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Photochemistry of Racemic and Resolved 2-Iodooctane. Effect of Solvent Polarity and Viscosity on the Chemistry

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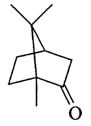
The photochemistry of racemic and resolved 2-iodooctane was examined in cyclopentane, methanol, and 2-methyl-2-propanol, media with differing polarities and viscosities. The photochemistry of racemic 2-iodooctane was also examined in the gas phase. The photochemistry of 2-deuterio- and 1,1,1-trideuterio-2-iodooctane in cyclopentane and methanol was also studied. The photoreactions in cyclopentane, 2-methyl-2-propanol, and the gas phase occurred exclusively through homolytic reactions, while in methanol, they occurred predominantly (>53%) through heterolytic reactions. By comparing the disappearance of the optically active substrate with its loss of optical activity, F, the fraction of the initially formed radical pair (RP) or ion pair (IP) resulting in product was determined for the three solvents. Because F contains contributions of both escape of the partners in the RP or IP into the bulk of the solvent and reaction within the RP or IP to yield products other than the substrate, there was no correlation between F and solvent viscosity. The F values will be valuable in assessing the photochemistry of 2-iodooctane in the same media with circularly polarized light.

Introduction

One of the triumphs of modern organic synthesis is the ability to make optically active molecules with high enantiomeric purity. The 2001 Nobel Prize in chemistry was awarded to three chemists who contributed significantly to this goal. Most of these asymmetric reactions are thermally activated.

Photochemistry has also been used for asymmetric synthesis, with mixed results. The most successful approach to date involves the photolysis of optically active crystals made up of optically inactive molecules.[1] This method works well but is limited to those relatively rare cases where enantiomorphic crystals are formed from achiral molecules. Optically active sensitizers have also proven useful in certain cases.[2] Photoreactions initiated with circularly polarized light (CPL), an easily prepared chiral form of light, is another approach. There are myriad ways in which CPL could be used in asymmetric synthesis, but this initial discussion will only consider two.

If one photolyzes a racemic mixture *R*/*S* with one enantiomeric form of CPL [left-handed CPL (LCPL) or right-handed CPL (RCPL)], one enantiomer of *R*/*S* will degrade more rapidly than the other, because it will have a slightly greater extinction coefficient (ϵ) than the other. In fact, the enantiomeric excess (ee) of recovered *R*/*S* approaches 100% as the time of the reaction becomes large. The problem with this approach is that one ordinarily destroys most of *R*/*S* before a large ee is obtained. This is a consequence of the fact that the differences in ϵ [$\Delta\epsilon$; determined by circular dichroism (CD)] are usually exceedingly small. Photolysis of racemic camphor (**1**) with CPL, for example, afforded recovered camphor with an ee of 20% after 99% of the camphor had been degraded.[3] Two-photon photochemistry of racemic tartaric acid (2) with CPL afforded a maximum ee for recovered tartaric acid of 7.5%.[4]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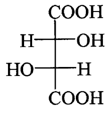
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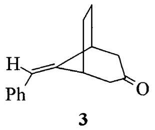
If one instead has a system in which *R* and *S* of the racemic mixture equilibrate photochemically but do not otherwise degrade, the ee at the photostationary state (pss) is $g_A/2$, where $g_A = (\epsilon_R - \epsilon_L)/(\epsilon_R + \epsilon_L)$, with ϵ_R and ϵ_L being the extinction coefficients for the *R* and *S* enantiomers at a given wavelength. This system is desirable in that *R*/*S* is not degraded, but it has the negative effect of yielding very small ee values because g_A is usually very small ($\epsilon_R - \epsilon_L$ is small and $\epsilon_R + \epsilon_L$ is large). For example, enone **3** underwent isomerization about the C−C double bond photochemically and yielded an ee of 1.6% when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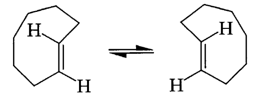

4 **4**

[†] Department of Chemistry.

[‡] Department of Physics.

[1] Feringa, B. L.; van Delden, R. A. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 3418.

[2] Inoue, Y.; Wada, T.; Asaoka, S.; Sato, H.; Pete, J.-P. *Chem. Commun.* **2000**, 250.

