic test of the feasibility of electron transfer within a radical pair.

Experimental Section

General Methods. Infrared spectra were recorded on a JASCO A-100 or a Shimadzu IR-27G grating sppctrophotometer. ^1H and ^{13}C NMR spectra were obtained in a chloroform-*d* or carbon tetrachloride solution containing 1% tetramethylsilane as an internal standard by using JEOL PMX-60 and FX-60 spectrometers. Mass spectra were measured with 20-eV bombardment by using a Hitachi RM-50GC gas chromatograph–mass spectrometer combination. Ultraviolet and visible spectra were recorded on a Shimadzu UV-300 spectrophotometer. Gas chromatographic analyses were performed on YANACO G-180 instrument with a temperature programmer operated at 60–120 or 60–180 °C and a 65-cm or a 1.5-m column of 10% Apiezon L grease.

Materials. 1-Bromo-1-hexyne (1a) was prepared in a reaction of 1-hexyne with potassium hypobromite in 32% yield according to the method reported by Schulte and Goes.[20] The product, boiling at 45 °C (16 torr) [lit.[20] mp 40–41 °C (15 torr)], was further purified by fractional distillation to give an experimental sample of >99% purity (by VPC). **1a**: IR (neat) 2930, 2900, 2840, 2180, 1460, 1420, 1370, 1320, 1100, 920, 740 cm^{-1}; ^1H NMR (CCl_4) δ 2.16 (t, 2 H), 1.2–1.7 (m, 4 H), 0.92 (t, 3 H); ^{13}C NMR ($CDCl_3$) δ 80.9 (s), 38.5 (s), 31.6 (t), 23.0 (t), 20.3 (t), 14.4 (q); MS, *m/z* (relative intensity) 162 (19), 160 (21), 120 (12), 118 (12), 81 (100), 79 (30), 66 (13), 65 (23), 56 (15), 53 (34), 43 (48), 41 (53), 39 (17); for UV spectral data, see Table I.

1-Iodo-1-hexyne (1b) was prepared in reactions of 1-hexyne with methyllithium and then with iodine in 50% yield according to the method described by Dieck and Heck.[21] The product, boiling at 80 °C (21 torr) [lit.[21] mp 75 °C (20 torr)], was purified by fractional distillation to a purity of >99%. **1b**: IR (neat) 2930, 2900, 2840, 2150, 1460, 1370, 1320, 1240, 1100, 950, 740, 560 cm^{-1}; ^1H NMR (CCl_4) δ 2.10 (t, 2 H), 1.2–1.7 (m, 4 H), 0.92 (t, 3 H); ^{13}C NMR ($CDCl_3$) δ 96.0 (s), 31.8 (t), 23.1 (t), 21.8 (t), 14.8 (q), –6.3 (s); MS, *m/z* 208 (100), 166 (29), 81 (38), 79 (43), 66 (29), 53 (62), 43 (38), 41 (81), 38 (52); for UV spectral data, see Table I.

Pentane and cyclohexane were distilled, shaken with concentrated sulfuric acid, washed with water and aqueous potassium carbonate, dried, passed through an activated alumina column, and then fractionally distilled. Methanol was refluxed overnight with magnesium turnings and then fractionally distilled. Dichloromethane was washed with 10% aqueous sodium carbonate and water, dried, and fractionally distilled. Ethylene glycol was used after distillation.

Triethylamine as an additive was distilled from potassium hydroxide prior to use. Reagent grade zinc powder was used as received. Cyclooctane and *n*-decane as internal standards for VPC analyses were purified in a manner similar to that employed for the hydrocarbon solvents.

Photolyses. A 300-W high-pressure mercury arc fitted with a quartz envelope was used as a light source. Except where indicated otherwise, quartz tubing (1 cm o.d.) was used. Irradiations of 0.05 M solutions (3 mL) of **1a** or **1b** were performed at room temperature under a nitrogen atmosphere in a merry-go-round apparatus; the samples were usually placed at a distance of 4 cm from the light source. The products and yields are shown in Tables II–IV. The products were identified mainly by comparison of their VPC retention times and mass spectra with those of the authentic specimens which were commercially available or independently synthesized. The yields were determined by

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(16) This argument is based on the assumption that the stabilization of the resulting cation through solvation is analogous in these three ions.

(17) Radom, L.; Hariharan, P. C.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 10.

(18) Breslow, R.; Hoffman, J. M. *J. Am. Chem. Soc.* **1972**, *94*, 2110.

(19) In a preliminary experiment, direct photolysis of iodobenzene (0.05 M) in methanol indeed gave anisole in ~2% yield along with the major product, benzene (90–95% yield).

(20) Schulte, K. E.; Goes, M. *Arch. Pharm.* **1957**, *290*, 118; *Chem. Abstr.* **1957**, *51*, 12817c.

(21) Dieck, H. A.; Heck, R. F. *J. Org. Chem.* **1975**, *40*, 1083.

