

Photochemistry of the carbon-halogen bond: some recent developments

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Abstract. The current status on the photochemistry of the carbon-halogen bond, incorporated in a wide variety of organic compounds, is presented. It mainly deals with the photolytic cleavage of the C-X bond in solution phase. The major development in this field has been the generation of saturated, vinyl and α -keto carbonium ions by photochemical methods. The factors that control the type of cleavage, viz, homolytic-heterolytic are discussed. The mechanistic aspects as well as the synthetic utility of the photoreactions of some organic halides are highlighted.

Keywords. Photoirradiation; homolytic cleavage; heterolytic cleavage; excited states; electron transfer.

1. Introduction

The photochemistry of organic halides has received extensive attention and quite a few review articles appeared on this topic during the period 1954-1973 (Stearie 1954; Major and Simmons 1964; Walling and Huyser 1963; Sammes 1973). In these studies, the common theme was the formation of radical products resulting from the homolytic cleavage of the carbon-halogen bond. However, in the mid-seventies, several research groups independently re-examined the photochemistry of various types of organic halides and it became evident that another competing primary photoprocess is the heterolytic cleavage of the carbon-halogen bond resulting in carbocation intermediates. This discovery not only helped to rationalize some of the seemingly anomalous previous results but also led to some novel synthetic applications. The aim of the present article is to highlight the recent developments in this field chiefly since 1975.

2. Alkyl halides

A major recent development in the photochemistry of alkyl halides is the demonstration for the first time of competing ionic and radical photobehaviour for a number of alkyl halides (Kropp *et al* 1976). These authors have shown that irradiation of alkyl bromides, and particularly iodides in solution is a convenient and powerful means for the generation of carbocations, especially of high energy. The synthetic utility of this method was shown by the generation of 1-bicyclo(2:2:1)heptyl cation which is not readily accessible by the conventional methods. Irradiation of

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1-iodobicyclo(2·2·1)heptane 1 in methanol afforded principally the ether 3 ($Y = \text{OCH}_3$, 76%), accompanied by a small amount of the radical product, viz, bicyclo(2·2·1)heptane 2 (12%). Similar type of photobehaviour was also observed in the case of 1- and 2-adamantyl iodides 4 and 5 which furnished essentially solvolysis products 7 (95%) and 8 (91%) respectively alongwith a trace of the reduction product 6.

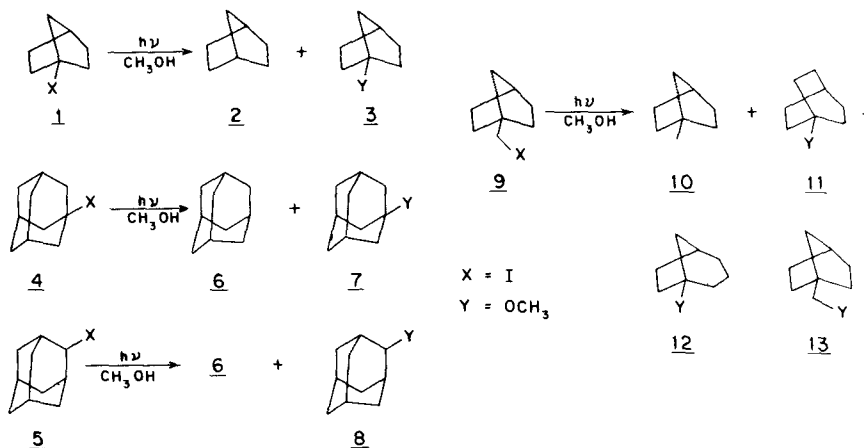
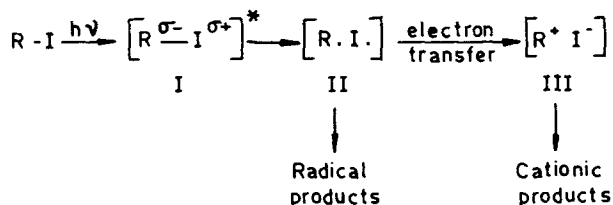


Chart 1.

Irradiation of iodide 9 in methanol, however, resulted in a mixture of the rearranged bicyclo(2·2·2) and bicyclo(3·2·1)octyl ethers 11 ($Y = \text{OCH}_3$, 37%) and 12 ($Y = \text{OCH}_3$, 47%). Significantly, the unrearranged ether 13 was found to be almost absent. Another interesting feature is that the iodide 9 displayed essentially an ionic photobehaviour as evidenced by the formation of the reduction product 10 only in trace amounts. This proclivity for rearrangement in the case of 9 has been ascribed to the involvement of 'free cations' (Keating and Skell 1970) generated by high energy processes with little or no solvent participation. The corresponding bromoanalogues displayed similar photobehaviour, although the radical products were preponderant.

The mechanism suggested by Kropp *et al* (1976) for the formation of cationic products is illustrated in scheme 1 for the alkyl iodide. It involves the photolytic generation of the radical pair II which can undergo an electron transfer to afford an ion pair III and ultimately the carbocationic products.

