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Photolytic Formation of Isomeric Vinyl Radicals from *cis*- and *trans*-Vinyl Iodides[1,2]

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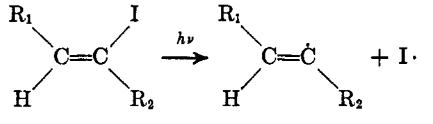
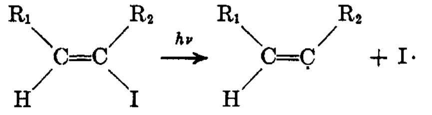
The isomeric vinyl iodides *cis*- and *trans*-4-iodo-3-heptenes have been synthesized, and their comparative solution phase photochemistry has been investigated using chloroform and pentane as solvents. Both isomers gave 3-heptyne and *cis*- and *trans*-3-heptenes as major products; the iodides isomerized; and 3,4-heptadiene was observed as a product under certain conditions. The product distributions were isomer and solvent dependent. The results are discussed in terms of the primary formation of vibrationally excited *cis*- and *trans*-3-hepten-4-yl radicals and their secondary reactions.

The photochemistry of vinyl iodides has received relatively little attention although these compounds are potential photolytic sources of isomeric vinyl radicals (reactions 1a and 1b). The configurational stability and relative chemical reactivity of such isomeric radicals are subjects of current interest,[3-10] and this prompts us to report the results of studies of the comparative solution phase photochemistry of *trans*- and *cis*-4-iodo-3-heptenes (1 and 2).


(1a)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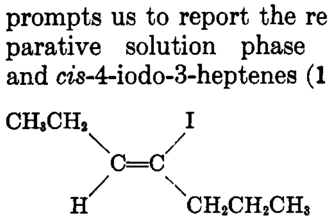
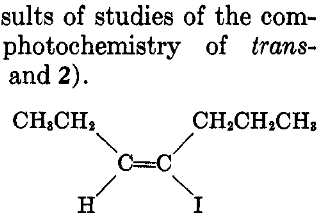

1
(*trans*)


2
(*cis*)

Organic monoiodides absorb light in the near-ultraviolet [$\lambda_{max} \simeq 250$ mμ ($\epsilon \sim 400$)], and photolysis in this region leads to efficient carbon–iodine bond homolysis.[11] It has been proposed that photolysis at shorter wavelengths can lead to a primary β-molecular elimination of hydrogen iodide (*e.g.*, reaction 2); however,

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

the evidence is sparse, and the process seems to be relatively inefficient.[11,12] Two secondary reactions following C–I homolysis can lead to products identical with those expected from a β-molecular elimination (reactions 3 and 4). Cage disproportionation of the

$$R_3CCR_2I \xrightarrow{h\nu} \overline{R_3C\dot{C}R_2\,I\cdot} \longrightarrow R_2C{=}CR_2 + RI \qquad (3)$$

$$R_3CCR_2I \xrightarrow{h\nu} R_3C\dot{C}R_2{}^* + I\cdot \longrightarrow R_2C{=}CR_2 + R\cdot \qquad (4)$$

initially formed geminate radical pair (reaction 3) would be expected in solution when the abstracted R was hydrogen, and fragmentation of a vibrationally excited radical (reaction 4), produced from the primary scission process, might occur in vapor phase experiments. Evidence is available for both reactions for vinyl iodides and iodoalkanes.[1a,11,12]

Previous studies of vinyl iodides have been restricted to 1-iodoethylene (vinyl iodide), 2-iodopropene, and *cis*- and *trans*-1-iodopropenes. Results from the photolysis of 1-iodoethylene in carbon tetrachloride indi-

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[1] (a) Photochemistry of Organic Iodides. III. Paper II: R. C. Neuman, Jr., and R. G. Wolcott, *Tetrahedron Lett.*, 6267 (1966). (b) Presented at the Pacific Conference on Chemistry and Spectroscopy, Anaheim, Calif., Oct 30–Nov 1, 1967.

[2] Support by the National Science Foundation (GP-4287 and GP-7349) is gratefully acknowledged.

[3] (a) L. A. Singer and N. P. Kong, *J. Amer. Chem. Soc.*, **89**, 5251 (1967); (b) L. A. Singer and N. P. Kong, *ibid.*, **88**, 5213 (1966).

[4] (a) E. I. Heiba and R. M. Dessau, *ibid.*, **89**, 3772 (1967); (b) E. I. Heiba and R. M. Dessau, *ibid.*, **89**, 2238 (1967).

[5] G. D. Sargent and M. W. Browne, *ibid.*, **89**, 2788 (1967).

[6] O. Simamura, K. Tokumaru, and H. Yui, *Tetrahedron Lett.*, 5141 (1966).

[7] G. M. Whitesides and C. P. Casey, *J. Amer. Chem. Soc.*, **88**, 4541 (1967).

[8] (a) R. M. Fantazier and J. A. Kampmeier, *ibid.*, **88**, 5219 (1966); (b) J. A. Kampmeier and R. M. Fantazier, *ibid.*, **88**, 1959 (1966); (c) J. A. Kampmeier and G. Chen, *ibid.*, **87**, 2608 (1965).

[9] P. S. Skell and R. G. Allen, *ibid.*, **86**, 1559 (1964).

