

The reversible concentration change in organic phase, which was caused by stirring, suggests a significant participation of the liquid-liquid interface in the equilibrium. The interfacial component is less than 3% for dithizone and then rises rather rapidly from 26% in MeDz to 82% in EtDz, to 99.9% in BuDz, and to all but  $7 \times 10^{-4}\%$  in hexyldithizone. These changes are indicative of the dramatic change in the heterogeneous acid-base equilibrium constant (up to a factor of  $10^5$ ) that occurs because the anionic alkylidithizonate (but not the neutral ligand) is surface active and is adsorbed into the interfacial region.<sup>39</sup>

The extraction kinetics of nickel and zinc with the alkylidithizonates<sup>39</sup> closely resembled those with dithizone and its analogues studied earlier,<sup>30</sup> in that the rate was first order each in metal and ligand and inverse first order in hydrogen ion. However, if one were to assume that the mechanism remained the same, i.e., that the rate-determining step was the formation of the 1:1 complex from metal and ligand anion in the aqueous phase, one would estimate increases in the second-order reaction rate constant with increasing size of alkyl group until, with the hexyldithizone, the values for both Ni and Zn would exceed the diffusion-limited rate constant for bimolecular reaction!

(39) Watarai, H.; Freiser, H. *J. Am. Chem. Soc.* **1983**, *105*, 191.

(40) Watarai, H.; Freiser, H. *J. Am. Chem. Soc.* **1983**, *105*, 189.

Having determined from the effect of stirring that the ligand anion is concentrated in the interface, however, one can reasonably assume that the locus for the formation of the 1:1 complex is the interfacial region. Calculating the correct value of the ligand anion concentration in the interface from the observed differences in  $\text{pH}_{1/2}$  values (vide supra) and assuming that since the metal ion is not surface active, its concentration in the interface is the same as it is in the bulk aqueous phase, we obtained values for rate constants that were eminently reasonable, i.e., essentially constant values for all the alkylated dithizonates.  $\log k_1$  for Ni and Zn are 5.13 and 8.08, respectively, which are consistent with those obtained for these metals in a broad cross section of ligand-substitution reactions. Essentially the entire cause of the unusual kinetic behavior, as well as of the unusual extraction equilibrium behavior, is the excess concentration of the ligand anion in the interfacial region, which is greatly enlarged by high-speed stirring.

Our studies are now directed toward characterizing the nature and the behavior of unsupported liquid-liquid interfaces, as well as the chemical reactions that occur in such an environment, an area of research that seems certain to be of significance to surface science in general as well as to extraction chemistry in particular.

*Much of the research described here was conducted with the support of the National Science Foundation.*

## Photobehavior of Alkyl Halides in Solution: Radical, Carbocation, and Carbene Intermediates

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*Received September 20, 1982 (Revised Manuscript Received September 1, 1983)*

One of the most conceptually simple and earliest studied chromophores is that of the carbon-iodine bond. The lowest lying transition involves promotion of one of the  $n$  electrons of iodine to the  $\sigma^*$  orbital of the bond. Since an antibonding orbital is now occupied and the transition occurs at an energy ( $\sim 380$  kJ/mol) far exceeding the carbon-iodine bond strength ( $\sim 215$  kJ/mol), it is not surprising that the bond undergoes efficient light-induced cleavage. From extensive early studies, conducted principally in the gas phase, it was demonstrated that the absorption of light by an alkyl iodide leads to homolytic cleavage of the carbon-iodine bond (eq 1) followed by ground-state reactions of the resulting alkyl radical and iodine atom.<sup>1,2</sup> In some cases molecular  $\beta$  elimination of HI (eq 2) was proposed as a competing minor pathway.<sup>3</sup>



Studies on the photobehavior of alkyl iodides in the liquid phase and in solution came later.<sup>4</sup> Once again the results were generally interpreted in terms of radical intermediates. It was here, however, that anomalous results began to appear, such as the isomerization of 1-iodopropane (1) to the 2-iodo isomer 2 and the formation of 2-butene (4) from 1-iodo-2-methylpropane (3).<sup>5</sup> Alkyl radicals do not normally undergo the type

(1) For an early review of the photobehavior of alkyl halides, see: Steacie, E. W. R. "Atomic and Free Radical Reactions", 2nd ed.; Reinhold: New York, 1958.

(2) For a more recent review of the gas phase photobehavior of alkyl halides, see: Majer, J. R.; Simons, J. P. *Adv. Photochem.* **1964**, *2*, 137-181.

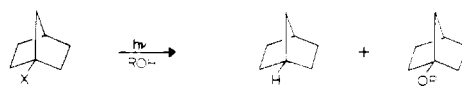
(3) See: Thrush, B. A. *Proc. R. Soc. London, Ser. A* **1958**, *243*, 555-560. Schindler, R.; Wijnen, N. H. *J. Z. Phys. Chem. Neue Folge* **1962**, *34*, 109-112.

(4) For a recent review of the solution phase photobehavior of alkyl halides, see: Sammes, P. G. In "Chemistry of the Carbon-Halogen Bond"; Patai, S., Ed.; Wiley: New York, 1973; Chapter 11.

(5) McCauley, C. E.; Hamill, W. H.; Williams, R. R., Jr. *J. Am. Chem. Soc.* **1954**, *76*, 6263-6266.