10.1021/jo020472r CCC: $22.00

photoequilibrated with CPL.[5] Photoequilibration of (*E*)- and (*Z*)-cyclooctene with CPL (190 nm from a synchotron source) afforded (*E*)-cyclooctene with a small enantiomeric enrichment.[6]

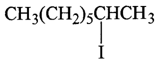
The first case, i.e., $R/S \rightarrow P$, is desirable because large ee values can be obtained regardless of the values of ϵ_R and ϵ_L, but only at the expense of degrading R/S significantly. The second case, i.e., $R \rightleftharpoons S$, is desirable because R/S is not degraded, but ee values will rarely be large. What may prove useful is a system that contains desirable features of both cases.

Reactions going through radical pairs (RPs) and/or ion pairs (IPs) have features of both cases (eq 1). The

$$\begin{tikzcd} R \arrow[r, shift left] & IN \arrow[l, shift left] \arrow[r, shift left] \arrow[d] & S \arrow[l, shift left] \\ & P & \end{tikzcd} \qquad (1)$$

enantiomers, R and S, photoequilibrate through the transient radical or ion pair (IN = intermediate) but ultimately yield products (P) through IN. It can be shown that the ee of recovered R/S depends on F, the fraction of IN that yields P.[7] When $F = 1$, i.e., IN → P 100% of the time, the system reverts to $R/S \rightarrow P$. When $F = 0$, i.e., IN never yields P, the system reverts to $R \rightleftharpoons S$. IN can yield P in two ways: (1) by the two components of the radical or ion pair diffusing apart and then reacting with solvent, for example, and (2) the two components of the radical or ion pair reacting with one another in a way that does not re-form R or S. Because F, in part, requires the two components of the intermediate to diffuse apart, F should depend on solvent viscosity.

The molecule chosen for this investigation was 2-iodooctane. It is easily prepared in racemic and optically active form.[8] Its chirooptical properties and thus g_A are



$$CH_3(CH_2)_5\underset{\displaystyle I}{\underset{|}{C}}HCH_3$$

easily measured by UV and CD spectroscopies. As shown herein, it yields an RP or IP, depending on solvent polarity, and a rich array of products. Its F values can be measured in a straightforward manner. This study is designed to provide a wealth of information on the dynamics of RPs and IPs as a function of solvent polarity and viscosity. Finally, the effect of g_A and F on the photolysis of racemic material with CPL can be probed.

This first paper will concentrate on the photochemistry of the racemic and optically active substrate with unpolarized light in four phases varying in polarity and viscosity and the measurement of F values. The results of the photochemistry with CPL will be reported elsewhere.

TABLE 1. Properties of the Reaction Phases

phase	$E_T(30)^a$	viscosity/cp (25 °C)^b	bond dissociation energy/kcal mol$^{-1\,c,d}$ C−H	O−H
gas	low	low		
cyclopentane	31	0.416	94.5	
methanol	55.4	0.551	94	104.4
2-methyl-2-propanol	43.3	4.438	100.5^e	105.1

[a] Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed.; VCH: Weinheim, Germany, 1988. [b] Riddick, J. A.; Bunger, W. B.; Sakuno, T. K. *Organic Solvents. Physical Properties and Methods of Purification*, 4th ed.; Wiley: New York, 1986. [c] Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976. [d] *CRC Handbook of Chemistry and Physics*, 63rd ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1982. [e] The value for neopentane (Bartmess, J., personal communication).

Results and Discussion

Cyclopentane, methanol, and 2-methyl-2-propanol were chosen as reaction media for this study. Cyclopentane and methanol have similar viscosities but different polarities, while 2-methyl-2-proponol is much more viscous and exhibits an intermediate polarity (Table 1). Because 2-iodooctane is volatile at room temperature, its photochemistry was also examined in the gas phase. Cyclopentane is a low-boiling, nonpolar liquid that should favor the formation of the RP, $CH_3(CH_2)_5{}^{\bullet}CHCH_3\ I^{\bullet}$. The organic radical can abstract hydrogen, dimerize, and disproportionate. The iodine atom is less prone to abstract H, because the bond dissociation energy of HI is so much less than the value of a typical C−H bond. The iodine atom could abstract H from the octyl radical in the RP, however; it could also dimerize. Because all 10 of its C−H bonds are equivalent, the number of products arising from cyclopentane will be minimized. Methanol, on the other hand, is a low-boiling, polar liquid that should favor the formation of the IP, $CH_3(CH_2)_5C^+HCH_3\ I^-$. The 2-octyl cation can, of course, be trapped by the solvent or isomerize to the 3-octyl cation, which in turn can be trapped. Trapping yields an ether and HI which could also be generated from iodide or other bases abstracting a proton from the carbocation. 2-Methyl-2-propanol has the highest viscosity of the three solvents, which should favor a chemistry occurring within the solvent cage. Unlike the other two solvents, its C−H and O−H bond strengths are sufficiently large to ensure that the 2-octyl radical will not likely abstract hydrogen from this solvent.