An essentially ionic photobehaviour has been observed for longibornyl iodide 14 and citronellyl iodide 18 (Gokhale *et al* 1976). The iodide 14 on irradiation in heptane



Scheme 1.

furnished the rearranged hydrocarbons 15 (40%), 16 (44%) and 17 (14%). The iodide 18 under similar conditions, furnished the simple elimination product 19 (52%) and yielded 20 (*cis* & *trans*, 42%) with π -participation alongwith minor amounts of 21 (6.0%). The formation of 16 is supposed to involve, 1,3-elimination while a transannular shift is considered to be responsible for the generation of 17. An ionic pathway has been preferred to rationalize the photoproducts as the radical derived products were found to be almost absent.

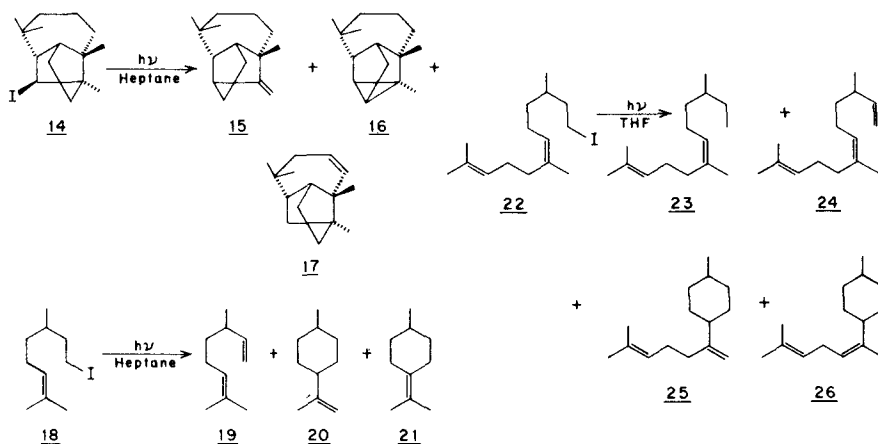


Chart 2.

Recently Saplay *et al* (1980) have extended their studies to systems of possible biomimetic interest and reported the formation of products arising from π -participation. These authors observed that photoirradiation of 2,3-dihydro-6(*Z*)-farnesyl iodide 22 in THF furnished 23 (5%), 24 (22%), 25 (40%) and 26 (21%) and three other minor unidentified products (12%). Similar irradiation of the corresponding *E*-isomer 27 afforded 28 (6%), 29 (35%), 25 (37%), 26 (18%) and two minor unidentified products (4%). The formation of these products has been rationalised using the concept of electron transfer.

Carbonium ions generated in a photolytic pathway appear to react differently from those formed in normal thermal reactions. For example, the primary 'free' cation generated by the photolysis of iodide 30 (Takaishi *et al* 1978) showed a preference for rearrangement yielding 31 while the same cation formed by the treatment of alcohol 32 with sulphuric acid afforded the hydrocarbon 33 by hydride abstraction.

A novel photobehaviour of isomeric chlorides present in the (2.2.1) and (2.2.2) bicyclic systems has been reported recently (Morrison and Miller 1980). Photolysis of a methanolic solution of *exo*-2-benzonorbornenyl chloride 34 with 254 nm light led to the cleavage of the C-Cl bond and furnished the products 35 (ϕ 0.12), 36 (ϕ 0.08), 37 (ϕ 0.03) arising from radical intermediates and the products 38 (ϕ 0.07), 39 (ϕ 0.13) and 40 (ϕ 0.03) involving the ionic intermediates. The formation of 40 is unique since it involves the hitherto unobserved 1,2-migration of the C₁-C₇ bridge in the 2-benzonorbornenyl cation. The generation of 'hot' carbocation by the aryl-initiated cleavage of the C-Cl bond has been suggested as being responsible for this rearrangement. The

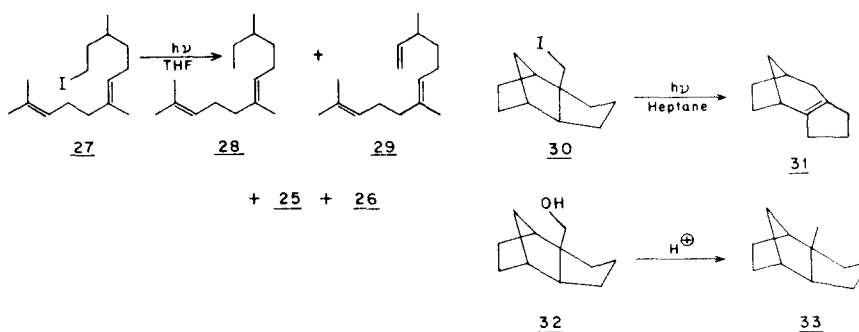


Chart 3.

corresponding *endo*-chloride, however, was found to be less (≈ 20 times) reactive than the *exo*-isomer 34. These products were shown to arise from the singlet excited state. The photolysis of isomeric chlorides in the bicyclo-(2:2:2)-octane system revealed an entirely opposite pattern of reactivity compared with that of the bicyclo-(2:2:1)-heptane system. For example, *endo*-2-chlorobenzo-bicyclo-(2:2:2)-*octa*-5-ene 41 was found to be more reactive (~ 5 times) than its *exo*-isomer 47 and on photolysis in methanol afforded the ionic products 43 (5%), 44 (37%), 45 (11%) and 46 (6%) together with some radical derived product 42 (22%). The rearranged ether 46 and the cyclopropane product 43 are supposed to have originated from a 'hot' carbocation. The product mixture from the photolysis of the *exo*-chloride 47 was less complex and comprised essentially the ionic products 44-46.