[10] A. A. Oswald, K. Griesbaum, B. E. Hudson, Jr., and J. M. Bregman, *ibid.*, **86**, 2877 (1964).

[11] (a) J. R. Majer and J. P. Simon, *Advan. Photochem.*, **2**, 137 (1964); (b) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1966, pp 522–528.

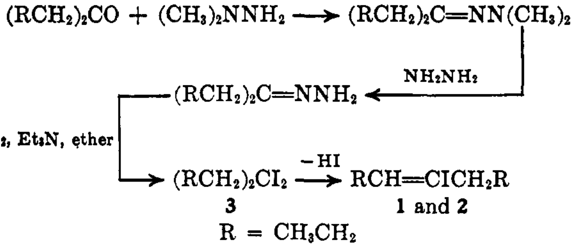
[12] R. C. Neuman, Jr., *J. Org. Chem.*, **31**, 1852 (1966).

cated that C–I homolysis was the only photoreaction of the iodide and that cage disproportionation to form acetylene (analogous to reaction 3) competed with diffusive separation of the initially formed geminate vinyl radical and iodine atom.[13] Pertinent conclusions from a vapor phase study of *cis*- and *trans*-1-iodopropenes were that C–I homolysis was probably the major primary process followed by some fragmentation (analogous to reaction 4), that some molecular elimination may have occurred at wavelengths less than 2400 Å, and that the product distributions were isomer independent.[12] Less detailed results from the solution phase photolysis of *trans*-1-iodopropene[12] agreed with the data for 1-iodoethylene.[13] Vapor phase photolysis of 2-iodopropene gave both methylacetylene and allene.[14]

The solution phase photochemical studies of **1** and **2** which constitute the subject of this paper have demonstrated a marked isomer dependence of the product distribution. For this reason we feel that the following description of the syntheses of these new vinyl iodides and the bases for their isomeric assignments are necessary.

Synthesis and Structural Assignments.—The synthentic sequence used to prepare *trans*- and *cis*-4-iodo-3-heptenes (**1** and **2**) is outlined in Scheme I. The procedure was a modification of that reported for 1,1-diiodoneopentane by Barton.[15] An unsubstituted hydrazone synthesis involving the intermediate N,N-dimethylhydrazone[16] was used in place of the more difficult direct hydrazone synthesis from 4-heptanone.

SCHEME I



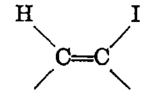
Attempts to purify 4,4-diiodoheptane (**3**) by glpc led to its efficient conversion into **1** and **2** in the ratio 4:1.[17] Sodium–liquid ammonia reduction[18] of **1** or **2** gave *trans*- or *cis*-3-heptene, respectively. Since these reductions proceed with retention of configuration,[19] the results offer confirmation of the isomeric assignments. Further proof of structure was derived from nmr and uv spectral data. The chemical shifts of the nmr resonance signals of the single vinyl proton in a series of vinyl iodides are given in Table I.[20] The cyclic compounds force a *cis* relationship between the vinyl proton and the neighboring iodine atom (**4**). The correspondence in chemical shifts between the vinyl proton of **2** and those of the cyclic iodides and the large upfield shift for the vinyl proton in **1** agree with the structural assignments. Additional confirmation is offered by the nmr data for *cis*- and *trans*-3-iodo-3-hexenes (Table I) whose structures were based on different evidence.[21,22] The C–I absorption band in the uv spectrum for *trans*-1-iodopropene (253 mμ), which has the geometry represented by **4**, is shifted by 5 mμ to a longer wavelength than that for *cis*-1-iodopropene (248 mμ).[12] Similarly, the C–I band for *cis*-4-iodo-3-heptene (**2**) (249 mμ), having the geometry of **4**, shows a 6-mμ longer wavelength shift compared with that of *trans*-4-iodo-3-heptene (**1**) (243 mμ).

TABLE I

CHEMICAL SHIFTS OF THE VINYL PROTON RESONANCE SIGNALS FOR A SERIES OF VINYL IODIDES[a]

Vinyl iodide	Vinyl hydrogen chemical shift, cps[b,c]
1-Iodocyclopentene[d]	−361
1-Iodocyclohexene[d]	−376
1-Iodocyclooctene[d]	−380
cis-3-Iodo-3-hexene[e]	−373
cis-4-Iodo-3-heptene (**2**)	−371
trans-3-Iodo-3-hexene[e]	−333
trans-4-Iodo-3-heptene (**1**)	−328

[a] Neat samples. [b] Reference, TMS. [c] Resonance signals were basically triplets in all cases. [d] Synthesized from the corresponding cycloalkanones. Structure proof based on microanalytical, chemical, and spectral data. Unpublished work of G. S. H. [e] Spectral data kindly furnished by Professor G. Zweifel.



4

Results

Solutions of **1** or **2** in chloroform or pentane were vacuum degassed and photolyzed at room temperature with stirring under nitrogen or oxygen atmospheres using the Vycor-filtered light (λ >2400 Å)[1a] of a medium-pressure mercury arc. The same quartz vessel and physical arrangement of the experimental apparatus were used in all runs, and the vapor phase region of the vessel was shielded from irradiation. Photolyzing mixtures were sampled at various time intervals, and the loss of starting material and formation of products were monitored by glpc.