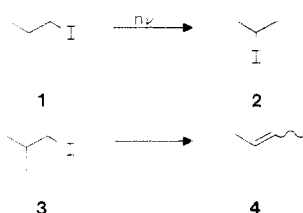
A native of Springfield, Ohio, Paul J. Kropp received his undergraduate training at the University of Notre Dame. After graduate studies at the University of Wisconsin and Stanford University, he joined the Miami Valley Laboratories of the Procter & Gamble Company. In 1970, he assumed his present position of Professor of Chemistry at the University of North Carolina at Chapel Hill. His research interests include photochemistry, reaction mechanisms, new synthetic methodology, and total synthesis.

Table I  
Irradiation of 1-Halonorbornanes.  
Effects of Changing Halogen and Solvent<sup>a</sup>

		
CH <sub>3</sub> OH		
X = Br	55%	30%
X = I	11%	89%
HOCH <sub>2</sub> CH <sub>2</sub> OH		
X = Br	6%	92%
X = I	trace	99%

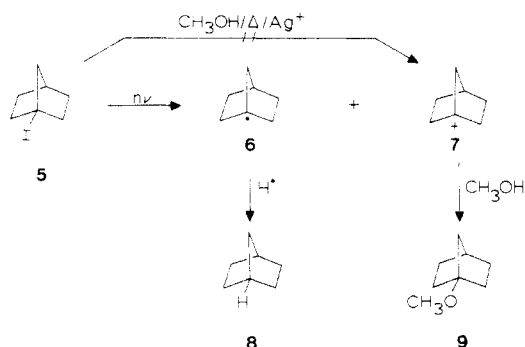
<sup>a</sup> Reference 6.

of rearrangement that would be required to account for these results, but carbocations do. Could it be that previously unsuspected cationic intermediates are sometimes involved in the liquid phase? Unfortunately, no one had conducted critical experiments that would permit a more clear distinction between radical and cationic intermediates. It was with this purpose in mind that we initiated an extensive study of the solution-phase photobehavior of alkyl halides.



### Carbocationic Intermediates

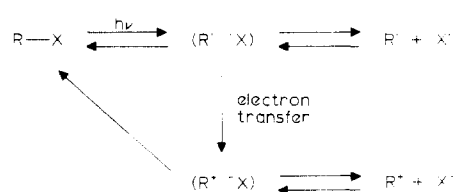
**The 1-Norbornyl Cation (7).** Although a tertiary iodide, 1-iodonorbornane (5) is remarkably inert toward solvolysis. For example, it can be recovered quantitatively from a methanolic solution heated under reflux for several days—even in the presence of added silver ion, which normally facilitates reaction by alkyl iodides.<sup>6</sup> The inertness of iodide 5 lies in the fact that carbocations normally prefer to be sp<sup>2</sup> hybridized and, hence, planar, but the 1-norbornyl cation (7) is structurally prevented from relaxing from the tetrahedral geometry at C-1. We found, however, that simply placing a solution of iodide 5 in the emission of a low-pressure mercury lamp, such as a germicidal lamp, results in rapid conversion of the iodide to two photoproducts (Table I).<sup>6</sup> The minor product, norbornane (8), is the



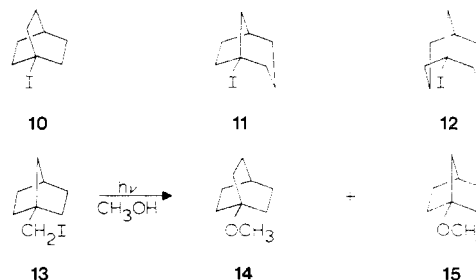
expected product from the traditional radical intermediate (6), whereas the major product, ether 9, is clearly an ionic photoproduct derived from nucleophilic

(6) Kropp, P. J.; Poindexter, G. S.; Pienta, N. J.; Hamilton, D. C. *J. Am. Chem. Soc.* 1976, 98, 8135–8144.

Scheme I



trapping of the 1-norbornyl cation (7). This single experiment demonstrated not only that an ionic photoproduct can be generated from an alkyl halide but that irradiation of alkyl halides has the potential of being a powerful method for the generation of carbocations not readily accessible by conventional ground-state methods. Subsequent studies showed that similar behavior is exhibited by the bridgehead iodides 10–12.<sup>7</sup> Ionic behavior is also displayed by 1-(iodomethyl)norbornane (13), which affords a mixture of the ring-expanded ethers 14 and 15 on irradiation in methanol.<sup>6</sup> The occurrence of Wagner–Meerwein rearrangements is yet another manifestation of ionic intermediates.

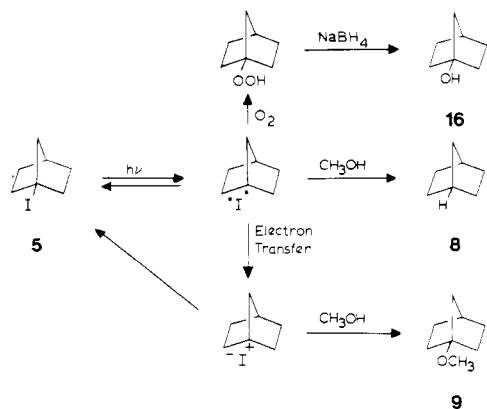


**Mechanism.** How do the ionic intermediates arise? Homolytic cleavage of the carbon–iodine bond is well-established for the n, σ\* state in the gas phase.<sup>1,2</sup> The ratio of ionic to radical product formation was found to be independent of wavelength, as expected for the involvement of a single excited state. An appealing mechanism was that outlined in Scheme I, in which initial homolytic cleavage is followed by electron transfer within the resulting caged radical pair. Competing diffusion from the cage would result in the observed formation of radical products.