Photolysis of racemic 2-iodooctane in the gas phase, where a radical pair yielding $F = 1$ is expected, afforded six hydrocarbon products: 1-octene, octane, (*E*)- and (*Z*)-2-octene, and *meso*- and *d,l*-7,8-dimethyltetradecane[9] (Table 2, Scheme 1). Although the yields of HI and I_2 were not determined, their yields could be estimated from the product distribution and hydrogen atom balance. About 80% of the time the iodine atom dimerizes to I_2 and 20% of the time it abstracts a hydrogen atom from C-1 or C-3 of the 2-octyl radical to form HI and the octenes. Octane (and a comparable amount of octenes) can also arise by disproportionation of the 2-octyl radical. The ratio of 2(octane)/tetradecanes of 0.19 is what is expected for the disproportionation of a secondary radical.[10]

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(3) Kagan, H. B.; Balavoine, G.; Moradour, A. *J. Mol. Evol.* **1974**, *4*, 41.

(4) (a) Shimizu, Y.; Kawanishi, S. *Chem. Commun.* **1996**, 819. (b) Shimizu, Y.; Kawanishi, S. *Chem. Commun* **1996**, 1333. (c) Shimizu, Y. *J. Chem. Soc., Perkin Trans. 1* **1997**, 1275.

(5) Zhang, Y.; Schuster, G. B. *J. Org. Chem.* **1995**, *60*, 7192.

(6) Inoue, Y.; Tsuneisci, H.; Hakashi, T.; Yagi, K.; Awazu, K.; Onuki, H. *Chem. Commun.* **1996**, 2627.

(7) The derivation assumes that the disappearance of *R* and *S* is first-order.

(8) San Filippo, J., Jr.; Romano, L. J. *J. Org. Chem.* **1975**, *40*, 1514.

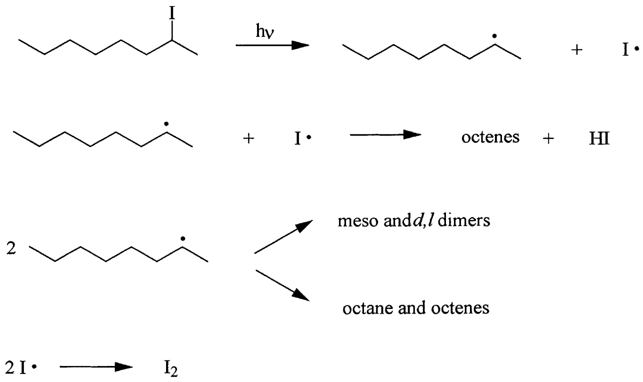
(9) We do not know which diastereomer is which.

TABLE 2. Photoproducts and Yields (%) from the Photochemistry of 2-Iodooctane[a]

	reaction phase			
photoproducts	gas	cyclo-pentane	methanol[b]	2-methyl-2-propanol[c]
1-octene	22	12	4	54
octane	6	22	17	2
(*E*)-2-octene	4	29	10	28
(*Z*)-2-octene	4	14	6	16
7,8-dimethyltetradecane				
isomer 1[d]	21	4	1	
isomer 2[d]	43	14	2	
iodocyclopentane		5		
unknown			7	
2-octanol			trace	trace
3-methoxyoctane			10	
2-methoxyoctane			38	
2-octanone			5	
iodine	76[e]	45	3	2[e]
hydrogen iodide	24[e]	50[f]	97[f]	98[e]

[a] Reactions usually contained unreacted starting material. Products normalized to 100%. [b] CH_3I is also formed in the reaction. [c] $(CH_3)_3CI$ is also a product of the reaction. [d] Meso or *d,l* isomer, shown in order of elution. [e] Estimated from product distribution and hydrogen atom balance. [f] Inferred from the amount of I_2 formed in reaction.

