Photochemistry of *cis*- and *trans*-1-Iodopropene[1]

ROBERT C. NEUMAN, JR.

Department of Chemistry, University of California,
Riverside, California 92502

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The iodo olefins *cis*- and *trans*-1-iodopropene have been synthesized. Photolysis in the vapor phase and in solution led to *cis–trans* isomerization, the photoelimination products acetylene, methylacetylene, and methyl iodide, and the photodissociation product propylene. The effects of oxygen, wavelength, and reaction phase on the various processes have been investigated and the possible mechanisms for these reactions are discussed in light of these results.

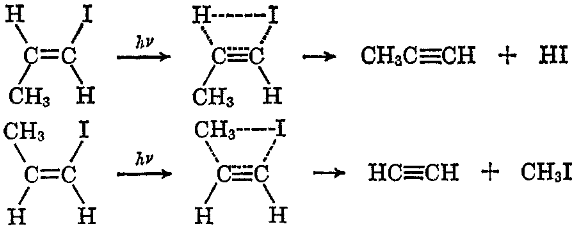
Photochemical studies of organic iodides have been largely restricted to the simple alkyl iodides[2-4] and aromatic iodides.[5] Mechanistic studies of the vapor phase photolysis of ethyl iodide suggest that photodissociation of the carbon–iodine bond (1) and photomolecular elimination of HI (2) both occur as primary processes.[3,6,7] Reaction 1 seems to be quite general for all organic iodides. This is expected because of the low values (~35–60 kcal/mole) for D(C–I).[8] In those systems in which reaction 2 is possible the observed products allow for its occurrence.[2,3] However, the evidence for such a process is not extensive.[6]

$$CH_3CH_2I \xrightarrow{h\nu} CH_3CH_2\cdot + I\cdot \qquad (1)$$

$$CH_3CH_2I \xrightarrow{h\nu} CH_2{=}CH_2 + HI \qquad (2)$$

Recently, we found that photolysis of 1,1-diiodopropane gave the volatile hydrocarbon products, methylacetylene, acetylene, and propylene.[9] A closer examination of this reaction showed that, in fact, *cis*- and *trans*-1-iodopropene were the primary products and that the volatile hydrocarbons were formed by photolysis of these iodoolefins.

The formation of methylacetylene and acetylene suggested that two types of photomolecular eliminations could have occurred: (1) the elimination of hydrogen iodide to yield methylacetylene; and (2) the elimination of methyl iodide to yield acetylene.[10] It seemed attractive to think of these processes as arising from the *trans* and *cis* isomers, respectively, as shown in reactions 3 and 4.



(3)

(4)

A search of the literature revealed that the only previous photochemical study of an iodo olefin was reported by Emschwiller in 1934.[11,12] He found that photolysis of liquid vinyl iodide yielded approximately equal amounts of acetylene and ethylene. His mechanistic proposals are vague, but apparently he favored an α elimination of hydrogen iodide and a subsequent hydrogen shift to give acetylene. The results of a more recent study[13] on the photolysis of *cis*-1,2-dichloroethylene and of a photolytic study[14] of several vinyl chlorides in the frozen state have been interpreted in terms of β-molecular eliminations of HCl. However, in these studies the question of a preferred geometric isomer for the elimination reaction was not considered.

In order to determine whether the photochemistry of the iodopropenes was different for the two geometric isomers, a study of *cis*- and *trans*-1-iodopropene was undertaken.

Results

Preparation and Spectral Properties of the Iodopropenes.—A mixture of *cis*- and *trans*-1-iodopropene was synthesized by dehydrohalogenation of 1,1-diiodopropane.[15] Vapor phase chromatography of this mixture using a silicone fluid (SF-96) liquid phase yielded analytically pure 1-iodopropene. The 1-iodopropene was further separated into its *cis* and *trans* isomers by preparative vapor phase chromatography using a γ-nitro-γ-methylpimelonitrile liquid phase. Characterization of these isomers was accomplished by an analysis of their ultraviolet, nmr,[16] and infrared spectral data. A comparison of the infrared data with those for the known *cis*- and *trans*-1-bromopropene[17,18] and *cis*- and *trans*-1-chloropropene[17] allowed the isomeric assignments to be made with a high degree of confidence (Table I).