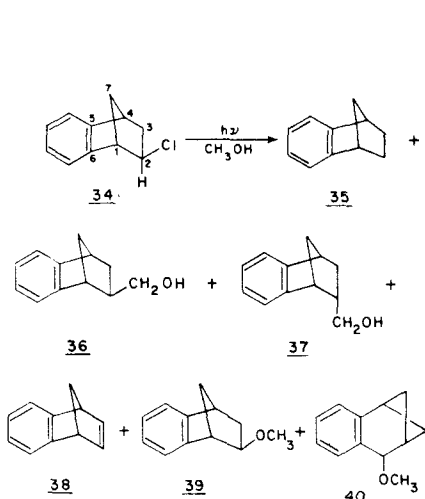


Chart 4.

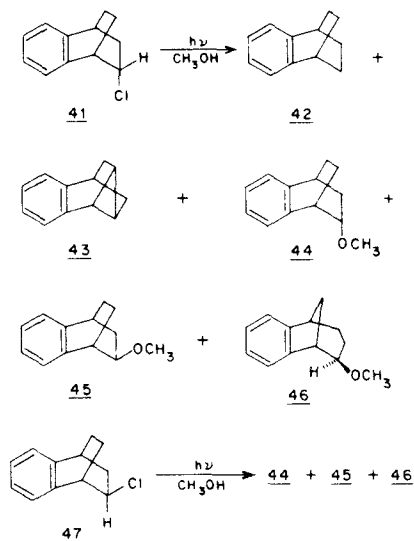


Chart 5.

The photochemistry of 4-phenyl-1-iodobutane 48 and 4-phenyl-2-iodomethyl-1-butane 50 has been studied (Charlton *et al* 1980). The irradiation of primary iodide 48 in acetonitrile furnished the olefin 49 as the only product, which was considered to be

radical-derived as its yield was reduced when the irradiation was carried out in presence of oxygen. The iodide 50 under similar conditions of irradiation afforded the cationic products 51 (37%) and 52 (28%). Another study of the photochemistry of 48 in alcoholic solvents resulted mostly in ionic products comprising 49 (60%), 53 (23%) and 54 (7%). Similar irradiation of 56 offered the ionic product 57 exclusively, suggesting the possible involvement of the phenonium ion (Bhale Rao 1978).

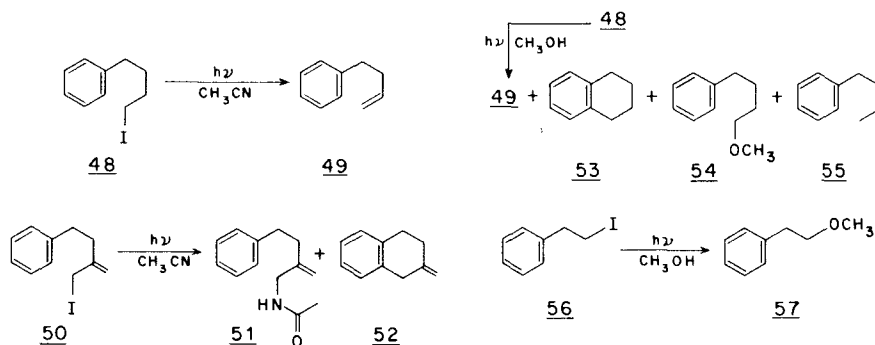


Chart 6.

The photochemistry of a number of ω -(4-halo phenoxy)-alkyl bromides 58 a, b have been studied in methanol (Davidson and Goodin 1980). These authors observed a selective cleavage of stronger aryl-halogen bonds (Ph-Cl = 94.5 kcal/mole, Ph-Br = 79.2 kcal/mole) rather than alkyl-bromine bonds (CH₃CH₂-Br = 60 kcal/mole) to give 59 in all cases except for 58b with $n = 2$. The absence of the reaction of the alkyl-bromine bond has been attributed to the inefficient energy transfer from the aryloxy group to the CH₂-Br bond.

It has been shown that intramolecular sensitized homolysis of alkyl-bromine bonds can occur efficiently in 60 with $n = 2$ and 3 only as these were found to be far more

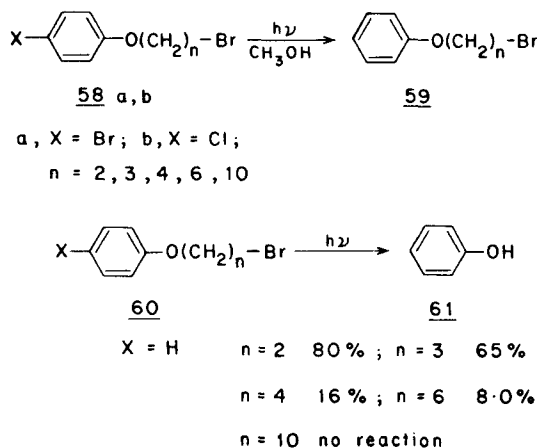


Chart 7.













reactive in giving the phenol 61 than the corresponding higher homologues. In the above cases, aryl-halogen bond cleavage was shown to involve the first excited singlet state. Similar observations have been reported in the photochemistry of alkyl bromides and iodides incorporated in naphthyl ethers (Kessar *et al* 1980).