In accordance with this mechanism, irradiation of a methanolic solution of iodide 5 in the presence of oxygen resulted not only in a total quenching of the radical product norbornane (8) but also in a substantial quenching of the ionic product 9. There was a concomitant formation of a new product, the corresponding hydroperoxide, which was characterized by reduction to 1-norbornanol (16).

**Bromides vs. Iodides.** As shown in Table I, irradiation of 1-bromonorbornane in methanol afforded a mixture of the same two photoproducts as the iodo analogue. However, in this case the reduction product norbornane was formed predominantly.<sup>6</sup> We have generally observed that the ratio of ionic to radical products is substantially larger for iodides than bromides. It would be expected on the basis of electronegativities that electron transfer would occur more readily for bromides. There are thus apparently overriding factors that determine the facility of electron transfer, such as the greater polarizability of iodine and the fact that formation of iodide ion involves generation of a

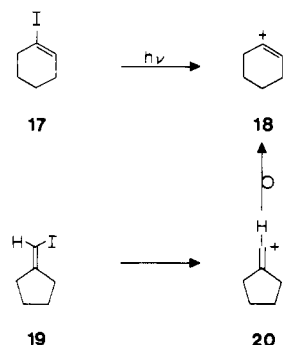
(7) Kropp, P. J.; Worsham, P. R.; Davidson, R. I.; Jones, T. H. *J. Am. Chem. Soc.* 1982, 104, 3972–3980.



lesser point charge density. Another factor might be the difference in reactivity of the bromine and iodine radicals toward hydrogen abstraction; bromine is sufficiently reactive to abstract hydrogen atoms from solvent molecules, thereby precluding competing electron transfer, whereas iodine is not sufficiently reactive.

**Solvent: The Effect of Viscosity.** As also seen in Table I, going to the more viscous solvent 1,2-ethanediol resulted in a substantial increase in the ratio of ionic to radical products. The increased lifetime of the radical pair cage in a more viscous solvent apparently allows electron transfer to compete more effectively with diffusion from the cage. The effect is particularly dramatic for the bromide, which exhibits almost exclusive ionic photobehavior in the more viscous solvent. Change of solvent is thus a simple means for inducing a higher degree of ionic behavior in alkyl bromides.

**Formation of Vinyl Cations.** Our attention next turned to extending the irradiation of alkyl halides to the formation of other cationic intermediates that are not readily available by conventional ground-state procedures. Vinyl cations fall into this class, particularly cyclic vinyl cations, which are structurally prevented from assuming the preferred linear geometry of the positive carbon, and "primary" vinyl cations, which bear only hydrogen substituents on the charged carbon. Thus cyclohexyl derivatives undergo solvolysis very reluctantly.<sup>8</sup> However, irradiation of 1-iodocyclohexene (17) was found to afford mixtures of the reduction product cyclohexene and products from nucleophilic trapping of the 1-cyclohexenyl cation (18).<sup>9</sup> These



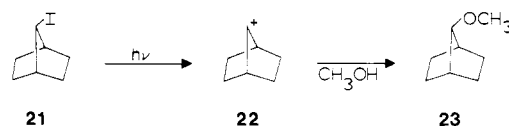
latter products were also obtained on irradiation of (iodomethylene)cyclopentane (19), along with the reduction product methylenecyclopentane.<sup>9</sup> Interestingly,

(8) Pfeifer, W. D.; Bahn, C. A.; Schleyer, P. v. R.; Bocher, S.; Harding, C. E.; Hummel, K.; Hanack, M.; Stang, P. J. *J. Am. Chem. Soc.* 1971, 93, 1513-1516. Subramanian, L. R.; Hanack, M. *Chem. Ber.* 1972, 105, 1465-1470.

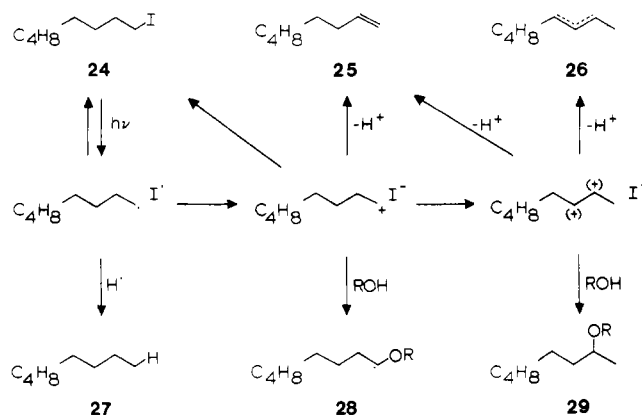
(9) Kropp, P. J.; McNeely, S. A.; Davis, R. D.; Davidson, R. I. *J. Am. Chem. Soc.* 1983, 105, 6907-6915.

the corresponding vinyl cation 20, which can assume a linear geometry but is  $\alpha$ -unsubstituted, has undergone rearrangement to the 1-cyclohexenyl cation (18), which is  $\alpha$ -substituted but cannot become linear. Irradiation of a number of other vinyl iodides was similarly found to be an efficient source of vinyl cations.<sup>9</sup>