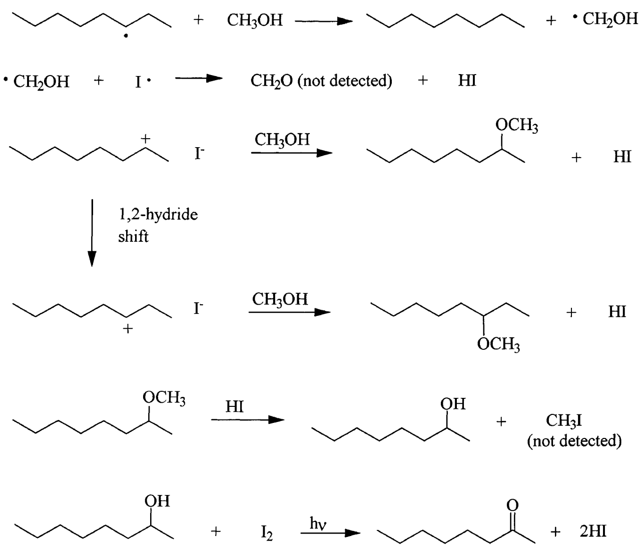
SCHEME 1



The photoreaction of 2-iodooctane in deoxygenerated cyclopentane, where a radical pair and $F \neq 1$ are expected, occurs rapidly at first but becomes progressively slower as the reaction progresses. This is undoubtedly due in some fashion to the buildup of I_2, a major photoproduct in the reaction. The reaction yields the same six hydrocarbons seen in the gas-phase plus iodocyclopentane (Table 1). The reaction also yields significant amounts of I_2. HI is also a product of the reaction, although it could not be detected in situ (lack of triiodide bands between 300 and 400 nm) because it is insoluble in cyclopentane. However, it could be trapped, in part, and detected in water (pH, AgI precipitate).

The free radical reaction in cyclopentane affords considerably more octane than observed in the gas phase reaction. If the disproportion-to-dimerization ratio of 0.2 holds here, only about 5% of the octane is formed from the disproportionation of two 2-octyl radicals. The remainder must arise by the 2-octyl radical abstraction of a hydrogen atom from the solvent. This reaction should be approximately isoenergetic. This interprepation is confirmed by the presence of iodocyclopentane in the product mixture. Of note is the lack of other cyclopentane-containing products including bicyclopentyl in the product mixture. Low-boiling products such as cyclopentene would have escaped detection, however.

SCHEME 2



Much more HI is formed in cyclopentane than in the gas phase. In the gas phase, no RP is formed ($F = 1$), and the 2-octyl radical and iodine atom escape each other instantly. In cyclopentane, the two radicals are formed in a cage. The radicals can react to regenerate the reactant or to produce HI and octenes and escape the cage. On the basis of the yields of I_2 and the two dimethyltetradecanes, escape products, one sees that about one-half of the radical pairs escape into the bulk solvent. Thus, F contains two contributions, reaction to yield HI and octenes and escape.

The photoreaction of 2-iodooctane in deoxygenerated methanol, which is faster than in cyclopentane, especially at longer reaction times, also yields the six hydrocarbons seen in the gas phase and cyclopentane (Table 2, Scheme 2). The reaction also yields 2-methoxyoctane (major product), 3-methoxyoctane, 2-octanol, 2-octanone, and an unknown compound. Trace amounts of unidentified compounds are also found. On the basis of their gas chromatographic retention times, some of these are likely (*E*)- and (*Z*)-3- and 4-octene and 4-methoxyoctane. UV/vis spectroscopy of the reaction solution shows the presence of triiodide, but not I_2. Thus, HI, which is soluble in methanol, is formed in greater amounts than I_2. Very little *meso*- and *d,l*-7,8-dimethyltetradecane are formed here, implying that little of the octane is formed by the disproportionation of the 2-octyl radical. Most of the octane undoubtedly arises by the 2-octyl radical abstraction of the C−H hydrogen atom from the solvent, a reaction which is approximately isoenergetic. Unlike octane, 2- and 3-methoxyoctane, 2-octanol, and 2-octanone arise via heterolytic chemistry, as shown below. The 2-octanol is undoubtedly formed by cleavage of 2-methoxyoctane by HI; the alcohol in turn is photooxidized by I_2 to form 2-octanone.[11]

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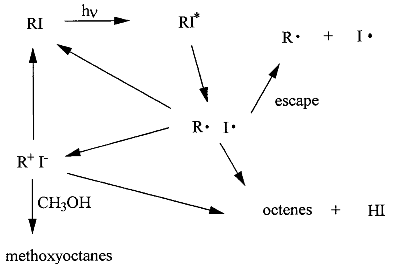
(10) Lowry, T. H.; Richardson, K. S. *Mechanisms and Theory in Organic Chemistry*, 3rd ed.; Harper and Row: New York, 1987; chapter 9.

(11) Itoh, A.; Kodamu, T.; Masaki, Y. *Chem. Lett.* **2001**, 686.