The photochemistry of diiodomethane has been elegantly utilized for the cyclopropanation of various types of olefins (Kropp *et al* 1981). This photolytic method appears to be significantly less subject to steric effects than the traditional Simmons-Smith method (Simmons *et al* 1973). The α -iodo cation, viz, ICH_2^+ is suggested as the methylene transfer species in the cyclopropanation. Representative examples of photocyclopropanation of a few alkenes are presented in scheme 2.

The photochemistry of some bridgehead iodides has been described recently (Kropp *et al* 1982). The iodides 62, 63 and 64 on irradiation in methanol afforded principally the ionic products 68 (90%), 69 (91%) and 70 (81%) accompanied by small amounts of reduction products 65 (2%), 66 (4%), and 67 (15%) respectively. It has been demonstrated that the ionic products 68–70 originate from the bridgehead carbocations and not by the protonation of bridgehead alkenes. By contrast, deuterium labelling studies revealed the intermediacy of the bridgehead alkene in the genesis of the ionic product 76 in the photolysis of 71 in methanol.

3. Allylic and benzylic halides

Cristol *et al* (1978) have reported the photochemistry of allylic halides incorporated in the dibenzobicyclic nonatriene and benzoctadienyl systems. The halide 79 on irradiation at 254 nm in aqueous CH_3CN was transformed into a mixture of 80, 81, 82 and 83. These products are considered to arise from photo-Wagner-Meerwein rearrangement and photochemical Ritter reaction. Irradiation of 79 in different solvents showed that the quantum efficiency decreased with the lowering of solvent polarity and the product composition also depended on the solvent polarity. Quenching experiments revealed that photosolvolytic products arise from the singlet

Alkene	Cyclopropane	Yield* (%)	Alkene	Cyclopropane	Yield* (%)
		68 (33)			76 (16)
		60 (47)			83 (42)
		75 (36)			30 (0)

* Numbers in parentheses are yields of Simmons - Smith method

Scheme 2.

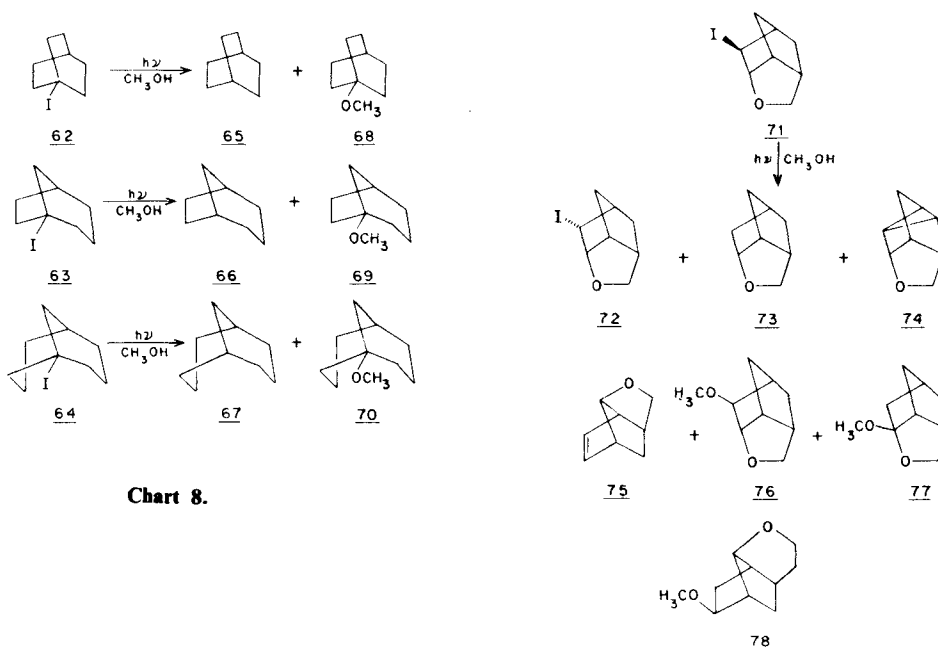


Chart 8.

Chart 9.

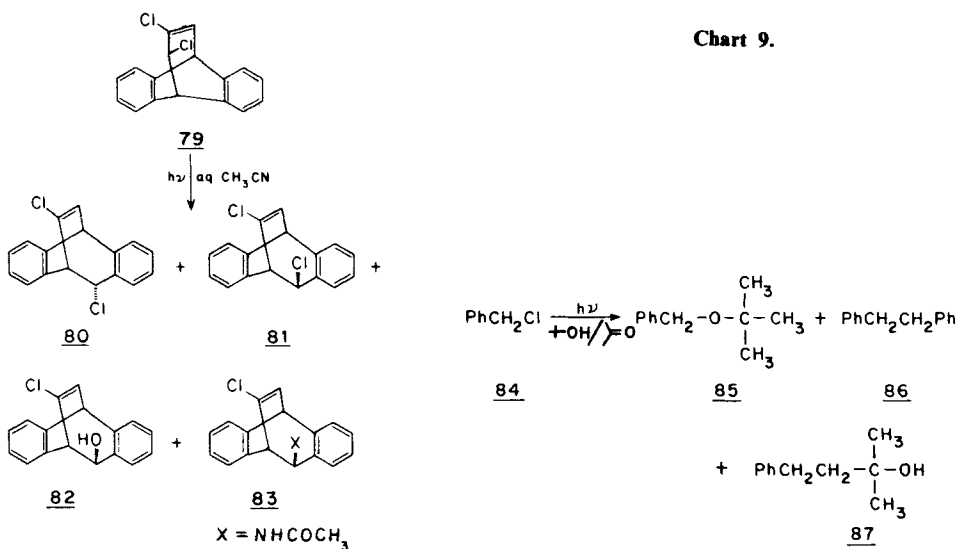


Chart 10.