Table VII. Photolysis of (*E*)-1,2-Dibromo-1-hexene (4E) in Cyclohexane[a]

irradn time, min	yield, %					
	4E	4Z	2	3	6	1-bromo-1-hexenes[b]
5	70	23	*c*	*c*	*c*	2.6
10	61	24	*c*	*c*	*c*	4.0
30	44	20	*c*	0.6	0.3	5.1
50	36	18	0.3	0.8	0.4	8.4

[a] Irradiation of a 0.05 M solution of 4E, containing small amount (4.6%) of 4Z, was run under the same photochemical conditions as mentioned in Table II. [b] Characterized only by the mass spectra; structures not fully established. [c] Trace amount.

Table VIII. Thermal Addition of HBr to 1a in Cyclohexane in the Absence/Presence of Triethylamine

[1a], M	$[Et_3N]$, M	product ratio, 4Z/4E
0.05	0	9^a–5.5^b
0.05	0.005	*c*
0.05	0.01	*d*

[a] The ratio at ca. 10% conversion. [b] The ratio at ca. 50% conversion. [c] Negligible, but detectable, amounts of 4 were produced. [d] Product not detectable on VPC.

VPC analyses. No significant decomposition of **1a** or **1b** was observed during the VPC analysis. The FID responses for the products were calibrated; where the specimens were not available, the TCD responses were taken as proporsional to the molar concentrations.

Irradiations of **1a** (0.05 M) in the presence of 0.005–0.05 M triethylamine were performed for 5 min in cyclohexane in a merry-go-round apparatus under the same photochemical conditions as mentioned above to give the same photoproducts in reduced yields along with a significant amount of triethylammonium bromide as white precipitate, the infrared spectrum of which was entirely identical with that of the authentic specimen. The results are shown in Table III.

Irradiation of a 0.05 M cyclohexane solution of (*E*)-1,2-dibromo-1-hexene (**4E**) was carried out under the same conditions mentioned above. As can be seen from Table VII, the major photochemical process is the $E \rightleftarrows Z$ isomerization, although slow debromination does occur to give (*E*)- and (*Z*)-1-bromo-1-hexenes in an average ratio of 2.5:1. The bromohexenes were characterized by their VPC retention times (close to that of **1a**) and by the fact that their mass spectra resemble each other. *E* form: *m/z* (relative intensity) 164 (23), 162 (25), 83 (57), 56 (100), 55 (84), 43 (67), 41 (68). *Z* form: *m/z* (relative intensity) 164 (25), 162 (28), 83 (37), 56 (100), 55 (66), 43 (53), 41 (66).

Thermal Addition of HBr to 1a. Hydrogen bromide, generated by adding hydrobromic acid to concentrated sulfuric acid and dried over calcium chloride, was introduced with the aid of slow nitrogen gas flow into a solution of **1a** (0.05 M) containing varying amounts of triethylamine at room temperature. The product ratios were determined at the initial and intermediate stages of reaction by VPC (see Table VIII).

Authentic Specimens. (*E*)- and (*Z*)-1,2-Dibromo-1-hexene (4*E* and 4*Z*). Bromination of 1-hexyne was conducted in chloroform at room temperature according to the method described by Uemura et al.[22] The product was a 21:1 mixture of **4*E*** and **4*Z*** and was characterized as a mixture. **4**: IR (neat) 3080, 2950, 2850, 1730, 1720, 1460, 1430, 1380, 1210, 1120, 790, 770, 720, 705, 645 cm^{-1}; ^{1}H NMR (CCl_4) δ 6.47 (s, vinyl of **4*Z***), 6.33 (s, vinyl of **4*E***), 2.57 (t, 2 H), 1.2–1.8 (m, 4 H), 0.96 (t, 3 H); GC/MS (**4*E***), *m/z* (relative intensity) 244 (10), 242 (19), 240 (11), 202 (11), 200 (20), 198 (11), 121 (16), 119 (15), 81 (100), 43 (83), 42 (18), 41 (29); GC/MS (**4*Z***), *m/z* (relative intensity) 244 (10), 242 (18), 240 (10), 202 (12), 200 (20), 198 (12), 141 (17), 121 (17), 119 (17), 97 (12), 85 (12), 83 (12), 82 (15), 81 (100), 71 (15), 57 (17), 43 (81), 42 (20), 41 (29).

1,1,2-Tribromo-1-hexene. 1-Bromo-1-hexyne (**1a**) was brominated in similar procedures as above.[22] The product tribromohexene showed the following spectral data: IR (neat) 2980, 2950, 2880, 1730, 1470, 1450, 1385, 1220, 1130, 840, 815, 770, 660 cm^{-1}; ^{1}H NMR (CCl_4) δ 2.65 (t, 2 H), 1.2–1.8 (m, 4 H), 0.95 (t, 3 H); ^{13}C NMR ($CDCl_3$) δ 131.0 (s), 88.1 (s), 41.9 (t), 30.9 (t), 22.9 (t), 15.1 (q); MS, *m/z* (relative intensity) 325 (7), 323 (15), 321 (15), 319 (7), 201 (15), 199 (31), 197 (17), 161 (19), 159 (20), 123 (7), 121 (8), 81 (5), 80 (14), 79 (20), 43 (100), 42 (8), 41 (26).