**The 7-Norbornyl Cation.** Another type of carbocation not readily generated is the 7-norbornyl cation (22). Due at least in part to the inability of the bond angle at C-7 to assume the preferred 120° of an  $sp^2$ -hybridized center, 7-norbornyl derivatives undergo solvolysis at exceptionally slow rates.<sup>10</sup> However, we have found that simple exposure of a methanolic solution of 7-iodonorbornane (21) to ultraviolet light results in rapid conversion to a mixture of ionic products consisting principally of the nucleophilic substitution product 23.<sup>11</sup>



**Nucleophilic Substitution vs. Elimination.** In addition to nucleophilic trapping, another common property of carbocations is loss of a proton to afford an unsaturated product. Since each of the preceding cationic intermediates is structurally incapable of readily undergoing deprotonation, it is not surprising that nucleophilic substitution was observed as the principal course of reaction. By contrast, systems capable of readily undergoing elimination usually afford unsaturated products predominately. Thus, for example, irradiation of 1-iodooctane (24) in alcoholic solvents affords principally 1-octene (25) accompanied by only a small amount of the reduction product 27 and the ether 28.<sup>6</sup> Also formed are small amounts of a mixture

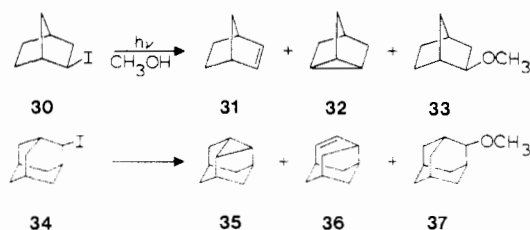


of the rearranged alkenes 26 and ether 29. Similarly, 2-iodonorbornane (30) affords principally a mixture of the elimination products 2-norbornene (31) and nor-tricyclene (32) in methanol, accompanied by only a small amount of ether 33.<sup>12</sup> 2-Iodoadamantane (34) represents an intermediate case, affording principally the ether 37, accompanied by smaller amounts of the elimination products 35 and 36.<sup>13</sup>

(10) Winstein, S.; Shafavsky, M.; Norton, C.; Woodward, R. B. *J. Am. Chem. Soc.* 1955, 77, 4183-4184. Woods, W. G.; Carbon, R. A.; Roberts, J. D. *Ibid.* 1956, 78, 5653-5657. Su, T. M.; Sliwinski, W. F.; Schleyer, P. v. R. *Ibid.* 1969, 91, 5386-5388.

(11) Kropp, P. J.; Davidson, R. I.; Tise, F. P.; McCraw, G. L.; Underwood, G. A., manuscript in preparation.

(12) Kropp, P. J.; Jones, T. H.; Poindexter, G. S. *J. Am. Chem. Soc.* 1973, 95, 5420-5421.

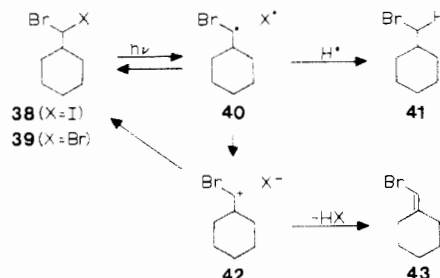


How are the elimination products generated? Before we had demonstrated that carbocationic intermediates are formed on irradiation of alkyl iodides, it was generally assumed that the elimination products arise via either a concerted 1,2 molecular loss of HI from the alkyl iodide (eq 2)<sup>3</sup> or disproportionation within the caged radical pair (eq 3). Although the former cannot

$$[\text{R}\cdot\text{I}] \rightarrow [\text{alkene} + \text{HI}] \quad (3)$$

be excluded as a possible contributing pathway in the formation of simple 1,2-elimination products such as 1-octene (25) and 2-norbornene (31), it is obviously not involved in the formation of either the rearranged elimination products 26 and 36 or the 1,3-elimination products 32 and 35. Such products are also not characteristic of radical behavior.

Additional evidence against the radical disproportionation route to unsaturated products is found in a comparison of the behavior of iodides and their corresponding bromides. For example, the bromo iodide 38 affords principally the vinyl bromide 43, whereas the dibromide 39 affords principally the reduction product 41.<sup>14</sup> Similarly, 1-bromooctane affords principally the



reduction product octane (27).<sup>6</sup> The radical pair formed in each case differs only in the identity of the halogen atom X. Although the bromine atom is normally much more prone toward hydrogen atom abstraction than the less active iodine atom, much less unsaturated product is obtained from the bromides.

On the other hand, the formation of elimination products with rearrangement, the formation of 1,3-elimination products, and the predominance of elimination products from iodides as opposed to bromides are all consistent with the involvement of carbocationic intermediates in the elimination process. And the fact that elimination predominates over nucleophilic substitution except in the cases in which elimination is structurally inhibited is generally true for carbocationic processes in which the intermediate is generated by a high-energy process involving little or no solvent participation.<sup>15</sup>

**Quantum Yields: Recombination.** From the considerations noted in the introduction, the carbon-iodine bond would be expected to undergo photodissociation

(13) Kropp, P. J.; Gibson, J. R.; Snyder, J. J.; Poindexter, G. S. *Tetrahedron Lett.* **1978**, 207-210.

(14) Kropp, P. J.; Pienta, N. J. *J. Org. Chem.* **1983**, *48*, 2084-2090.

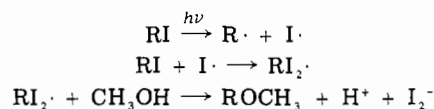
(15) Keating, J. T.; Skell, P. S. *Carbonium Ions* **1970**, *2*, 573.