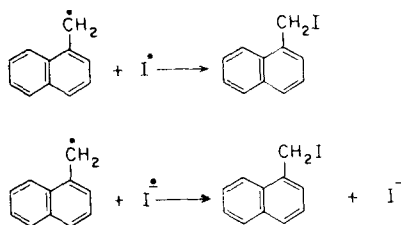
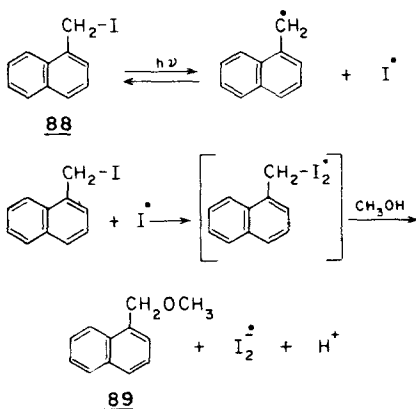
excited state. An analogous type of photobehaviour has been displayed by the halides derived from benzooctadienyl systems.

Recently, several research groups have studied the photochemistry of benzyl halides under a variety of conditions. Most of the work deals with the effects of direct irradiation, photosensitization and solvent variation upon quantum yields of photo-induced heterolysis and homolysis of the carbon-halogen bond. Appleton *et al* (1980) have examined the photochemistry of benzyl halides in methanol and *t*-butyl alcohol.

They report that the ionic products and the products derived from non-ionic mechanisms are formed in either direct or sensitized photolysis. The significant feature of the mechanism proposed by them is the interconversion of loose singlet and triplet radical pairs and electron transfer in the singlet pair to give a solvent separated ion pair.

A detailed investigation of the photochemistry of benzyl chloride **84** and a number of its *m*- and *p*-substituted derivatives in *t*-butyl alcohol has been carried out (Cristol and Bindel 1980). Both the types of products, viz, photosolvolysis product benzyl *t*-butyl ether **85** and photohomolysis products bibenzyl **86** and 4-phenyl-2-methyl-2-butanol **87** were observed in both direct and photosensitized irradiations. Furthermore, these authors have reported that bond heterolysis is favoured in sensitized conditions while direct irradiation favours homolytic cleavage. Cristol and Bindel (1981) in their study of the photochemistry of a number of substituted benzyl chlorides, have employed a variety of sensitization and quenching techniques. The results obtained are rationalized by the assumption that there are two triplet states of benzyl chlorides—one, a short-lived upper state which leads to solvolysis products and another, a long-lived lower energy state.

An altogether different mechanism has been proposed for the formation of the ether **89** in the photolysis of iodomethylnaphthalene **88** in methanol (Slocum *et al* 1981). The product generating step has been shown to involve a complex between the iodine atom and the starting halide. The complex thus formed, would rapidly dissociate into separate ions or react directly with the solvent (scheme 3).



4. Vinyl halides

The photochemistry of vinyl halides has received relatively less attention although these compounds could be potential sources of vinyl radicals and vinyl cations depending upon the mode of cleavage of the carbon-halogen bond. It must be pointed out that in most of the cases reported so far, photoreduction of the vinyl radicals occurs almost exclusively (Stecie 1954; Major and Simmons 1964; Walling and Huysen 1963; Sammes 1973). Vinyl cation intermediates have been reported only in a very few recent investigations.

The photoinduced homolytic cleavage of the carbon-halogen bond has been utilized in the synthesis of deuterated olefins from the corresponding vinyl halides (Muller *et al* 1976). For example, irradiation of **90** for 2.5 hours in deuterated methanol gave the deuterated olefin **91** (60%). The high stereospecificity observed in this case is somewhat surprising especially with the involvement of vinyl radical intermediates. Irradiation of **92** under similar conditions gave **93** in a high yield (94%).