1-Cyclohexyl-1-hexyne (5). According to the method reported by Brown et al.,[23] a tetrahydrofuran solution of lithium hexynylide, prepared in a reaction of 1-hexyne with *n*-butyllithium, was added at 0 °C to tricyclohexylborane, prepared by hydroboration of cyclohexene. To the resultant mixture was added iodine in ether at −78 °C. A workup gave the cyclohexylhexyne **5** as a colorless liquid: bp 94 °C (1.0 torr); IR (neat) 2950, 2880, 2220, 1455, 1380 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.0–2.6 (m, 3 H), 1.1–2.0 (m, 14 H), 0.9 (t, 3 H); MS, *m/z* (relative intensity) 164 (53), 135 (32), 123 (16), 122 (100), 121 (53), 109 (16), 108 (26), 107 (84), 95 (21), 94 (42), 93 (100), 91 (16), 83 (21), 82 (42), 81 (100), 80 (68), 79 (95), 69 (16), 68 (42), 67 (100), 57 (16), 55 (37), 54 (26), 43 (16), 41 (16).

Iodocyclohexane (3b). Addition of cyclohexene to a mixture of potassium iodine and 85% phosphoric acid and the subsequent reflux for 3.5 h[24] gave iodohexane: bp 74 °C (27 torr) [lit.[24] 48–49.5 °C (4 torr)]; IR (neat) 2950, 2850, 1450, 1330, 1250, 1180, 1100, 995, 890, 810, 660, 500, 450 cm^{-1}; ^{1}H NMR (CCl_4) δ 4.27 (tt, 1 H), 2.03 (br, 4 H), 1.58 (br, 6 H); ^{13}C NMR ($CDCl_3$) δ 41.2 (t), 33.6 (d), 28.9 (t), 27.1 (t); MS, *m/z* (relative intensity) 210 (17), 83 (100), 55 (66).

1,2-Diiodo-1-hexene (8). An equimolar mixture of 1-hexyne and iodine was refulxed in methanol for 23 h to give the diiodohexene **8**: bp 86 °C (1.0 torr); IR (neat) 3060, 2950, 2850, 1460, 1430, 1380, 1200, 1110, 950, 770, 570 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.77 (s, 1 H), 2.50 (t, 2 H), 1.2–1.7 (m, 4 H), 0.96 (t, 3 H); ^{13}C NMR ($CDCl_3$) δ 106.4 (s), 81.7 (s), 46.3 (t), 32.1 (t), 23.3 (t), 16.2 (q); MS, *m/z* (relative intensity) 336 (59), 294 (28), 167 (59), 82 (27), 81 (100), 67 (21), 53 (13).

1-Chloro-1-hexyne. To an aqueous 2 M sodium hydroxide solution (20 mL) containing 4 mL of commercial sodium hypochlorite solution (Antiformin, 10% active chlorine) was added 0.5 g (6.1 mmol) of 1-hexyne at 0 °C, and the mixture was stirred vigorously at room temperature for 6 days. Extraction with pentane, evaporation of the solvent, and trap-to-trap distillation gave 1-chloro-1-hexyne: IR (neat) 2960, 2930, 2860, 2240, 1460, 1430, 1380, 1325, 1080, 930, 740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.16 (t, 2 H), 1.51 (m, 4 H), 0.90 (t, 3 H); MS, *m/z* (relative intensity) 118 (4), 116 (12), 103 (6), 101 (17), 81 (100), 79 (21), 65 (26), 56 (12), 53 (15), 43 (52), 41 (47), 39 (13).

All the other compounds produced in the photolyses were commercially available, except dichloroiodomethane, which was tentatively assigned by the characteristic fragment pattern of the mass spectrum.

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Registry No. **1a**, 1119-64-8; **1b**, 1119-67-1; **2**, 693-02-7; **3a**, 626-62-0; **4E**, 49677-13-6; **4Z**, 49677-14-7; **5**, 42049-52-5; **8**, 74966-64-6; potassium hypobromite, 13824-97-0; methyllithium, 917-54-4; iodine, 7553-56-2; (*E*)-1-bromo-1-hexene, 13154-13-7; (*Z*)-1-bromo-1-hexene, 13154-12-6; 1,1,2-tribromo-1-hexene, 53977-98-3; lithium hexynylide, 17689-03-1; tricyclohexylborane, 1088-01-3; cyclohexene, 110-83-8; sodium hypochlorite, 7681-52-9; 1-chloro-1-hexyne, 1119-66-0.

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