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[1] (a) Partial support by the National Science Foundation through Grant GP 4287 is gratefully acknowledged; (b) presented at the First Western Regional American Chemical Society Meeting, Los Angeles, Calif., Nov. 18–20, 1965.

[2] See E. W. R. Steacie, "Atomic and Free Radical Reactions," Vol. 1, 2nd ed, Reinhold Publishing Corp., New York, N. Y., 1954, pp 397–405.

[3] J. R. Majer and J. P. Simons, *Advan. Photochem.*, **2**, 137 (1964).

[4] D. C. Blomstrom, K. Herbig, and H. E. Simmons, *J. Org. Chem.*, **30**, 959 (1965).

[5] See W. Wolf and N. Kharasch, *ibid.*, **30**, 2493 (1965).

[6] R. Schindler and M. H. J. Wijnen, *Z. Physik. Chem.* (Frankfurt), **34**, 109 (1962); **38**, 285 (1963).

[7] See also (a) R. H. Webbe, Jr., and J. E. Willard, *J. Am. Chem. Soc.*, **81**, 761 (1959); (b) H. A. Gillis, R. R. Williams, Jr., and W. H. Hamill, *ibid.*, **83**, 17 (1961).

[8] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp 47–53.

[9] R. C. Neuman, Jr., unpublished results.

[10] Molecular eliminations of hydrogen halides, both photochemical and thermal, have been previously proposed (*vide infra*). However, to our knowledge, molecular eliminations in which carbon–halogen bonds are formed (*e.g.*, CH_3I formation) have not been previously proposed.

[11] G. Emschwiller, *Compt. Rend.*, **198**, 464 (1934).

[12] (a) Only one study of vinyl iodide discusses the organic products.[11] Two other studies[12b,c] have been reported which are not pertinent to this discussion. (b) G. Emschwiller, *Bull. Soc. Chim. France*, **6**, 561 (1939); (c) W. West and B. Paul, *Trans. Faraday Soc.*, **28**, 688 (1932).

[13] M. H. J. Wijnen, *J. Am. Chem. Soc.*, **83**, 4109 (1961).

[14] D. H. Volman, K. A. Maas and J. Wolstenholme, *ibid.*, **87**, 3041 (1965).

[15] (a) For a preliminary report on the synthesis of this diiodide, see R. C. Neuman, Jr., *Tetrahedron Letters*, 2541 (1964); (b) R. C. Neuman, Jr. and M. J. Rahm, *J. Org. Chem.*, **31**, 1857 (1966).

[16] An analysis of the nmr spectral data for the 1- and 2-iodopropenes will be published separately: R. C. Neuman, Jr., and D. Roark, *J. Mol. Spectry.*, in press.

[17] K. E. Harwell and L. F. Hatch, *J. Am. Chem. Soc.*, **77**, 1682 (1955).

[18] P. S. Skell and R. G. Allen, *ibid.*, **80**, 5997 (1958).

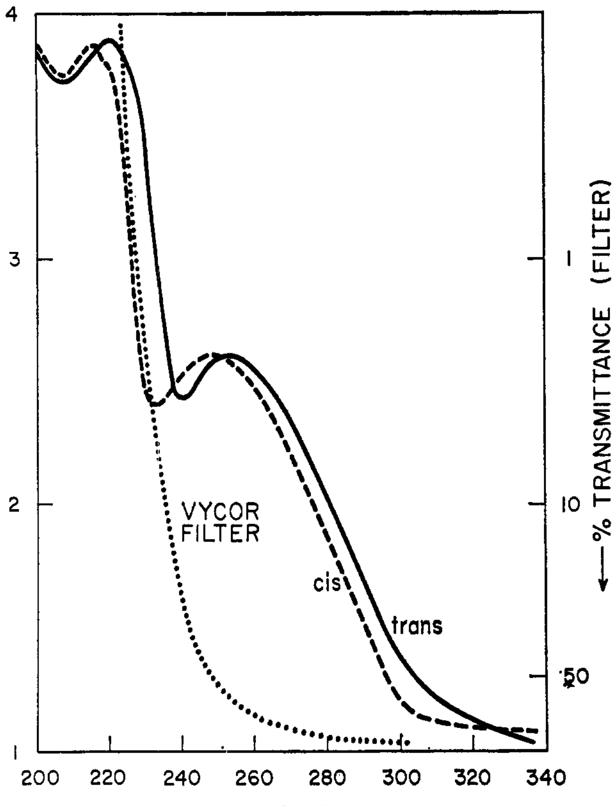

Figure 1.—Ultraviolet spectra of *cis*- and *trans*-1-iodopropene in cyclohexane. Vycor filter transmittance was used in these runs.