The only detectable products formed from either **1** (expt 1–5) or **2** (expt 6–9) were *cis*- and *trans*-3-heptenes, 3-heptyne, 3,4-heptadiene, and the geometric isomer of the starting iodide (Table II). These products typically accounted for about 60–65% of the starting

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(13) C. Roberge and J. A. Herman, *Can. J. Chem.*, **42**, 2262 (1964).

(14) R. C. Neuman, Jr., and S. Moje, unpublished work.

(15) (a) D. H. R. Barton, R. E. O'Brien, and S. Sternhell, *J. Chem. Soc.*, 470 (1962); (b) see also A. J. Fry and J. N. Cawse, *J. Org. Chem.*, **32**, 1677 (1967); (c) see also R. C. Neuman, Jr., and M. L. Rahm, *ibid.*, **31**, 1857 (1966).

(16) G. R. Newkome and D. L. Fishel, *ibid.*, **31**, 677 (1966).

(17) Base-catalyzed dehydrohalogenation of **3** led to the same products. Since **1** and **2** were to be purified by glpc subsequent to their preparation, we saw no need to use the base-catalyzed dehydrohalogenation for synthetic purposes since the desired elimination of HI from **3** occurred efficiently in the injector block of the gas chromatograph (see Experimental Section).

(18) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965, p 77.

(19) M. C. Hoff, K. W. Greenlee, and C. E. Boord, *J. Amer. Chem. Soc.*, **73**, 3329 (1951).

(20) The iodocycloalkenes were synthesized from the corresponding cycloalkanones. Proof of structure is based on microanalytical, chemical, and spectral data. G. Holmes, M.S. Thesis, University of California at Riverside, Riverside, Calif., 1967.

(21) G. Zweifel and C. C. Whitney, *J. Amer. Chem. Soc.*, **89**, 2753 (1967).

(22) The authors are grateful to Professor G. Zweifel for copies of the nmr and ir spectra of *cis*- and *trans*-3-iodo-3-hexenes.

TABLE II

PRODUCT DATA FOR PHOTOLYSES OF 1 AND 2[a,b]

Expt[c]	Time, min	Convn, %	Yield, %	Isomerization, %	Mol %				
					3-Heptene				
					cis	*trans*	3-Heptyne	3,4-Heptadiene	Isomerized iodide[d]
1-1 C N 3.2	10	8	62	1.0	11	10	61	0	17
	20	14	52	2.8	10	9	52	0	29
	30	18	63	3.8	11	10	54	0	26
	40	21	66	5.4	11	10	51	0	29
2-1 C N 6.3	3	1			[8]	[8]	[45]	[19]	[20]
	5	2			[8]	[8]	[50]	[14]	[20]
3-1 C N 3.2[e]	10	8	52	1.0	9	9	46	15	21
NaOH	26	22	48	2.4	11	11	46	15	17
4-1 C O 2.9	20	11	68	2.6	4	4	64	0	29
5-1 P N 2.1	10			1.9	[5]	[10]	[56]	[0]	[29]
6-2 C N 1.7	10	17	68	6.0	14	21	26	0	39
	20	27	64	9.9	13	20	26	0	41
	33	38	60	15.4	14	20	26	0	41
7-2 C N 5.0	3	1			[14]	[22]	[24]	[0]	[40]
8-2 C O 1.8	10	16	45	4.3	12	24	23	0	41
9-2 P N 3.1	10			3.5	[2]	[40]	[18]	[0]	[40]

[a] A description of the various column headings is given in the text. [b] Bracketed numbers based on assumed yields of isomerized iodide. [c] The first number in the experiment code refers to the experiment number; 1 and 2 stand for *trans*- and *cis*-4-iodo-3-heptenes, respectively; N and O stand for nitrogen and oxygen, respectively; C and P stand for chloroform and pentane, respectively; the last numbers are the molar concentrations of starting iodide $\times 10^2$. [d] 2 in expt 1–5; 1 in expt 6–9. [e] Chloroform solution (5 ml) stirred in contact with ~2 ml of 0.1 *N* aqueous sodium hydroxide solution.

iodide which disappeared.[23] The individual mole percentages of each product, based on the total number of moles of detectable products formed, are given as the unbracketed numbers in the last five columns of Table II. The bracketed numbers in these columns are the mole percentages based on an assumed yield of isomerized iodide.

The code used in column 1 to describe the experimental conditions is explained in the footnotes of Table II. Columns 2 and 3 contain the photolysis time and corresponding per cent consumption of the starting isomeric iodide. The true over-all product balances are given in column 4, and column 5 indicates the per cent contamination of the remaining 4-iodo-3-heptene by the geometric isomer opposite that of the starting material.

Examination of the product data for expt 1 and 6 shows that their per cent yields are relatively insensitive to photolysis time or extent conversion within each experiment. This was also observed in the other experiments (with the exception of expt 2), although not all of the data have been reported. Thus, some characteristic product ratios have been summarized in Table III according to the starting vinyl iodide and the reaction conditions without reference to photolysis time or extent conversion of iodide.