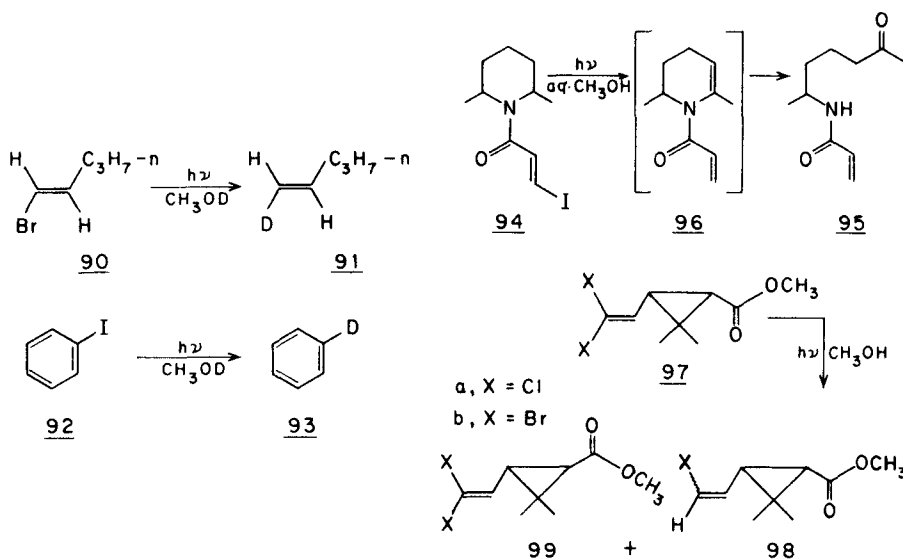


Chart 12.

A new method of remote functionalization involving the photoinduced cleavage of the carbon-halogen bond has been attempted in the case of various β -iodoacrylamides (Wilson and Commons 1975). For instance, irradiation of **94** in aq. methanol gave the keto-amide **95** (77%) with a newly functionalized carbon. The probable mechanism suggested by the authors involves the abstraction of a hydrogen atom β - to the amide nitrogen by the vinyl radical leading to the enamide intermediate **96** which can rapidly hydrolyze to the final product.

The modern synthetic pyrethroids containing the haloethylenic moiety are known to possess enhanced insecticidal potency with higher photostability (Elliot and James 1978). The photoprocesses of this class of compounds include reductive dehalogenation and *cis-trans* isomerization at the cyclopropane ring. The compounds **97a, b** on irradiation in methanol at 254 nm resulted mainly (Ruzo and Casida 1979) in **98a, b** (*a*, 92%; *b*, 58%) and **99a, b** (*a, b*: 8% each). Sensitization and quenching studies showed that the triplet excited state was responsible for the isomerization at the cyclopropane ring.

There are some recent reports which show that photolysis of certain vinyl halides is a particularly facile route to the corresponding vinyl cations. Suzuki *et al* (1976) have observed a novel photoinduced 1,2-anisyl migrations leading to the corresponding tolanes **101a-c** (*a*, 53%; *b*, 86%; *c*, 50%) in the irradiation of 2,2-dianisyl vinyl bromides **100a-c** in benzene. By contrast, photolysis of **100d** in benzene did not afford the corresponding tolanes but gave a mixture of 9-phenylphenanthrene **102** (40%) and 1,1-

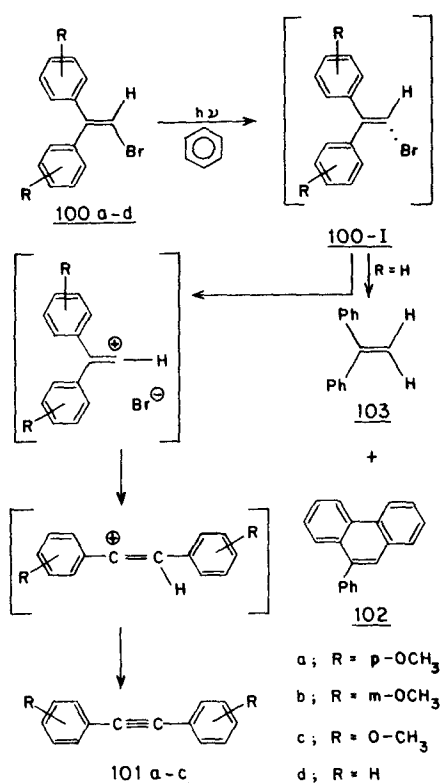


Chart 13.

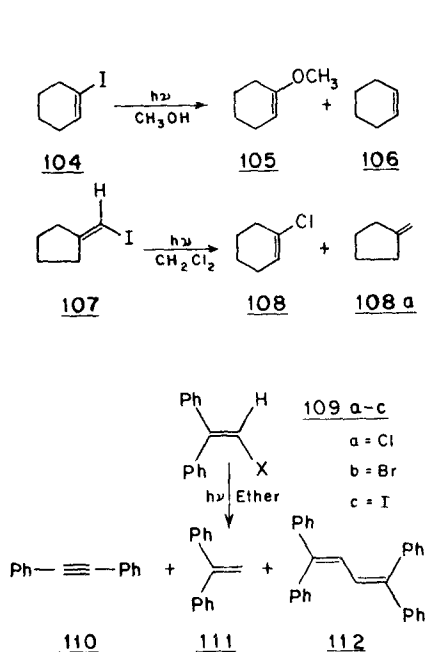


Chart 14.

diphenyl ethylene **103** (13%) as a result of radical reactions via the radical pair **100-I**.

Simultaneously, McNeely and Kropp (1976) have observed that cycloalkenyl halides as well as halomethylene cycloalkanes on photoirradiation result in vinyl-cation derived products together with radical products. Irradiation of **104** in methanol furnished the ionic product **105** (65%) accompanied by the reduction product **106** (25%). Similar ionic behaviour was exhibited by **107** which gave the ring-expanded product **108** (23%) alongwith the radical product **108a** (50%). As mentioned earlier in the case of alkyl halides, these reactions have also been interpreted to involve electron transfer within the initially generated radical pair affording vinyl cations.