TABLE I

INFRARED SPECTRAL DATA FOR THE ISOMERIC 1-HALOPROPENES[a]

Halogen	*cis* isomer	*trans* isomer
Cl[b]	7.65	8.13
	13–15	10.75
Br[c]	7.61, 7.69	8.17
	14.6, 14.8	10.54, 10.72
I[d]	7.68, 7.74	8.32, 8.39
	15.4, 15.7	10.28, 10.32

[a] All absorptions are strong and given in microns. [b] Pure liquid sample.[17] [c] Gas sample; 10-cm cell.[17,18] [d] Gas sample; 10-cm cell (this work).

The ultraviolet spectra of cyclohexane solutions of *cis*- and *trans*-1-iodopropene are shown in Figure 1. The spectra of the isomers are very similar except that the spectrum of the *cis* isomer shows a blue shift of $\sim$5 mμ.

Direct Photolysis.—Irradiation of the iodopropenes was carried out in the vapor phase at atmospheric pressure (nitrogen atmosphere) in a quartz vessel using the full arc of a medium pressure mercury lamp. The observed reaction products (*vide supra*) have led us to divide the possible photochemical processes into three convenient categories: (1) photoisomerization; (2) photoelimination; and (3) photodissociation. Subsequent discussion will indicate that these may or may not be truly separable.

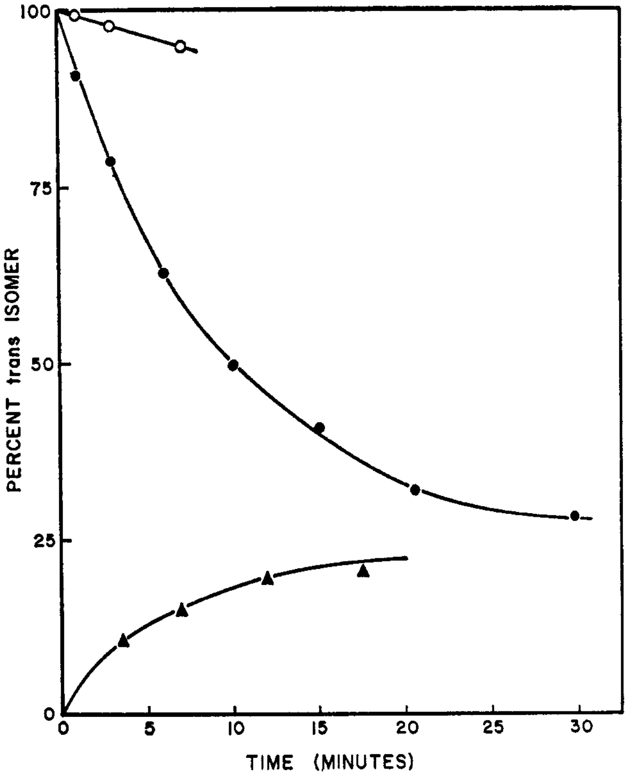

Figure 2.—Isomerization of *cis*-1-iodopropene (▲) and *trans*-1-iodopropene (●) during direct photolysis in a nitrogen atmosphere. Isomerization of *trans*-1-iodopropene during direct photolysis in an oxygen atmosphere (○).

Direct photolysis of either isomer led to *cis–trans* isomerization and the data in Figure 2 show that the isomer ratio was approaching a photostationary state of about 75% *cis* and 25% *trans*. An accurate determination of this photostationary state was prevented by the simultaneous photodecomposition of the iodopropenes into acetylene, methylacetylene, and propylene. The relative rates of photodecomposition of the *trans* and *cis* compounds appeared to be the same within experimental error and the initial relative rates of photodecomposition and photoisomerization were about 1:4. Hence the competing photodecomposition reactions should not have affected the photostationary state.