Table II  
Quantum Yields for Disappearance

iodide	solvent	$\phi$	ref
5	CH <sub>3</sub> OH	0.10	6
	CH <sub>3</sub> OH <sup>a</sup>	0.13	
21	CH <sub>3</sub> OH	0.09	11
38	CH <sub>2</sub> Cl <sub>2</sub>	0.35	14
	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	0.48	

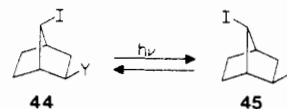
<sup>a</sup> Saturated with oxygen.

Scheme II



with high efficiency.<sup>16</sup> However, the quantum yields for disappearance of iodides 5, 21, and 38 given in Table II are substantially less than 1. The low values are attributable at least in part to recombination within both the radical pair and ion pair cages. Such recombination leads to inefficiency from an energy standpoint but has no effect on the chemical yields since the starting iodide is regenerated.

The occurrence of recombination is manifested not only in reduced quantum yields but also in epimerization of the starting iodide. Thus, for example, irradiation of the syn iodides 44 results in rapid equilibration with the anti epimers 45.<sup>11</sup> At photoequilibrium the



anti:syn ratio is approximately 8:1 for Y = Cl and 3.5:1 for Y = OCH<sub>3</sub>. On extended irradiation products attributable to the 7-norbornyl cation are obtained. The photoepimerization affords a convenient method of preparing the anti epimers from the readily available syn isomers.

### A Comment on Benzylic Halides

A number of benzylic halides have been observed to undergo photosolvolysis.<sup>17</sup> Although in most cases these reactions apparently involve carbocationic intermediates, it is not clear that they arise via initial homolytic cleavage followed by electron transfer as appears to be the case in the alkyl systems described here. Indeed, many important differences in behavior between alkyl and benzylic systems have been observed. Photomethanolysis of at least one benzylic system 1-(iodomethyl)naphthalene, apparently does not involve an ionic intermediate; the alternative mechanism outlined in Scheme II has been proposed in this case.<sup>18</sup>

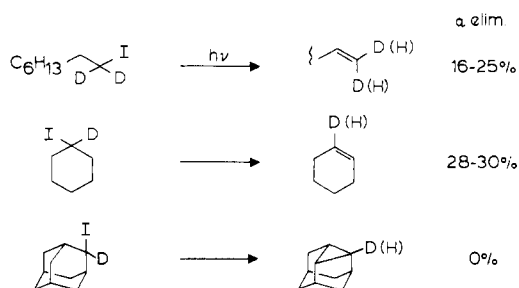
It is important to note that this latter mechanism does not apply to simple alkyl systems. For example,

(16) It has long been assumed that the photodissociation of alkyl iodides occurs with a quantum yield of unity. However, the quantum yield of photodissociation of ethyl iodide in the gas phase has recently been reported to be only 0.31. See: Shepson, P. B.; Heicklen, J. *J. Phys. Chem.* **1981**, *85*, 2691-2694.

(17) Zimmerman, H. E.; Sandel, V. R. *J. Am. Chem. Soc.* **1962**, *85*, 915-922. Ivanov, V. B.; Ivanov, V. L.; Kuz'min, M. G. *J. Org. Chem. USSR (Engl. Transl.)* **1973**, *9*, 345-347. Cristol, S. J.; Greenwald, B. E. *Tetrahedron Lett.* **1976**, 2105-2108. Appleton, D. C.; Brocklehurst, B.; McKenna, J.; McKenna, J. M.; Thackeray, S.; Walley, A. R. *J. Chem. Soc., Perkin Trans. 2* **1980**, 87-90. Cristol, S. J.; Bindel, T. H. *J. Org. Chem.* **1980**, *45*, 951-957; *J. Am. Chem. Soc.* **1981**, *103*, 7287-7293.

(18) Slocum, G. H.; Kaufman, K.; Schuster, G. B. *J. Am. Chem. Soc.* **1981**, *103*, 4625-4627.

Table III  
 $\alpha$  Elimination<sup>a</sup>

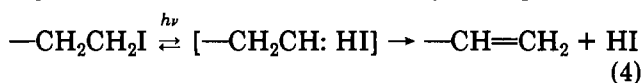


<sup>a</sup> Reference 21. Ranges result from use of various solvents.

the quantum yield for the formation of ether 9 from 1-iodonorbornane (5) is substantially decreased by the presence of oxygen,<sup>6</sup> in agreement with the proposed mechanism of Scheme I but not that of Scheme II. Moreover, the quantum yield for photoconversion of iodide 24 in methanol is independent of concentration, and iodide 24 is inert in a methanolic solution containing I $\cdot$  generated by irradiation of iodine at wavelengths >280 nm.

### Carbene Intermediates

The fact that alkyl iodides have such a striking propensity for undergoing elimination rather than nucleophilic substitution led us to question whether primary and secondary systems did not form unsaturated products via initial  $\alpha$  elimination followed by 1,2 or 1,3 internal insertion of the resulting carbene intermediate (eq 4).<sup>19</sup> Since alkylcarbenes normally undergo internal



insertion more rapidly than intermolecular addition,<sup>20</sup> the absence of nucleophilic substitution products would be readily explained.