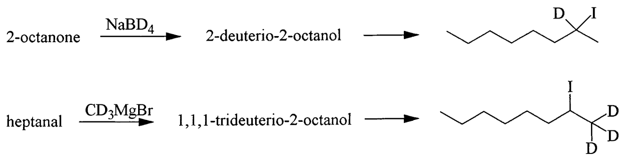
TABLE 3. % Deuterium Content of Selected Photoproducts

	photolysis of 2-iodo-2-deutereooctane				photolysis of 2-iodo-1,1,l-trideuteriooctane					
	cyclopentane		methanol		cyclopentane		methanol			
product	d_1	d_0	d_1	d_0	d_3	d_2	d_3	d_2	d_1	d_0
1-octene	100	0	100	0	100	0		30	52	17
octane	53	47	66	4	0	100	100	51	32	16
(*E*)-2-octene	~96	~4	70	30	0	100		20	54	26
(*Z*)-2-octene	~96	~4	66	34	0			34	50	16
2-methoxyoctane			100	0				70	30	
3-methoxyoctene			100	0				73	27	

SCHEME 3



SCHEME 4



The product distribution reveals that at least 53% of the reaction occurs through the 2-octyl cation and at least another 20% through the 2-octyl radical. How the remaining 27% of the product is formed is unclear, because all of the octenes can be formed from the RP or IP. Although the RP and IP may be formed independently from the excited state of 2-iodooctane, it is reasonable to assume that they form sequentially, as shown in Scheme 3. The low yields of I_2 and the dimethyltetradecanes suggest that very little of the radicals in the RP escape into the bulk solvent. On the basis of the extensive literature on solvolysis reactions and their associated ion pairs, it is reasonable to assume that most of the ionic chemistry takes place within the IP and little of the relatively unstable 2-octyl cation and iodide escape into the bulk solvent.

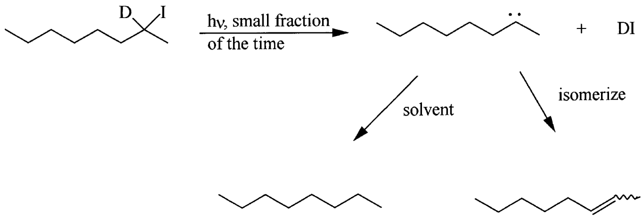
The photochemistry of the substrate in 2-methyl-2-propanol, whose polarity is intermediate between that of cyclopentane and methanol, occurs surprisingly completely through free radicals (Table 2). As little I_2 and no dimethyltetradecanes are formed here, it is reasonable to assume that virtually all the chemistry takes place within the RP.

The photochemistry of two deuterated analogues of 2-iodooctane, 2-deuterio-, and 1,1,1-trideuterio-, whose syntheses are shown in Scheme 4, was investigated in cyclopentane and methanol.

Photolysis of 2-iodooctane-d_3 in cyclopentane gives the expected results: 1-octene with two Ds and (*E*)- and (*Z*)-2-octene with three Ds (Table 3). Octane is formed with three Ds only.

Any octane formed in this reaction by disproportionation does not transfer a D at C-1 in one radical to the other, as this would generate octane with four Ds. Transfer of an H at C-3 is consistent with the results. Interestingly, there is much less octane formed here (7%) than is seen in the nondeuterated case (22%).

SCHEME 5



Photolysis of 2-iodooctane-d_1 in cyclopentane is also informative. As in the previous case, only a small amount of octane is produced (5%), 47% of which contained no deuterium. This is consistent with the photoreaction yielding a small amount of the 2-octyl carbene (Scheme 5). This result has precedent in Kropp's study of the photochemistry of alkyl halides, where carbenes are often observed.[12] Once formed the carbene could abstract hydrogen from the solvent to form octane or isomerize to (*E*)- and (*Z*)-2-octene, all with no deuterium. The 2-butyl carbene, an analogue of the 2-octyl carbene, is known to preferentially yield the two 2-butenes.[13]

Unlike in cyclopentane, the photochemistry of 2-iodooctane-d_1 in methanol yields considerable amounts of octane, approximately 34% of which contains no deuterum (Scheme 6). Thus, more carbene is formed in methanol than in cyclopentane. Some of the unlabeled (*E*)- and (*Z*)-2-octene must arise from the 2-octyl carbene. The rest arises from 1,2-hydride shifts starting from the 2-octyl cation. Interestingly neither 3-methoxyoctane nor 2-methoxyoctane has any D, which is expected for their formation from the 3-octyl and 2-octyl cations, respectively. This yields the rather surprising result that none of the 2-methoxyoctane arises from the insertion of the 2-octyl carbene into the solvent's O−H bond.