The *cis–trans* isomerization was quenched by oxygen and this is shown in Figure 2 for photolysis of the *trans* isomer. However, an atmosphere of isobutene appeared to have no effect on the isomerization process.

Isomerization was caused mainly by absorption of light of wavelength greater than 240 mμ. When the light was passed through a Vycor filter which transmitted as shown in Figure 1, the initial rate of isomerization was decreased only by a factor of 1.5.

Direct photolysis of either *cis*- or *trans*-1-iodopropene led to essentially the same ratio of acetylene and methylacetylene (photoelimination products). Though the rate of photoelimination was about one-fourth that of isomerization, an inspection of the data in Table II shows that the similarity in product ratios starting with either the *cis* or *trans* isomer cannot be explained by the simultaneous isomerization process. The data in the last column of Table II show the *cis–trans* ratio which existed when the product ratios were determined.

Although *cis–trans* isomerization was quenched by oxygen, the formation of methylacetylene and acetylene

TABLE II

RELATIVE PRODUCT YIELDS AND ISOMER DISTRIBUTION FROM DIRECT PHOTOLYSIS OF *cis*- AND *trans*-1-IODOPROPENE[a]

Starting isomer	Reaction conditions[b]	Time, min	Acetylene	Methylacetylene	Propylene	*cis–trans* ratio
trans[c]	nitrogen	1.0	3.34	1.00	0.09	0.10
		3.0	4.30	1.00	0.14	0.27
		6.0	4.10	1.00	0.25	0.59
		10.0	3.90	1.00	0.50	0.99
		15.0	4.00	1.00	0.43	1.41
		20.5	4.44	1.00	0.49	2.14
		30.0	4.76	1.00	0.38	2.42
cis[d]	nitrogen	3.5	3.98	1.00	0.05	7.27
		7.0	4.10	1.00	0.33	5.66
		12.0	4.44	1.00	0.43	4.10
		17.5	4.20	1.00	0.44	3.88
trans	oxygen	1.0	2.06	1.00	0.01	0.0
		3.0	2.26	1.00	0.01	0.01
		7.0	2.82	1.00	0.01	0.05

[a] Determined by vapor phase chromatographic analyses; see Experimental Section; molar ratios. [b] See Experimental Section. [c] Relative rates of isomerization and elimination were 4:1. [d] Relative rates of photolysis of *trans* and *cis* appeared to be the same.

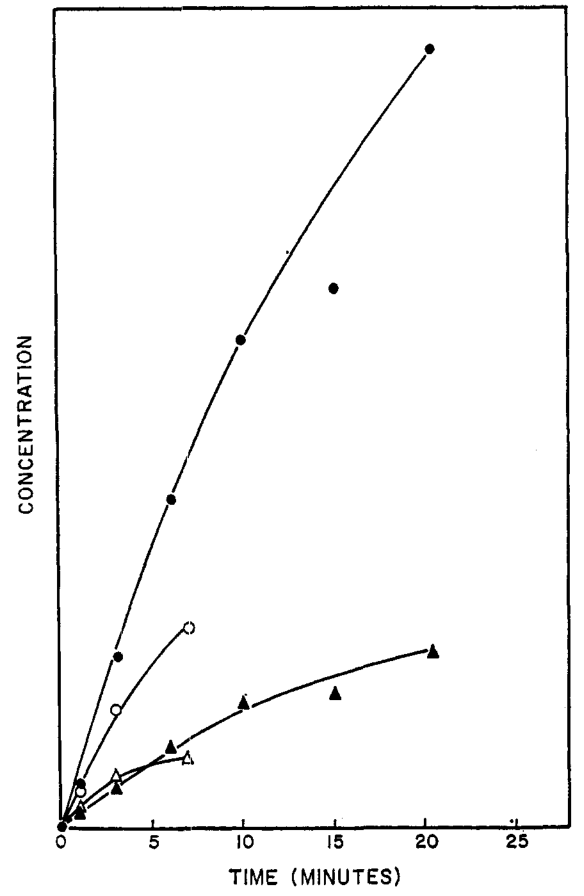

Figure 3.—Formation of the photoelimination products acetylene [nitrogen atmosphere (●), oxygen atmosphere (○)] and methylacetylene [nitrogen atmosphere (▲), oxygen atmosphere (△)] during direct photolysis of *trans*-1-iodopropene.

was comparatively unaffected (Figure 3).[19] However, the ratio of methylacetylene to acetylene was found to be quite wavelength dependent. When the *trans* isomer was irradiated with light which had been passed through a Vycor filter (see Figure 1) the rates of acetylene and methylacetylene formation decreased by factors of 18 and 4, respectively.