Accurate analyses of the *cis-/trans*-3-heptene ratios were difficult because the two peaks were incompletely resolved by the gas chromatographic column. Similarly, base line resolution of 3,4-heptadiene and 3-heptyne was not accomplished. However, the large differences between the product distributions arising from 1 and 2 in comparable experiments (Tables II and III) are well outside of experimental error as determined from duplicate studies. It was necessary to monitor loss of iodide and product formation on separate glpc columns. This may have been a source of the large and somewhat random variation in the over-all yield data given in the fourth column of Table II.[23]

TABLE III

SUMMARIZED PRODUCT RATIOS FOR PHOTOLYSES OF 1 AND 2[a]

Iodide	Conditions[b]	3-Heptyne/ 3-heptene	*cis*-3-Heptene/ *trans*-3-heptene	Heptyne + heptadiene + I[c]/3-heptene
1	$CHCl_3$, N_2	~2.7	~1.1	~4
	$CHCl_3$, N_2, NaOH	~2.4	~1.0	~4
	$CHCl_3$, O_2	~9.0	~1.0	~12
	Pentane, N_2	~3.8	~0.5	
2	$CHCl_3$, N_2	~0.8	~0.7	~2
	$CHCl_3$, O_2	~0.7	~0.5	~2
	Pentane, N_2	~0.4	<0.1	

[a] Data extracted from Table II. [b] See text and Table II. [c] The symbol "I" stands for isomerized iodide.

The allene 3,4-heptadiene was detected as a reaction product only from the *trans* iodide 1 and only at low conversions (compare expt 1 and 2). However, in the presence of dilute aqueous sodium hydroxide (expt 3) it was a significant reaction product even at high conversions of starting iodide. No dark reactions occurred in the latter experiment.

The rates of photolysis of 1 and 2 in chloroform were essentially the same under nitrogen or oxygen atmospheres, and the per cent iodide isomerization and *cis-/trans*-3-heptene ratios (Table III) were also unaffected. However, oxygen caused a marked increase in the heptyne/heptene ratio from 1 (Table III), while the product distribution from photolysis of 2 in chloroform appears to be oxygen insensitive (Tables II and III).

Insufficient data are available for an adequate comparison of the pentane experiments with those using chloroform. However, the product ratios in Table III show that a major difference was in the relative amounts of *cis*- and *trans*-3-heptenes formed. The relative percentage of *trans* olefin increased markedly for both 1 and 2 using pentane as solvent.

Control experiments using a chloroform light filter in addition to the Vycor filter showed no detectable differences in product distribution, rates of product

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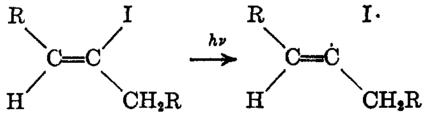
[23] No other products with molecular weights similar to the starting iodides or to the hydrocarbon products were detected by glpc. The origin of the low product balance is not definitely known; however, it could have been due in part to addition of S· (most often $\cdot CCl_3$) or HI to starting iodide and to experimental inaccuracies in the glpc analyses (see text).

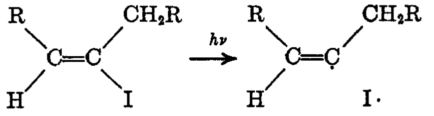
formation, or yields compared with those without the chloroform filter. The color of all of the photolyzing solutions under a nitrogen atmosphere turned light yellow with the exception of those for **1** in pentane which became purple. Under an oxygen atmosphere, all solutions rapidly turned dark purple.

Discussion

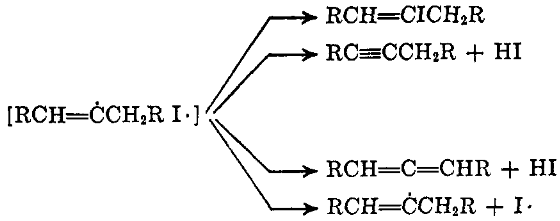
The most likely primary photochemical processes of **1** and **2** under these experimental conditions would seem to be the formation of the geminate radical pairs shown in reactions 5 and 6 ($R = CH_3CH_2$). Secondary reactions potentially available to the geminate pairs could include reactions 7–11 and *cis–trans* isomerization of the vinyl radical prior to separative diffusion of the geminate pair.



1 (5)



2 (6)



$$[RCH{=}\dot{C}CH_2R\ I\cdot] + SH \longrightarrow RCH{=}CHCH_2R + I\cdot + S\cdot \quad (11)$$

Reactions 10 and 11 represent diffusion and cage scavenging, respectively. The most probable reaction of either isomeric vinyl radical subsequent to diffusion is hydrogen abstraction from solvent (reaction 12).

$$RCH{=}\dot{C}CH_2R + SH \longrightarrow RCH{=}CHCH_2R + S\cdot \quad (12)$$

The similarity of the rates of formation of products and product distribution with or without an external chloroform filter suggests that initiation of detectable reactions due to photolysis of chloroform did not occur, and this was expected to be largely precluded by the use of the Vycor filter.[1a] The possible existence of chain reactions leading to the observed products also seems to be unlikely, at least in chloroform, in view of the ready availability of easily abstractable solvent hydrogen atoms.