The question was easily resolved with deuterium-labeling studies. The answer, somewhat to our surprise, is that at least some, probably most, primary and secondary alkyl iodides do indeed undergo  $\alpha$  elimination (Table III).<sup>21</sup> However, in none of the cases that we examined was  $\alpha$  elimination the principal route to an unsaturated product. In one case studied, that of 2-iodoadamantane (34), the unsaturated product, 35, was obtained without any detectable  $\alpha$  elimination and is apparently formed exclusively via 1,3 deprotonation of the corresponding 2-adamantyl cation.<sup>22</sup>

An interesting example is that of 1-(iodomethyl)-norbornane (13). Irradiation of this iodide in methanol-*d* resulted in partial deuterium incorporation in the

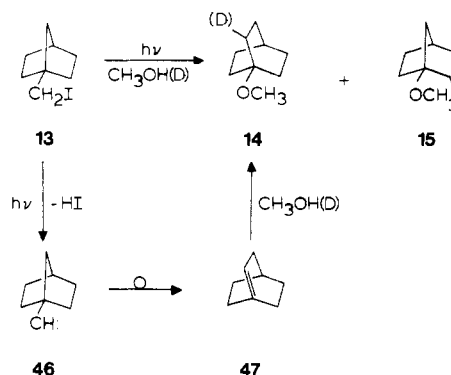
(19) The possibility of  $\alpha$  elimination occurring on irradiation of alkyl iodides in solution had been previously suggested but not established experimentally. See: Rama Rao, K. V. S.; Prasad, D.; Shankar, J. *Ind. J. Chem.* 1973, 11, 1045-1047. The formation of methylene in low yield on irradiation of iodomethane in the gas phase at short wavelengths had been previously observed. See: Chou, C. C.; Angleberger, P.; Rowland, F. S. *J. Phys. Chem.* 1971, 75, 2536-2638.

(20) See: "Carbenes"; Jones, M., Jr., Moss, R. H., Ed.; Wiley: New York, 1973, Vol. 1.

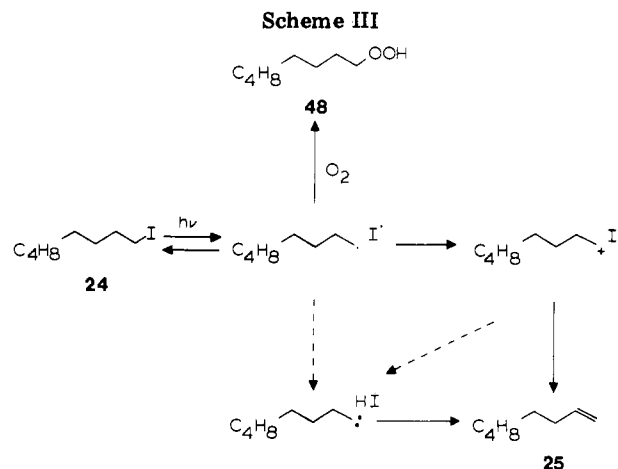
(21) Kropp, P. J.; Sawyer, J. A.; Snyder, J. J. *J. Org. Chem.*, in press.

(22) It is not clear whether  $\alpha$  elimination simply does not occur in this case or whether the corresponding carbene intermediate, adamantylidene, is formed but undergoes addition of HI, regenerating the starting iodide 34. It is known that adamantylidene undergoes 1,3 insertion to the highly strained 2,4-dehydroadamantane (35) sufficiently slowly that intermolecular trapping can compete, a property quite unusual for a dialkylcarbene. See Moss, R. A.; Chang, M. J. *Tetrahedron Lett.* 1981, 22, 3749-3752.

bicyclo[2.2.2]octyl ether 14 but not in the accompanying bicyclo[3.2.1]octyl ether 15.<sup>21</sup> It has been shown previously that the corresponding carbene 46 undergoes ring expansion to 1-bicyclo[2.2.2]octene (47) but not to the bicyclo[3.2.1]octenyl analogue.<sup>23</sup> Thus  $\alpha$  elimination contributes to the formation of photoproduct 14 but not 15 and is in competition with the carbocationic route, which affords both products.



How do the carbene intermediates arise? Apparently not via concerted loss of HI from the alkyl iodide as depicted by path A of Scheme III. Irradiation of 1-iodooctane (24) in methanol saturated with oxygen, followed by reductive workup, results in substantial quenching of the formation of 1-octene (25) with concomitant formation of the hydroperoxide 48.<sup>6</sup> When such an irradiation was repeated with iodide 24 that was labeled at the  $\alpha$  positions with deuterium, the 1-octene (25) that was still formed was generated via  $\alpha$  elimination to the same extent as in the absence of oxygen.<sup>21</sup> This is inconsistent with path A, which should not be affected by the presence of oxygen. Of the remaining paths, B and C, the available data do not permit a distinction.



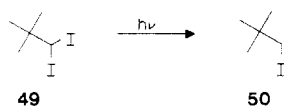
### Geminal Diiodides: Photocyclopropanation

Our attention next turned to geminal diiodides, which exhibit ultraviolet absorption spectra that are much more complex than those of monoiodides and are substantially red-shifted. Do geminal diiodides undergo selective photocleavage of a single carbon-iodine bond, in analogy with the behavior of monoiodides, or simultaneous cleavage of both carbon-iodine bonds to afford a carbene intermediate?