When *trans*-1-iodopropene was photolyzed in cyclohexane solution, the products formed were acetylene, methylacetylene, and propylene in the relative molar amounts 0.01, 1.00, and 0.60, respectively. The same results were obtained from a mixture of the *cis* and *trans* isomers in cyclohexane.

The formation of acetylene and methylacetylene by photoelimination reactions required the simultaneous formation of methyl iodide and hydrogen iodide, respectively. The former has been detected and its rate of formation parallels that of acetylene; however, we have not attempted to observe hydrogen iodide. It is interesting to note that although acetylene formation is relatively unaffected by oxygen the formation of methyl iodide is quenched.

The third major hydrocarbon product, propylene, behaved somewhat differently than the acetylenes. An inspection of Table II shows that the ratio of propylene to the acetylenic products increased with time. Also, the formation of propylene was quenched by oxygen (Table II). It did not appear that there was any significant wavelength effect on propylene formation.

The rate of disappearance of *trans*-1-iodopropene was accelerated by a factor of 2–3 when the nitrogen atmosphere was replaced by oxygen, and under these conditions propionaldehyde was detected as a photolysis product. When the photolyses were conducted under a nitrogen atmosphere, analyses of the reaction mixtures showed no detectable "nongaseous" products other than the starting iodopropenes and methyl iodide. In particular, no six-carbon compounds were detected.

Discussion

Photoisomerization.—We have considered three possible mechanisms for the observed *cis–trans* isomerization reaction (summarized in eq 5–7). Reaction 5

$$cis\text{-}CH_3CH{=}CHI \overset{I\cdot}{\rightleftharpoons} trans\text{-}CH_3CH{=}CHI \qquad (5)$$

$$cis\text{-}CH_3CH{=}CHI \overset{h\nu}{\rightleftharpoons} CH_3CH{=}CH\cdot + I\cdot \rightleftharpoons trans\text{-}CH_3CH{=}CHI \qquad (6)$$

$$cis\text{-}CH_3CH{=}CHI \overset{h\nu}{\rightleftharpoons} \text{excited state(s)} \rightleftharpoons trans\text{-}CH_3CH{=}CHI \qquad (7)$$

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[19] The small decrease which occurred in the acetylene–methylacetylene ratio may well have been due to a wavelength effect (*vide infra*). The reaction cell rapidly became iodine-colored when photolyses were carried out in an oxygen atmosphere.

represents the well-known iodine-catalyzed mechanism for isomerization of olefins.[20] In reaction 6 isomerization proceeds through an intermediate vinyl radical which loses its stereochemical integrity.[21] Reaction 7 represents nondissociative isomerization mechanisms which proceed through excited electronic states.[22]

The fact that isomerization was apparently unaffected by isobutene suggests that reactions 5 and 6 may not be important isomerization pathways. It would be expected that the rate of isomerization by reaction 5 would be significantly retarded since isobutene should act as an iodine trap, and it might be expected that vinyl radicals (and also iodine atoms) produced in reaction 6 would similarly react with isobutene.

Added oxygen would be expected to quench isomerization proceeding by reactions 5 and 6, and oxygen quenching has been observed. However, if *cis–trans* isomerization occurred by way of a triplet state, one would similarly expect quenching by oxygen. The presence of the heavy atom iodine in these olefins should enhance the efficiency of intersystem crossing from an excited singlet to a triplet state.[23] Thus, all of the data are consistent with a triplet state isomerization mechanism. However, the effect of wavelength on isomerization must also be considered. These data suggest that absorption in the long-wavelength band (λ_{253} mμ, *trans;* λ_{248} mμ, *cis*) is responsible for isomerization. This band may be the "normal" n,σ^* transition observed in alkyl iodides and may not involve the π system.[3,24] Such a transition would not be expected to lead to isomerization by reaction 7, but more likely to a dissociative mechanism such as represented in reaction 6.[3] Further studies are in progress on this question.