The stability of 3,4-heptadiene in the presence of aqueous base and its disappearance at conversions above 5% in the absence of base (*vide supra*) indicate that it was destroyed by hydrogen iodide produced during the course of the photolysis of **1**. Possible reactions are represented in eq 13 and 14 shown below.

$$RCH{=}C{=}CHR + HI \longrightarrow RCH{=}ClCH_2R \quad (13)$$

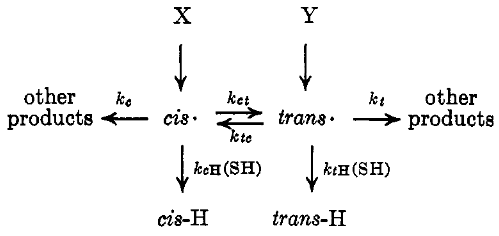
$$RCH{=}C{=}CHR + HI \longrightarrow RC{\equiv}CCH_2R \quad (14)$$

Reaction 13 could give both starting iodide and its geometric isomer, and there is an indication that the per cent yield of the isomerized iodide was slightly decreased when aqueous base was present (expt 1 and 3).[24] Similarly, if a part of the 3-heptyne arose by allene isomerization (reaction 14), the heptyne/heptene ratio would be lower in the presence of aqueous base, and a comparison of these ratios (Table III) shows such a trend.[25]

With the exception of 3,4-heptadiene, the insensitivity of the other product ratios to the extent of conversion of starting iodide and photolysis time within each experiment indicates that significant secondary reactions involving the products did not occur. In particular, a comparison of expt 2 and 7, in which product data were obtained when the per cent conversion of the starting iodide was less than one, seems to confirm that the isomer dependence of the product distribution was not due to secondary reactions in these systems, and, although HI could conceivably react with all of the products including the starting vinyl iodides,[23,24] the absence of any significant differences (with the exception of 3,4-heptadiene) between the product distributions of expt 1 and 3 suggests that this did not occur.

In previous studies of isomeric vinyl radicals, a wide range of results has been obtained for the ratio of *cis/trans* olefin arising from vinyl radical hydrogen abstraction from solvent or other hydrogen donor.[3-10] In most cases, no isomer dependence has been observed indicating that isomerization was much faster than hydrogen abstraction, but, recently, in studies by Singer[3] and Sargent,[5] the *cis/trans* olefin ratio has been found to be isomer dependent implying that the radicals produced in these cases were trapped prior to complete isomerization. If isomerically distinct vinyl radicals arise from separate sources represented by X and Y in Scheme II, the ratios of *cis/trans* olefin from either source, designated as (*cis*-H/*trans*-H)$_x$ and (*cis*-H/*trans*-H)$_y$, will be given by eq 15 and 16.

SCHEME II



Since

$$(cis\text{-}H/trans\text{-}H)_x = (k_{cH}/k_{tH})\{[k_{tc} + k_{tH}(SH) + k_t)]/k_{ct}\} \quad (15)$$

$$(cis\text{-}H/trans\text{-}H)_y = (k_{cH}/k_{tH})\{k_{tc}/[k_{ct} + k_{cH}(SH) + k_c]\} \quad (16)$$

these individual ratios will depend not only on the ratio k_{cH}/k_{tH} but also on the relative magnitudes of the rate constants for reactions in competition with hydro-

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[24] (a) Hydrogen iodide might also add to 3,4-heptadiene to give the allyl iodide 3-iodo-4-heptene. Although no new peak was observed in glpc traces, the retention time of this compound is unknown and might be identical with that of **1** or **2**. However, it is known that addition of HI to allene yields only 2-iodopropene and 2,2-diiodopropane.[24b] If 4,4-diiodoheptane (**3**) was formed in these systems by HI addition to **1** or **2**, its major photolysis products would have been **1** and **2**.[1a] (b) K. Griesbaum, W. Naegele, and G. G. Wanless, *J. Amer. Chem. Soc.*, **87**, 3151 (1965).

[25] The low per cent conversion in expt 2 precluded a determination of the yield of isomerized iodide. However, making the assumption that it was the same as that in expt 3 gives product distributions for these two experiments which are remarkably similar. This tends to support our proposals concerning the existence of reactions 13 and/or 14.

gen abstraction, they may vary considerably from system to system.[26] However, it becomes clear from an examination of the kinetic expressions given in eq 17 and 18 that the ratio $(\textit{cis}\text{-H}/\textit{trans}\text{-H})_x/(\textit{cis}\text{-H}/\textit{trans}\text{-H})_y$ cannot be less than unity. Based on the *a priori* assumption that reactions 5 and 6 represent the respective primary processes of **1** and **2**, the radical sources Y and X (Scheme II) are **1** and **2**, respectively, and thus the ratio defined by eq 17 and 18 is (*cis-/trans*-3-heptene)$_2$/(*cis-/trans*-3-heptene)$_1$. However, an inspection of the data in Table III shows that this ratio was always *less* than unity under comparable reaction conditions. Although these results could indicate incorrect structural assignments of **1** and **2**, the supporting structural evidence is strong (*vide supra*). Rather, we propose that this seeming anomaly may be due to the initial production of vibrationally excited *trans*- and *cis*-vinyl radicals from **1** and **2**, respectively.