The existing literature reports were enigmatic. Irradiation of diiodide 49 was reported to afford only the

(23) Wolf, A. D.; Jones, M., Jr. *J. Am. Chem. Soc.* 1973, 95, 8209-8210.

reduction product **50**.<sup>24,25</sup> There was no detectable



formation of 1,1-dimethylcyclopropane, which would be the expected product of a carbene intermediate.<sup>26</sup> Similarly, we had found that dibromide **39** affords principally the reduction product **41** and bromo iodide **38** the vinyl bromide **43**.<sup>14</sup> On the other hand, there were several reports that irradiation of either diiodomethane or dibromomethane in the presence of alkenes had been found to afford cyclopropane adducts.<sup>24,27</sup> Although the mechanism of the photocyclopropanation process was not clear, a carbene intermediate could not be excluded. We decided to explore both the scope of the photocyclopropanation process and its mechanism.

**Scope.** Irradiation of diiodomethane was found to effect cyclopropanation of a wide variety of alkenes in high yield.<sup>28,29</sup> Several examples are given in Table IV. In none of the approximately 30 examples we studied was there any detectable competing formation of C-H insertion products. As seen for alkenes **52**–**54**, photocyclopropanation can be effected in the presence of other functional groups. The addition reaction is stereospecific, with *cis*- and *trans*-alkenes affording *cis*- and *trans*-cyclopropanes, respectively.<sup>27a,28</sup> There was some tendency for cyclopropanation to occur *cis* to the hydroxyl group of 3-cyclopentenol (**54**), but the addition did not proceed with the stereospecificity exhibited by the more conventional Simmons–Smith procedure,<sup>30</sup> which involves treatment of diiodomethane with zinc–copper couple.<sup>31</sup>

As seen in Table V, the photocyclopropanation reaction displays progressively increasing rates in going from mono- to tetrasubstituted alkenes. By contrast, the Simmons–Smith procedure shows a decrease in rate on going from 1-methylcyclohexene (**57**) to the tetrasubstituted analogue **58**, which is apparently due to offsetting steric effects in the more highly substituted alkene. The relative lack of sensitivity to steric effects gives the photocyclopropanation reaction a synthetic advantage over the Simmons–Smith procedure in some cases. Thus, for example, the photochemical procedure effects cyclopropanation of the sterically hindered alkene **51** in good yield, whereas the Simmons–Smith method is totally ineffective.<sup>28</sup> Another interesting contrast is seen in the case of limonene (**59**) (Table VI). Photocyclopropanation occurs more rapidly at the more

(24) Neuman, R. C., Jr.; Wolcott, R. G. *Tetrahedron Lett.* 1966, 6267–6272.

(25) For a more detailed study of the photobehavior of diiodide **49** and other diiodides, see ref 14. See also: Moret, E.; Jones, C. R.; Grant, B. *J. Org. Chem.* 1983, 48, 2090–2092.

(26) Friedman, L.; Shechter, H. *J. Am. Chem. Soc.* 1959, 81, 5512–5513. Kirmse, W.; Horn, K. *Chem. Ber.* 1967, 100, 2698–2709.

(27) (a) Blomstrom, D. C.; Herbig, K.; Simmons, H. E. *J. Org. Chem.* 1965, 30, 959–964. (b) Marolewski, T.; Yang, N. C. *J. Chem. Soc., Chem. Commun.* 1967, 1225–1226.

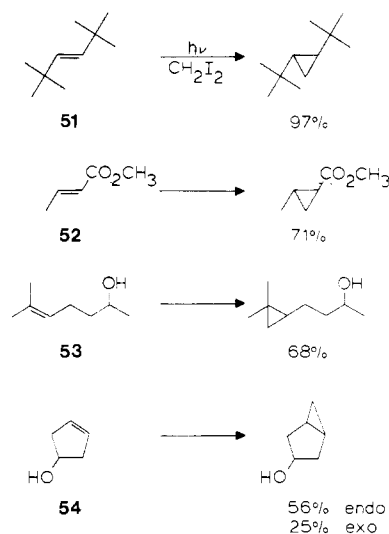
(28) Kropp, P. J.; Pienta, N. J.; Sawyer, J. A.; Polniaszek, R. P. *Tetrahedron* 1981, 37, 3229–3236.

(29) Davis, R. D. Ph.D. Dissertation, University of North Carolina at Chapel Hill, Chapel Hill, NC, 1982.

(30) Winstein, S.; Sonnenberg, J.; de Vries, L. *J. Am. Chem. Soc.* 1959, 81, 6523–6524. Winstein, S.; Sonnenberg, J. *Ibid.* 1961, 83, 3235–3244. Corey, E. J.; Dawson, R. L. *Ibid.* 1963, 85, 1782–1787.

(31) For a review of the Simmons–Smith procedures, see: Simmons, H. E.; Cairns, T. L.; Vladuchick, S. A.; Holness, C. M. *Org. React.* 1973, 20, 1–130.

Table IV  
Photocyclopropanation of Various Alkenes<sup>a</sup>



<sup>a</sup> References 28 and 29.

Table V  
Relative Rates of Cyclopropanation

	55	56	57	58
$\text{CH}_2\text{I}_2, h\nu^a$	0.3	1.0	3.6	8.7
$\text{CH}_2\text{I}_2, \text{Zn}(\text{Cu})^b$	0.1	1.0	2.1	0.9, 0.6 <sup>c</sup>

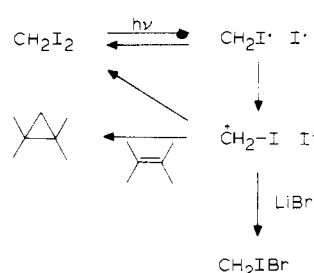
<sup>a</sup> Reference 28. <sup>b</sup> Reference 32. <sup>c</sup> Reference 33.