Recently, 1,1-diphenyl-2-haloethenes **109 a-c** have been subjected to a detailed photochemical study in different solvents (Sket and Zupon 1979). Competing ionic and radical behaviour has been observed for these vinyl halides. Free radical intermediates were supposed to be involved in the formation of **111** (a, 28%; b, 34%; c, 51%) and **112** (a, 10%; b, 10%; c, 6%) while **110** (a, 25%; b, 23%; c, 19%) was ascribed to an ionic intermediate. The products were rationalized using the mechanism of electron transfer.

An example of nucleophilic trapping of a photolytically generated vinyl cation is provided by Kitamura *et al* (1979). These authors irradiated the vinyl bromide **113** in acetone in presence of tetrabutylammonium azide and obtained the oxazoline **116** (90%) as the final product. The vinyl cation was trapped by the azide ion and the

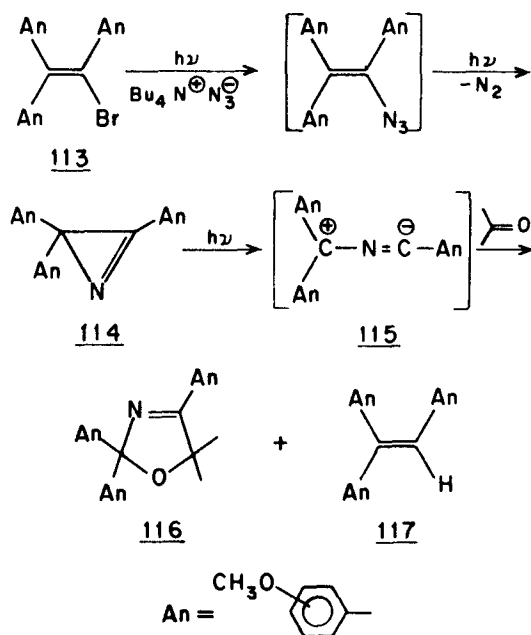


Chart 15.

resulting vinyl azide gave the azirine **114** by loss of nitrogen. On further photolysis, **114** gave the product **116** via the nitrile **115** by a cycloaddition reaction with acetone. The reduction product **117** was obtained in a poor yield (5%).

Direct evidence for vinyl cation intermediates in the case of vinyl halides has been obtained by ^{13}C NMR (Siehl *et al* 1974) as well as flash photolysis studies (Kitamura *et al* 1980). In the ^{13}C NMR spectrum of 1,1-dimethyl-2-(*p*-anisyl)-2-fluoroethylene when recorded in the presence of SbF_5 , the observed downfield shift (30 ppm) of the signal of the carbon carrying methoxyl group was considered as evidence for the vinyl cation at C_2 (Siehl *et al* 1974).

The photolysis of β,β -bis(*o*-methoxyphenyl)-substituted vinyl bromides **118** ($R = \text{H}, \text{CH}_3, \text{Ph}$) in benzene has been reported to give essentially the benzofurans **119** and **120** (Suzuki *et al* 1981). With α -aryl substituted systems, the benzofuran is derived essentially from the unrearranged vinyl cation **118I** but when the α -substituent is methyl or hydrogen, benzofuran from the rearranged vinyl cation **118II** is also formed. With the α -methyl substituent, the allene **121** (20%) was also observed.

A systematic investigation carried out on the photochemistry of vinyl halides derived from camphene revealed the occurrence of competing radical and ionic photoprocesses (Sonawane *et al* 1984a). The unsubstituted vinyl halides **122** and **123** on direct irradiation in methanol furnished exclusively the radical-derived product **124**, while the halides **125** and **126** on similar irradiation afforded both the radical products, viz, *E/Z* isomers of ω -methyl camphene **127** (65%) and the ionic product **128** (35%). Similarly, ω -phenyl substituted halide **129** on direct irradiation resulted in the radical and ionic products **130** (24%) and **131** (76%) respectively. However, these vinyl halides when irradiated in nonpolar solvents such as cyclohexane and methylene chloride gave exclusively the radical-derived products. These results suggest that the competing

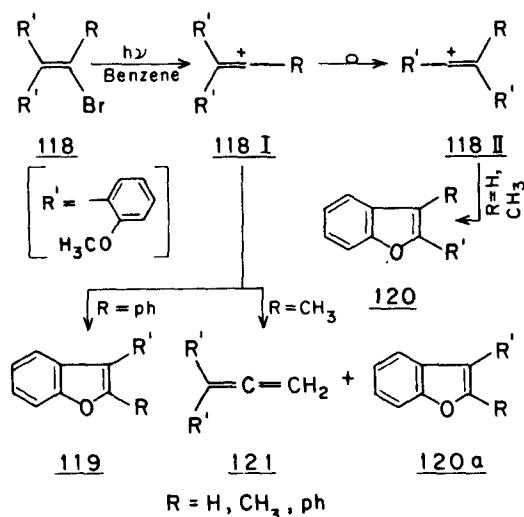


Chart 16.

radical and ionic photobehaviour of these vinyl halides is governed mainly by two factors, namely: (1) the nature of the α -stabilizing substituent, and (2) the polarity of the medium. The sensitization and quenching studies carried out with these substrates clearly established for the first time that the triplet excited state is responsible for the radical products while the ionic products are derived from the singlet excited state.