The photochemistry of 2-iodooctane-d_3 in methanol is also informative. The products show evidence for the loss of one, two, and even three deuteriums. This is a consequence of the fact that HI is generated in the reaction and it can re-add to the octene to re-form 2-iodooctane (3-iodooctane is not seen) (Scheme 7).[14] Thus, 1-octene-d_2 formed in the deprotonation of the 2-octyl cation forms, in addition to HI, 2-iodooctane-d_2, which can then react photochemically again. This hy-

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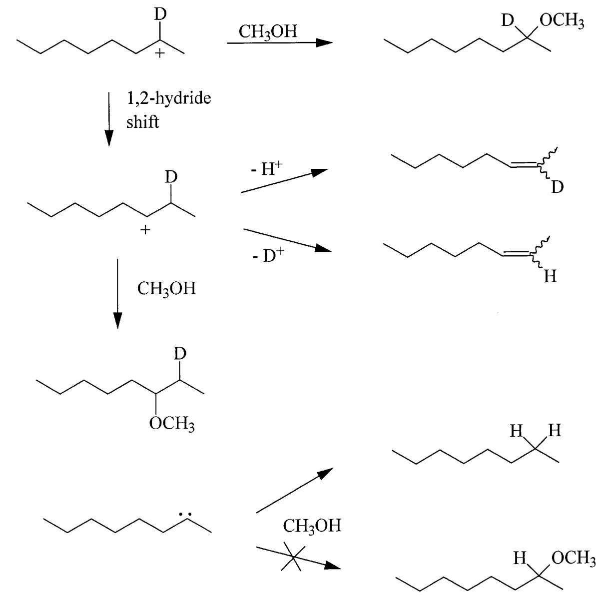
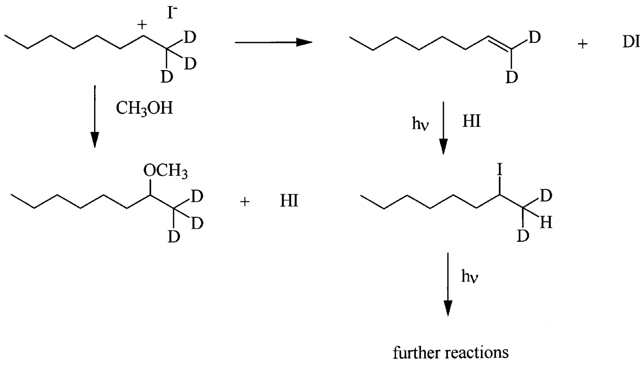
[12] Kropp, P. J.; Sawyer, J. A.; Snyder, J. J. *J. Org. Chem.* **1984**, *49*, 1583.

[13] Platz, M. S. In *Advances in Carbene Chemistry*; Brinlar, V. H., Ed.; JA1 Press: Stanford, CT, 1998; Vol. 2, p 131.

SCHEME 6



SCHEME 7



pothesis is also born out by the fact that recovered 2-iodooctane consists of 63%-d_3 and 37%-d_2 after most of the overall reaction is complete (>99%).

Solvolysis reactions yielding IPs have been characterized, in part, by various kinds of rate constant measurements including k_t, from the titration of acid formed in the reaction; k_α, from the loss of optical activity of the solution; and k_{rac}, from the loss of optical activity in the reactant. *F*, the fraction of the IP going to product, can be deduced from these measurements. Similar data for photoreactions proceeding through RPs and/or IPs will also yield *F* values.

The kinetics of unimolecular photochemical reactions has been worked out by Kagan,[15] Inoue,[16] and others.[17] If the absorbance (A) of the substrate and products is small (A < 0.01), the rate of disappearance of reactant is close to first-order. At higher values of A, the dependence of the rate on substrate concentration is quite complex, although it may appear to be zero-order when A is large.[16]

If an optically active substrate R reacts photochemically with unpolarized light according to the scheme in eq 1, it is easy to show that, under first-order conditions, the disappearance of substrate, i.e. [R] + [S], and the loss of optical activity, as measured by [R] − [S], yields, respectively

$$[R] + [S] = [R]_o e^{-kFt}$$

$$[R] - [S] = [R]_o e^{-kt}$$

where [R] = [R]$_o$ and [S] = 0 at t = 0, k is the phenomenological rate constant, and F is the fraction of IN going to product.[18] Plots of ln([R] + [S])/[R]$_o$ and ln([R] − [S])/ [R]$_o$ versus time yield straight lines with slopes of kF and k. If the reactions have the appearance of being zero-order, plots of ([R] + [S])/[R]$_o$ and ([R] − [S])/ [R]$_o$ versus time yield straight lines whose ratio of slopes yields F.