Photoelimination.—Two extreme mechanisms may be considered for the unimolecular formation of methylacetylene and acetylene from *cis*- and *trans*-1-iodopropene. These are molecular eliminations[25] and "hot" radical fragmentations[26] represented for the general elimination of RI by eq 8 and 9, respectively.

$$R_2C{=}CHI \xrightarrow{h\nu} RC{\equiv}CH + RI \qquad (8)$$

$$R_2C{=}CHI \xrightarrow{h\nu} R_2C{=}\overset{*}{C}H\cdot + I\cdot \longrightarrow R\cdot + RC{\equiv}CH + I\cdot \quad (9)$$

The concerted *trans*- or *cis*-elimination of R· and I· (not shown) would be expected to have features of both eq 8 and 9 and hence will be discussed below where appropriate.

Reaction 9 is appealing because it would not be expected to depend on the geometry of the starting iodopropene, thus agreeing with the data in Table II. Such a mechanism can be best thought of as arising from vibrationally excited species and is suggested by the inhibition of acetylene formation on photolysis in cyclohexane solution. The energy required for C–I bond homolysis should be approximately the same for the *cis* and *trans* isomers. Thermochemical calculations[26,27] then show that reaction 10 is favored over reaction 11 by about 12 kcal/mole. A similar difference in activation energies is also expected.[28]

$$CH_3CH{=}CH\cdot \longrightarrow CH_3\cdot + CH{\equiv}CH \quad -28 \text{ kcal/mole} \quad (10)$$

$$CH_3CH{=}CH\cdot \longrightarrow H\cdot + CH_3C{\equiv}CH \quad -40 \text{ kcal/mole} \quad (11)$$

The data in Table II agree qualitatively with these calculations, however the large decrease in the acetylene–methylacetylene ratio when light below 240 mμ was filtered out seems to require that at least some of the methylacetylene arises by reactions other than reaction 11. It would not be expected that the process with the greater energy requirement (methylacetylene formation) would be favored by light of lower energy. It has also been shown that oxygen does not significantly inhibit the formation of the acetylenes (Figure 3 and Table II). This makes the intermediacy of "hot" vinyl radicals less appealing,[6] but does not absolutely rule out their existence.

Molecular elimination processes should be insensitive to oxygen.[6] The similarity in product ratios from photolysis of either *cis*- or *trans*-1-iodopropene (Table II) rules out the very simple molecular elimination mechanisms proposed in reactions 3 and 4. However the data are accommodated by (1) molecular eliminations of CH_3I and HI from a common nonplanar excited state which can be reached by excitation of either isomer; or (2) molecular eliminations of CH_3I and HI from two different excited states which are populated in essentially the same ratio by excitation of either the *cis* or *trans* isomer.

The wavelength effect on the elimination reactions suggests that absorption in the short wavelength band (λ_{220} mμ, *trans;* λ_{215} mμ, *cis*) is primarily responsible for their occurrence and this band may be due to a π,π^* transition. The fact that these eliminations are not quenched by oxygen strongly suggests that they arise from singlet rather than triplet states. If the iodine atom is not conjugated to the double bond, the first excited singlet state will have an energy minimum when the molecule is twisted ~90° about the double bond and this state would probably be common to both isomers; however, if the iodine is conjugated, the situation becomes more complicated.[29] Since the

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(20) See ref 8, pp 302–308.

(21) See R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

(22) See G. S. Hammond, *et al.*, *J. Am. Chem. Soc.*, **86**, 3197 (1964).

(23) J. Saltiel, *Surv. Progr. Chem.*, **2**, 240 (1964).

(24) (a) The problem of band assignments in potentially conjugated iodine compounds is complicated.[24b] (b) H. H. Jaffé, and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, pp 251–252.

(25) (a) Reports of photochemical molecular eliminations have been previously mentioned.[6,13,14] Thermal molecular eliminations of hydrogen halides from alkyl halides have recently been discussed.[25b,c] (b) S. W. Benson and A. N. Bose, *J. Chem. Phys.*, **39**, 3463 (1963). (c) S. W. Benson and G. R. Haugen, *J. Am. Chem. Soc.*, **87**, 4036 (1965).