$$\frac{(\textit{cis}\text{-H}/\textit{trans}\text{-H})_x}{(\textit{cis}\text{-H}/\textit{trans}\text{-H})_y} = \frac{[k_{tc} + k_{t\mathrm{H}}(\mathrm{SH}) + k_t][k_{ct} + k_{c\mathrm{H}}(\mathrm{SH}) + k_c]}{k_{tc}k_{ct}} \tag{17}$$

$$\frac{(\textit{cis}\text{-H}/\textit{trans}\text{-H})_x}{(\textit{cis}\text{-H}/\textit{trans}\text{-H})_y} = \{1 + [k_{t\mathrm{H}}(\mathrm{SH})/k_{tc}] + (k_t/k_{tc})\}\{1 + [k_{c\mathrm{H}}(\mathrm{SH})/k_{ct}] + (k_c/k_{ct})\} \tag{18}$$

The value of D(C–I) for the vinyl iodides is probably between 55 and 60 kcal/mol,[27] while the energy of the light corresponding to their $\lambda_{\max}$ is on the order of 110 kcal/einstein,[28] indicating that excess vibrational energy may have remained in the vinyl radicals after C–I homolysis. This is supported by earlier observations that photolysis of methyl iodide at 2537 Å produced methyl radicals with ~32 kcal/mol of excess vibrational energy[29] and that propenyl radicals formed from vapor phase photolysis of *cis*- or *trans*-1-iodopropene (Vycor-filtered light) apparently possessed sufficient vibrational energy to fragment relatively efficiently into methyl radicals and acetylene, a process requiring energy on the order of 30 kcal/mol.[12] Although the barrier to vinyl radical isomerization seems to vary with structure, it is reasonable to assume that it is less than 15 kcal/mol in these systems,[30] and thus it is likely that the vinyl radicals initially produced from **1** or **2** had an energy content in excess of that corresponding to the inversion-transition state. If a portion of this energy found its way into the reaction coordinate for isomerization, prior to collisional deactivation, the initially formed *cis* or *trans* excited vinyl radicals could have each produced both *cis* and *trans* ground-state radicals. If the excited *trans* and *cis* radicals from **1** and **2**, respectively, partitioned to give different ground-state radical distributions such that $(\textit{cis}\cdot/\textit{trans}\cdot)_1$ was greater than $(\textit{cis}\cdot/\textit{trans}\cdot)_2$, the experimental results can be qualitatively justified if hydrogen abstraction was competitive with isomerization of the ground-state radicals. Excluding the possible occurrence of secondary reactions (*vide supra*), the different *cis-/trans*-3-heptene ratios from **1** and **2** support the latter contention. While no firm evidence can be cited to support the proposal that the excited radicals would partition as suggested above, the likely energy relationships $E_2 > E_1$,[31] $E(\textit{cis}\cdot) > E(\textit{trans}.)$,[3,5] and $[E\ (\textit{trans}\cdot^*) - E_1] \cong [E(\textit{cis}\cdot^*) - E_2]$[32] do not preclude such an occurrence.[33]

The apparent absence of an oxygen effect on the yields of isomerized iodide from either **1** or **2** (compare expt 1 and 4 and expt 6 and 8, Table II) indicates that they were formed by radical recombination (reaction 7) during the initial geminate encounter prior to separative diffusion (reaction 10).[33] Additionally, the absence of an apparent oxygen effect on any of the products from **2** (expt 6 and 8) implies that all were formed prior to diffusion. However, the data for **1** (expt 1 and 4), while supporting a cage disproportionation source for 3-heptyne (and presumably 3,4-heptadiene; reactions 8 and 9), indicate that a portion of the 3-heptenes was formed from scavengeable radicals. While these differences in the effect of oxygen on the product yields of **1** and **2** may be significant, it is conceivable that other unanticipated reactions were introduced by the addition of oxygen and thus we hesitate to speculate on their meaning without additional supporting data.

The significantly larger 3-heptyne/3-heptene ratios arising from **1** compared with those from **2** suggest that disproportionation was a more facile reaction for the geminate pairs produced from the former than from the latter. If it is assumed that all of the products arose from "cold" vinyl radicals, these data and our previous discussion concerning the partitioning of the excited radicals into ground-state radicals suggest that disproportionation (reactions 8 and 9) was more facile for *cis*- than for *trans*-vinyl radicals; however, we can offer no explanation for the apparent absence of 3,4-heptadiene in photolyses of **2**. While both of these products could have been formed by fragmentation of the initial vibrationally excited radicals, such processes would require on the order of 40 kcal/mol of energy[12] and, in view of our previous work,[12] seem unlikely under these experimental conditions.

Hydrogen iodide is an excellent hydrogen donor to carbon radicals, and its presence in these systems could have led to its participation in this role. Since disproportionation was a more significant process for photolyses of **1** compared with those of **2**, the differences in hydrogen iodide concentration in the respective systems might have led to some of the observed differences in product distribution. However, the similarity of the *cis-/trans*-3-heptene ratios from **1** in chloroform in the absence and presence of dilute aque-

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(26) The rate constants k_c and k_t (Scheme II) represent, respectively, aggregates of all other possible reactions (not specifically shown) of the *cis*- and *trans*-vinyl radicals.