Photolysis of optically active (*R*)-2-iodooctane[8] in methanol, cyclopentane, and 2-methyl-2- propanol was followed by quantitative GC/MS and polarimetry as a function of time.[19] The normalized results are shown in the table in the Supporting Information. The methanol data afforded linear (zero-order) plots of ([R] + [S])/ [R]$_o$ and ([R] − [S])/ [R]$_o$ versus time for the first half of the reaction. From the slopes, one obtains $F(CH_3OH) = 0.60 \pm 0.05$. A like analysis of the 2-methyl-2-propanol data yields $F[(CH_3)_3COH] = 0.74 \pm 0.05$. A similar analysis of the cyclopentane data was difficult, because the log and nonlog plots deviated quite early in the reaction. It is clear from the data that *F*(cyclopentane) is close to 1. Using the data points through 1 h of the reaction yields *F*(cyclopentane) = 0.70 ± 0.12, although a value larger than 0.80 is likely.

The photolysis solutions have rotations close to or at 0° when the reactions are near completion. The unreacted 2-iodooctane is racemic at this time. The chiral 7,8-dimethyltetradecane isomer must also be racemic. This is not surprising, as the hydrocarbon arises by dimerization of the achiral 2-octyl radical that has escaped the RP cage. 2- And 3-methoxyoctane must also be racemic or nearly so.

It is possible to dissect the behavior of the radical and ion pairs in three solvents (Table 4). In the gas phase there is, of course, no caged intermediates. Except in methanol, where a sizable fraction of the reaction proceeds through ion pairs, the chemistry is dominated by free radicals. *F* is large in all cases through varying degrees of escape of the caged intermediates into the bulk solvent and reaction within the cage to form products other than the reactant. Escape of the radicals in the RP in cyclopentane is large, while very small in 2-methyl-

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[14] HI does not add to 1-octene in methanol at room temperature. The temperature inside the photoreactor is approximately 31−32 °C. The addition must be photoactivated. HI forms H$^\bullet$ and I$^\bullet$ under our reaction conditions: Calvert, J. G.; Pitts, J. N., Jr. *Photochemistry*; Wiley: New York, 1966.

[15] Balavoine, G.; Moradpour, A.; Kagan, H. B. *J. Am. Chem. Soc.* **1974**, *96*, 5152.

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[18] Equation 1 is the simplest scheme for describing the photochemistry of resolved 2-iodooctane. A more involved scheme would involve "fight" and "loose" ion/radical pairs, each of which could give P. Intimate and solvent-separated ion pairs are well-known from solvolysis chemistry. The mathematics for the more complex scheme but gives solutions similar in form to those described in the text. Because there is no evidence for the more complex behavior, the simplest scheme was used.

[19] The HI formed in the reactions does not racemize the (*R*)-2-iodooctane.

TABLE 4. Fractional Behavior of 2-Octyl/Iodine Radical/Ion Pair

phase	fraction of reaction that is free radical	F	return to reactant (1 − F)	escape	reaction in cage to form octenes and octane
gas	1	1[a]	0[a]	1	
cyclopentane	1	>0.80	<0.20	~0.50	~0.40
methanol	0.20 < fraction <0.47	0.60	0.40	0.03[b]	0.57
2-methyl-2-propanol	~1	0.74	0.26	0.02	0.72

[a] Assumed. [b] From RP. Escape from IP unknown but assumed to be 0.

2-propanol, reflecting the 10-fold difference in viscosity of the two media. The *F* value in methanol, a solvent with a viscosity similar to that of cyclopentane, is smaller than in the other two solvents. This is a reflection of the fact that the reaction in methanol is dominated by an IP, where escape of the ions likely does not occur.