(26) (a) Very little attention has been given to the possible fragmentations of radicals derived from organic iodides by photolysis. However, a brief discussion of the possible fragmentation reactions of a "hot" propyl radical has been presented.[26b] (b) See ref 2, vol. 2, pp 583–585.

(27) (a) Standard thermochemical calculations were performed using the values ΔH_f (propylene), 5 kcal/mole;[27b] ΔH_f (methane), −18 kcal/mole;[8] ΔH_f (propyne), 46 kcal/mole;[27c] ΔH_f (acetylene), 54 kcal/mole;[27c] D(CH_3-H) 102 kcal/mole;[8] D(H–H), 104 kcal/mole;[8] and D($CH_3CH{=}CH$—H), 105 kcal/mole.[27d] (b) E. J. Prosen and F. D. Rossini, *J. Res. Natl. Bur. Std.* **36**, 269 (1946). (c) D. D. Wagman *et al.*, *ibid.*, **35**, 467 (1946). (d) This value is a reasonable guess based on data given for D($CH_2{=}CH$—H).[8] However, since this number is included in the thermochemical calculations for both reactions 10 and 11, the choice of an absolute value cannot affect the difference $\Delta H_{10} - \Delta H_{11}$.

(28) (a) It has recently been found[28b] that photolysis of methyl iodide at 2537 A produces methyl radicals with ~32 kcal/mole excess energy. The photolyses of the iodopropenes were performed using the full arc of the mercury lamp and hence one might expect an even greater energy excess in the first formed propenyl radical. (b) D. Lewis and G. Mains, Abstract, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 4–9, 1965, 18S.

(29) See ref 24b, pp 175–177, 424–426.

nature of the long-wavelength band in the spectra of these compounds is unclear,[24] it is not possible to guess whether the iodine atom conjugates strongly to the double bond or not, and further speculation concerning the geometry of excited states is unwarranted.

The fact that methyl iodide formation was quenched by oxygen could be construed as support for the intermediacy of a methyl radical formed by reaction 10, however methyl iodide photolyzes under these conditions and its rapid disappearance in an oxygen atmosphere is expected.[30]

Concerted *cis* or *trans* eliminations of the elements $CH_3\cdot$ (or $H\cdot$) and $I\cdot$ have not been discussed. First, the relative energetics of such processes would be expected to parallel those of reactions 10 and 11 and hence would not agree completely with the wavelength effect; secondly, the necessity exists to account for the same product ratios beginning with the two different isomers; and thirdly, the distinction between a concerted *cis* elimination and a molecular elimination would seem to be rather impossible.

Several bimolecular elimination mechanisms may be considered; these are represented in eq 12–14.[3] In the

$$R_2C{=}CH\cdot + I\cdot \longrightarrow RI + RC{\equiv}CH \tag{12}$$

$$R_2C{=}CHI + I\cdot \longrightarrow RI + RC{\equiv}CH + I\cdot \tag{13}$$

$$2\,CH_3CH{=}CH\cdot \longrightarrow CH_3C{\equiv}CH + CH_3CH{=}CH_2 \tag{14}$$

first place neither reactions 12 nor 14 would be expected to compete with oxygen, and none of these reactions would be expected to show the wavelength dependence observed. Reaction 14 should have yielded equal amounts of methylacetylene and propylene which is obviously not what was observed (Table II). Although propylene could have been consumed by reaction with HI to give propyl iodides these were not observed and only trace amounts of propane were detected.

Photodissociation.—It is proposed that the propylene which was formed arose mainly from reaction of thermal propenyl radicals with hydrogen iodide. Such a reaction has precedent in studies of iodoalkanes[6] and agrees with the data. In particular, the oxygen inhibition and the increase in the relative amount of propylene with time suggest that propenyl radicals and hydrogen iodide, respectively, were involved in a bimolecular reaction.

We are continuing our studies on these and related systems.