(27) (a) D(C–I) for methyl iodide is 56 kcal/mol,[27b] and the bond dissociation energies for vinyl carbon–X bonds are similar to those for the analogous CH_3–X bonds.[27b] (b) S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965).

(28) See J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1966, p 12.

(29) D. Lewis and G. Mains, Abstracts, 149th National Meeting of the American Chemical Society, Detroit, Mich., April, 1965, p 8S.

(30) Assuming a frequency factor of 10^{13} sec^{-1}, such a barrier corresponds to a rate constant of 10^2 sec^{-1}; see ref 3a.

(31) The relative stabilities of **1** and **2** have not been determined; however, it is generally found for simple internal alkenes of the structure $R_1CH{=}CHR_2$ that the *trans* isomer is more stable than the *cis* isomer. Additionally, the *cis* isomers of 1-halopropenes ($CH_3CH{=}CHX$) appear to be thermodynamically more stable than the *trans* isomers.[12] Both of these observations suggest that $E_2 > E_1$.

(32) This assumes the same excess energy input into **1** and **2** beyond that required to break the C–I bond.

(33) Alternative explanations involving isomerization in electronically excited states prior to homolytic scission or the direct production of vinyl radicals of the configuration opposite that of the starting iodide cannot be excluded.

ous sodium hydroxide indicates that hydrogen iodide was not involved as a free-radical hydrogen donor to the vinyl radicals. In the less reactive solvent pentane, it was observed that photolyzing solutions of **1** became iodine colored in the absence of oxygen, and this suggests that hydrogen iodide did act as a hydrogen donor. Since it was present in much lower concentrations in photolyzing pentane solutions of **2**, it apparently did not participate as seen by the absence of any iodine-color formation (see Results). The most notable difference between the chloroform experiments and those using pentane is seen in a comparison of the *cis-/trans*-3-heptene ratios for **1** or **2** in the two different solvents (Table III). Since the ground-state *trans*-vinyl radical is probably more stable than the ground-state *cis*-vinyl radical $[E(cis\cdot) > E(trans\cdot)]$, the significantly lower *cis-/trans*-3-heptene ratios in pentane may reflect the poorer competition of hydrogen abstraction with isomerization in this medium of lower hydrogen-donating ability. The higher *cis-/trans*-3-heptene ratio from **1** compared with that from **2** could have been due to the intervention of HI as a hydrogen donor in the former case as discussed above.

Other less complicated sources of these radicals are under investigation, and it is hoped that these studies will assist in clarifying the results reported here.

Experimental Section

4-Heptanone-N,N-dimethylhydrazone.—A mixture of 240 g (4.0 mol) of anhydrous N,N-dimethylhydrazine (Matheson Coleman and Bell), 114 g (1 mol) of 4-heptanone (Matheson Coleman and Bell), and sufficient absoute ethanol to give a homogeneous solution was refluxed for 3 hr,[16] and the excess dimethylhydrazine was stripped from the reaction mixture. Vacuum distillation yielded 156 g (1.0 mol) of 4-heptanone-N,N-dimethylhydrazone: bp 55–57° (8 mm); ir 1635 cm^{-1} (C═N); nmr multiplets at τ 7.78 (2), 8.50 (2), and 9.08 (3) and singlet at 7.74 (3).

4-Heptanonehydrazone.—The purified 4-heptanone-N,N-dimethylhydrazone was refluxed for 24 hr with a fivefold molar excess of anhydrous hydrazine (Matheson Coleman and Bell) in sufficient absolute ethanol to give a homogeneous solution.[16] The excess hydrazine and resulting N,N-dimethylhydrazine were stripped from the reaction mixture along with the ethanol at 50° *in vacuo*. The crude hydrazone was not purified because such attempts led to azine formation.

4,4-Diiodoheptane.—The crude hydrazone and a twofold molar excess of triethylamine were dissolved in 100 ml of anhydrous diethyl ether, and a saturated ether solution of iodine was added dropwise with stirring over a period of about 1 hr until a dark red-brown color persisted indicating an excess of iodine.[15] After additional stirring for 1 hr the solution was decanted off the resulting triethylammonium iodide. This residue was washed with ether, and the combined solutions were washed successively with 100-ml portions of 2 *N* hydrochloric acid, water, sodium bisulfite, water, and saturated sodium bicarbonate solution and dried over anhydrous calcium carbonate (Drierite) (magnesium sulfate led to apparent decomposition of the product). The ether solvent was stripped off on a rotary evaporator. The nmr spectrum of this product showed multiplets at τ 9.0, ~8.4, and ~7.8 in the approximate ratio of 3:2:2; the uv spectrum showed λ_{max} 285 and 295 mμ (shoulder). The over-all yield from 4-heptanone was about 55%.

***cis*- and *trans*-4-Iodo-3-heptenes.**—On attempted purification of the crude 4,4-diiodoheptane by glpc using a 4 ft × 0.375 in. aluminum column packed with 20% didecyl phthalate on Chromosorb W at 110° (injector block 120°), the chromatogram showed only a partially resolved doublet with a retention time anomalously short for the diiodoalkane. The nmr spectrum of this mixture collected from the column showed two triplets corresponding to vinyl protons at τ 3.83 and 4.53 anticipated for a spectrum of a mixture of *cis*- and *trans*-4-iodo-3-heptenes.