Concluding Remarks

There have been many studies of photoreactions in solution yielding RPs and/or IPs. The extensive work of Kropp on alkyl halides,[12,20,21] Givens on phosphate esters,[22] and Pincock on arylmethyl esters[23] comes to mind, with the work of Kropp having the closest relationship to the work reported herein.[24]

2-Iodooctane has a weak absorption band at ca. 270 nm, which is associated with an n → σ^* transition.[25] For the related compounds CH_3I and CH_3CH_2I, this results in homolytic cleavage of the C−I bond in the gas phase.[26] Similar behavior is seen for 2-iodooctane in the gas phase, where significant amounts of the dimeric *meso*- and *d*,*l*-7,8-dimethyltetradecane are formed. Similar behavior is also seen for the substrate in the nonpolar cyclopentane and the much more polar 2-methyl-2-propanol. Dimers are seen in cyclopentane but not in the more viscous 2-methyl-2-propanol. Interestingly, dimers are not formed in the photochemistry of 1-iodooctane.[12,24] A small amount of carbene-derived products are formed in cyclopentane. Kropp has shown in the case of 1-iodooctane, where some 1-octyl carbene is formed, that the carbene does not arise in a concerted loss of HI, but instead may derive from the RP or IP.[12,24] In methanol, considerably greater than half of the photoreaction occurs through an IP, with the rest through an RP. A small amount of the 2-octyl dimers are formed in methanol. 2-Iodooctane affords more carbocation in methanol than does 1-iodooctane; the secondary 2-octyl cation is, of course, more stable than the 1-octyl cation. It is known that many solvolysis reactions proceed through two types of ion pairs: intimate and solvent-separated. Although it is clear that they are formed during the photolysis of 2-iodooctane in methanol, after all the “ion pair” goes back to reactant and forward to product, the data from the experiments herein do not directly address their nature.

Although a lot has been learned about RPs and IPs from time-resolved experiments, labeling experiments, and the like, the *F* values determined here are the first reported for RPs and the first for IPs generated in photochemical reactions. The *F* value for methanol is a composite, containing contributions from both its RP and IP. The experiments were not designed to resolve the *F* values into its contributors. The *F* values for the three solvents do not correlate with solvent viscosity. This is a consequence of the fact that the caged intermediates cannot only re-form the reactant and escape but also react within the cage to form the octenes. Nonetheless, it will now be possible to assess how the *F* values influence the photochemistry of 2-iodooctane in the three solvents with circularly polarized light.

Experiment Section

Samples. Racemic and optically active (*R*)-2-iodooctane were prepared from the corresponding alcohol by a literature procedure.[8] 2-Deuterio-2-octanol was prepared by reduction of 2-octanone with $NaBD_4$; further treatment afforded 2-deuterio-2-iodooctane. 1,1,1-Trideuterio-2-octanol was prepared by the reaction of heptanal with CD_3MgBr; further treatment afforded 1,1,1-trideuterio-2-iodooctane. Both substrates were isotopically pure by mass spectrometry. (*Z*)-2-octene was prepared by the direct irradiation of (*E*)-2-octene.

Photolyses. Photolyses were carried out in a reactor using 2537Å lamps. 2-Iodooctane has λ_{max} at 266 nm in cyclopentane. The samples in quartz tubes were degassed before photolysis. The gas-phase photolysis was carried out on a degassed, neat sample of the 2-iodooctane in the quartz tube. Because the substrate has a vapor pressure at room temperature, the quartz tube always contained equilibrated gaseous substrate. The light passed through the nonliquid-containing portion of the tube. Because there are no cage effects here, the gas-phase reaction occurred almost as fast as the solution phase ones.

Product Identification. The photoproducts were separated by GC/MS. The products were identified using known samples and literature mass spectra data and retention times. Deuterium analysis of the products obtained from the irradiation of the deuterated substrates was carried out by MS.

Controls. Experiments showed that HI did not react with 1-octene in methanol in the absence of light. It also did not racemize optically active 2-iodooctane under the reaction conditions.

UV/Vis Experiments. I_2 from photolyses in cyclopentane was quantified using the extinction coefficient determined in these laboratories. Likewise I_3^- in methanol was quantified using the extinction coefficient determined in these laboratories. Anhydrous HI was prepared by the method of Hoffman.[27] Bubbling HI into I_2 in cyclopentane did not yield I_3^-. Bubbling HI into I_2 in methanol did yield the characteristic bands of I_3^-.

Photolysis of (*R*)-2-Iodooctane. The disappearance of the substrate was followed by GC/MS, while the change in optical rotation was followed by polarimetry. Rotations of 0.001° could be measured on carefully equilibrated samples. How the data were analyzed is found in the Supporting Information.

Photolysis of a degassed solution of 2-octanol and I_2 in methanol under the conditions described above afforded 2-octanone. Similar behavior is known for benzylic and allylic alcohols.[28]

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Supporting Information Available: The data analysis from the photolysis of the optically active substrate and the derivation of the relevant mathematical equations. This material is available free of charge via the Internet at http://pubs.acs.org.

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