Experimental Section

***cis* and *trans*-1-Iodopropene.**—A 3.6-g (0.012 mole) sample of 1,1-diiodopropane[15] and 20 ml of ethylene glycol were placed in a 50-ml three-neck round bottom flask containing a stirring bar and fitted with a thermometer, a dropping funnel, and a simple vacuum distillation head with low holdup. The receiver flask connected to the head was immersed in a Dry Ice–isopropanol slush and the head was connected to the vacuum system through a cold trap. A solution prepared by dissolving 0.9 g (0.016 mole) of potassium hydroxide in 10 ml of ethylene glycol in a stoppered flask was then placed in the dropping funnel and the contents of the reaction flask were heated to 80° with stirring at a pressure of 35 mm. The potassium hydroxide solution was then added dropwise and heating was continued until distillation of the volatile iodopropene ceased. The lower layer of the distillate was removed and found to weigh 1.5 g (73%). Nmr analysis showed two groups of multiplets at τ 8.3 and 3.3–4.2 in the ratio 3:2 and a trace amount of 1,1-diiodopropane. This crude 1-iodopropene was purified by vapor phase chromatography at 91° using a 5 ft × 0.25 in. column packed with 20% SF-96-coated 60–80 firebrick.

Anal.[31] Calcd for C_3H_5I: C, 21.45; H, 3.00; I, 75.55. Found: C, 21.37, 21.17; H, 3.03, 3.02; I, 69.2, 72.7.

This sample was further separated into two isomers by vapor phase chromatography at 90° using a 12 ft × 0.25 in. column packed with 25% NMPN-coated 60/80 Chromosorb W. The shorter and longer retention time isomers, obtained in the ratio 1:2, were identified on the basis of their infrared spectral data (10-cm gas cell) as *cis*- and *trans*-1-iodopropene, respectively (see Table I). This was confirmed by an analysis of their nmr spectra.[16,32]

Vapor Phase Photolysis.—A quartz-reaction cell mounted on a short optical bench served as the reaction vessel. The vessel was evacuated and filled with nitrogen several times and finally left with an atmosphere of nitrogen. The vessel was shut off from the vacuum system and a 1.8-μl. sample of *cis*- or *trans*-1-iodopropene was injected into the vessel through a rubber serum stopper on a side arm. The volatile iodopropene vaporized in the vessel. The vaporized sample was then photolyzed for a known length of time using the light from a 140-w medium pressure mercury lamp (Hanovia, Type SH) passed through a mercury vapor filter. Two 2-ml gas samples were withdrawn after photolysis for analysis by vapor phase chromatography. The first sample was analyzed for *cis*- and *trans*-1-iodopropene and methyl iodide using a 12 ft × $^1/_8$ in. column packed with 20% Apiezon-L-coated 60–80 firebrick at 90° in conjunction with a thermal conductivity detector and the second sample was analyzed for the volatile hydrocarbon gases using a 20 ft × $^1/_8$ in. column packed with 20% SF-96-coated 60–80 firebrick at room temperature in conjunction with a flame ionization detector.

The cell was cleaned between runs. No methyl iodide or volatile hydrocarbon products were detected in analyses of 1-iodopropene vapor before photolysis. There were no dark reactions. The reaction cell was maintained at room temperature during the photolyses by air cooling.

The Vycor filter used in these runs was purchased from the Hanovia Company and was made of Corning glass no. 7910 (see Figure 1).

Vapor Phase Photolyses (Oxygen or Isobutene Atmosphere).—These runs were performed identically with the runs under nitrogen except that oxygen or isobutene replaced the nitrogen.

Solution Phase Photolysis.—A 20-μl. sample of *trans*-1-iodopropene was dissolved in 5 ml of spectral grade cyclohexane. The solution was photolyzed in a quartz vessel which had been covered in such a way as to avoid photolysis of the vapor. After photolysis for 12 hr, samples of both the liquid and vapor phase analyzed for volatile hydrocarbon gases using the flame ionization vapor phase chromatograph. The compounds acetylene, methylacetylene, and propylene were found in the relative molar amounts 0.01, 1.00, and 0.60, respectively, in both the solution and vapor analyses. The same results were obtained using a *cis–trans* isomer mixture.

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(30) See D. E. Hoare and G. S. Pearson, *Advan. Photochem.*, **3**, 83 (1964).

(31) The analyst reported difficulty with the iodine analyses.

(32) (a) Apparently, an impure sample of the mixed 1-iodopropenes has been previously prepared.[32b] (b) H. G. Viehe, *Chem. Ber.*, **93**, 1697 (1960).