Anal. Calcd for $C_7H_{13}I$: C, 37.52; H, 5.85; I, 56.63. Found: C, 37.45; H, 5.80; I, 56.42.

Separation of the two isomers was accomplished by lowering the column temperature to 85°. The previously purified mixture was rechromatographed at this temperature, and the separate components were collected. The shorter and longer retention time isomers **1** and **2**, respectively (see synthesis), were present in the approximate ratio 4:1. The nmr spectrum of **1** showed a triplet (1) at τ 4.55, multiplets (12) at 7.79, 8.49, and 9.08; of **2** showed a triplet (1) at 3.83, multiplets (12) at 7.80, 8.50, and 9.08. The uv spectrum of **1** showed λ_{max} 243 mμ (ϵ ~400); of **2** showed λ_{max} 249 mμ (ϵ ~400).

The identical vinyl iodides were formed by base-catalyzed dehydrohalogenation of crude 4,4-diiodoheptane.[17]

Sodium–Liquid Ammonia Reduction of 1 and 2.[18,19]—Sodium (1.5 g) was added in small pieces to liquid ammonia (20–25 ml) in a 50-ml round-bottom flask fitted with a serum cap and Dry Ice condenser and immersed in a Dry Ice–isopropyl alcohol slush. About 10 μl of **1** dissolved in 30 μl of pentane was injected into the flask, and the solution was stirred with cooling for 30 min. A 10-ml sample of pentane was added, and the reaction mixture was quenched by dropwise addition of saturated aqueous ammonium chloride solution. The pentane layer was removed, washed with water, dried over magnesium sulfate, and analyzed by flame ionization glpc on a 21 ft × 0.125 in. column of 20% SE-30 on Chromosorb W at 115°. The sole detectable olefinic product was *trans*-3-heptene. Analogous reduction of **2** gave predominantly *cis*-3-hexene. The *cis*- and *trans*-3-hexenes were identified by retention time comparison with authentic samples (*vide infra*) by mixing the known compounds with the reaction mixtures.

Analysis of Photolysis Reaction Products.—The hydrocarbon products from the photolyses of **1** and **2** were analyzed by flame ionization glpc at 115° using a 21 ft × 0.125 in. column containing 20% SE-30 Chromosorb W. The disappearance and isomerization of the vinyl iodides were followed by thermal conductivity glpc at 70° using a 6 ft × 0.125 in. column containing 20% SE-30 on Chromosorb W. The products were identified by comparison with authentic samples described below.

***cis*- and *trans*-3-Heptenes.**—*trans*-3-Heptene was a commercial sample (Matheson Coleman and Bell) and gave only a single peak on a glpc trace. Pure *cis*-3-heptene was not isolated, but its retention time was obtained from a commercial mixture of *cis*- and *trans*-3-heptenes (Matheson Coleman and Bell). Its identity was further confirmed by iodine-catalyzed photoisomerization of the *cis–trans* mixture in which that peak identified as *trans*-3-heptene increased simultaneously with the loss of the peak identified as *cis*-3-heptene.

3-Heptyne.—A 2-ml sample of crude 4,4-diiodoheptane in 20 ml of 10 *M* solution of potassium hydroxide in ethylene glycol was slowly heated to 180°, and the distillate was collected during the course of several hours. Purification of this distillate by glpc gave a fraction containing *cis*- and *trans*-4-iodo-3-heptenes and a fraction identified as 3-heptyne: ir 2175 cm^{-1} (w) (C≡C); nmr multiplet at τ 8.19 (4) and two overlapping multiplets at 8.6–9.5 (8).

Anal. Calcd for C_7H_{12}: C, 87.42; H, 21.57. Found: C, 87.57; H, 12.65.

3,4-Heptadiene.—Treatment of *trans*-1,2-diethyl-3,3-dibromocyclopropane[34] with magnesium metal[35] or with methyllithium in ether[36] gave as the major product a compound whose retention time fell between those of 3-heptyne and the 3-heptenes. The acetylene 3-heptyne was also formed in these syntheses. Although this compound proposed to be 3,4-heptadiene was not isolated and characterized, the synthetic origins (particularly the methyllithium preparation) are strong proof of structure. The glpc characteristics of the compound identified as 3,4-heptadiene in the photolysis experiments were identical with those of this compound.

Registry No.—**1**, 17497-50-6; **2**, 17497-51-7; 1-iodocyclopentene, 17497-52-8; 1-iodocyclohexene, 17497-53-9; 1-iodocyclooctene, 17497-54-0; *cis*-3-iodo-3-hexene, 16403-09-1; *trans*-3-iodo-3-hexene, 16403-13-7; 4-heptanone-N,N-dimethylhydrazone, 14090-58-5.

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(34) W. von E. Doering and A. K. Hoffman, *J. Amer. Chem. Soc.*, **76**, 6162 (1954).

(35) W. von E. Doering and P. M. La Flamme, *Tetrahedron*, **2**, 75 (1958).

(36) L. Skättebøl, *Acta Chem. Scand.*, **17**, 1683 (1963).