Table VI  
Cyclopropanation of Limonene (**59**)

$\text{CH}_2\text{I}_2, h\nu^a$	7%	47%
$\text{CH}_2\text{I}_2, \text{Zn}(\text{Cu})^b$	50%	

<sup>a</sup> Reference 28. <sup>b</sup> Reference 31.

Scheme IV

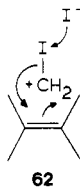


highly substituted cyclohexenyl double bond, whereas in the Simmons–Smith reaction cyclopropanation of the less hindered, but less highly substituted, isopropenyl double bond is preferred. No doubt many other examples will be found in which the two methods are synthetically complementary.

**Mechanism.** Both the lack of C–H insertion products and the high degree of selectivity for addition to

(32) Rickborn, B.; Chan, H.-H. *J. Org. Chem.* 1967, 32, 3576–3580.

(33) Blanchard, E. P.; Simmons, H. E. *J. Am. Chem. Soc.* 1964, 86, 1337–1347.



more highly substituted alkenes argue against involvement of the carbene  $\text{CH}_2$  in the photocyclopropanation reaction.<sup>34</sup> On the other hand, the presence of the usual carbocationic intermediate could be shown by the formation of bromiodomethane when diiodomethane was irradiated in the presence of lithium bromide (Scheme IV).<sup>28</sup> This same intermediate meets all of the requirements for serving as the methylene transfer agent (cf. 62): it would be highly electrophilic, not give C-H insertion products, and not have large steric demands. Thus the initial steps in the photobehavior of geminal dihalides apparently involve selective homolytic cleavage of one of the carbon-halogen bonds followed by electron transfer within the initially formed caged radical pair, in complete analogy with their monohalide analogues. The resulting  $\alpha$ -halo cation has highly interesting behavior.<sup>25</sup>

### Summary

The photobehavior of simple alkyl bromides and iodides in solution is intriguingly more complex than originally appreciated—involving radical, carbocationic, and carbene intermediates. For most iodides ionic behavior predominates and affords a convenient method for the generation of carbocationic intermediates that are not readily available by conventional ground-state procedures—including bridgehead, small-ring cyclic vinyl,  $\alpha$ -unsubstituted vinyl, and 7-norbornyl cations.<sup>35</sup> Bromides exhibit substantially more radical behavior, but in at least some cases cationic behavior

(34) For a review of the reactions of methylene, see ref 20.

(35) By contrast, attempts to generate 1-alkynyl cations by irradiation of the corresponding 1-alkynyl iodides have afforded only radical products. See McNeely, S. A., Ph.D. Dissertation, University of North Carolina at Chapel Hill, Chapel Hill, NC, 1976. Inoue, Y.; Fukunaga, T.; Hakushi, T. *J. Org. Chem.* 1983, 48, 1732-1737.

can be made to predominate by the use of a solvent of high viscosity.

The available data are most consistent with a mechanism involving initial light-induced homolytic cleavage of the carbon-halogen bond followed by electron transfer within the resulting caged radical pair to afford an ion pair (Scheme I). The resulting cationic intermediates display all of the behavior typical of carbocations—undergoing nucleophilic trapping, rearrangement, and deprotonation. Systems capable of readily undergoing elimination afford unsaturated products predominantly over nucleophilic substitution products, as is typical of carbocationic intermediates formed by high-energy processes. In many primary and secondary iodide systems the unsaturated products are also formed via a competing carbene route that appears to involve transfer of an  $\alpha$  hydrogen atom or proton (Scheme III, path B or C) in competition with  $\beta$ -proton transfer.

Irradiation of diiodomethane in the presence of alkenes results in the formation of cyclopropane adducts and is a synthetically useful alternative to the traditional Simmons-Smith procedure, especially for sterically hindered alkenes. This reaction apparently does not involve a carbene pathway but rather methylene transfer by the  $\alpha$ -iodo cation formed by initial homolytic cleavage of one carbon-iodine bond followed by electron transfer (Scheme IV). Similar behavior would probably be exhibited by other geminal dihalides not bearing a  $\beta$ -hydrogen substituent. However, those that do bear such a substituent undergo deprotonation to afford a vinyl halide in competition with methylene transfer.

Many important questions remain—including why electron transfer occurs so readily in these systems and whether it could be extended to other systems. These are the subject of our continuing investigation.

*I thank my colleagues, mentioned in the references, for their enthusiastic and inspiring work. Thanks is also due to the Alfred P. Sloan Foundation, the National Science Foundation, the University of North Carolina Research Council, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for generous financial support.*

## Proton-Transfer Reactions between Carbon and Oxygen

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Received June 10, 1982 (Revised Manuscript Received November 15, 1983)

Proton transfer from one atom to another is a fundamental reaction in chemistry. Brønsted, in his pioneering studies, used the proton-transfer process to

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classify an acid as a species having a tendency to lose a proton and a base as a species having a tendency to add a proton.<sup>1</sup> Bell's classic book "The Proton in Chemistry", was originally based on the Baker Lectures presented at Cornell University in 1958; however, in 1972 he prepared a second edition since:<sup>2</sup> "The subject as a whole has expanded greatly since 1959, especially in two fields, namely, the direct study of fast proton-

(1) Brønsted, J. N. *Recl. Trav. Chim. Pays-Bas* 1923, 42, 718-728.

(2) Bell, R. P. "The Proton in Chemistry"; Cornell University Press: Ithaca, NY, 1973.