The results obtained from the irradiation of cyclohexenyl halides 132–135 are noteworthy (Sonawane *et al* 1984b). It is significant to note that these halides on irradiation in methanol yielded only the radical-derived reduction products 136 and 137, thereby confirming the earlier findings (Sonawane *et al* 1984a). In the light of these

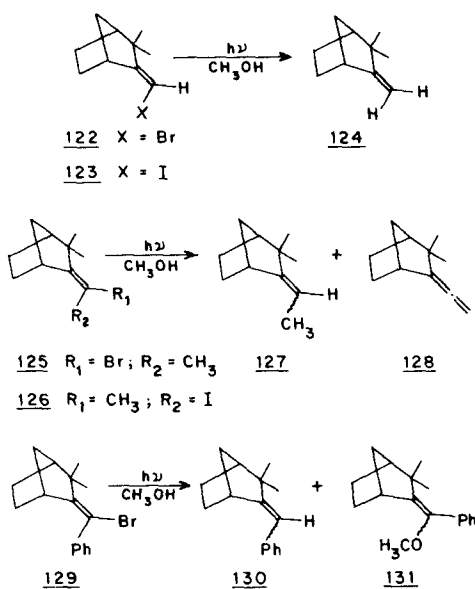


Chart 17.

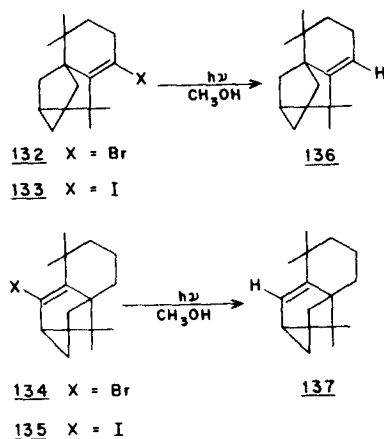


Chart 18.

results, the facile generation of vinyl cations in the photolysis of cycloalkenyl halides lacking α -stabilizing substituents (McNeely and Kropp 1976) appears somewhat surprising. It remains for future workers to rationalize these intriguing differences.

5. α -Halo ketones

The effect of the carbonyl moiety on the photochemistry of the carbon-halogen bond has been the subject of some recent studies. In this section, a few selected examples of the photobehaviour of this class of compounds are presented. Photolysis of 9- ω -bromo-acetylanthracene **138** (Matsumoto *et al* 1974) in cyclohexane led to the discovery of two photochemical reactions of this class of compounds. The main photoproducts were 1-acanthrone **140** and 9-bromo-anthracene **141**. The intermediate **139** detected spectroscopically is supposed to give **140** either by thermal or photochemical process with loss of HBr. The product **141** is suggested to arise from a concerted process involving loss of ketene.

A similar type of photocyclization giving indane-1-one **143** (62%) occurred (Bergmark 1978) especially in the case of α -chloro-*o*-methyl-acetophenone **142** but not its bromoanalogue which gave only the reduction product **144**. The cyclization product is supposed to involve photoenolization while **144** seems to be derived from the α -keto radical formed in the homolysis of the C-X bond. The fluorine substitution α - to the carbonyl group as in **145** is found to cause a dramatic effect with the exclusive formation of **146** providing a unique method for the synthesis of fluorinated cyclobutanols (Wagner and Thomas 1976). The alteration in the Norrish-II product ratio caused by α -fluorine substitution is considered to be due to hyperconjugative stabilization of the 1,4-diradical. However, fluorine substitution at the γ -position did not influence the product ratio.

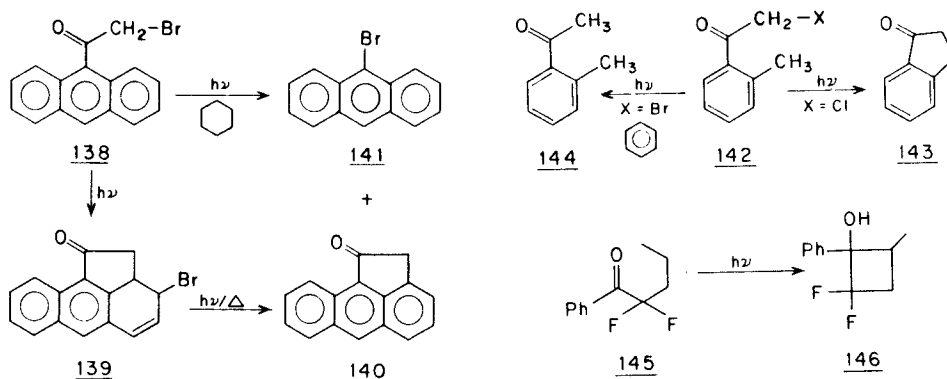


Chart 19.

Direct photolysis of 2-chlorocyclobutanone **147** has been well studied (Metcalf and Lee 1973) at different wavelengths (254–325 nm) and the primary photoproducts arising from ring cleavage and decarbonylation processes have been identified. A Favorskii type ring contraction has been observed in the photolysis of bicyclic chloroketones **148** and **149** in methanol furnishing **150 a, b** alongwith **151 a, b** (Jones

and McDonnell 1976). For the formation of cyclopropyl esters 150 a, b a mechanism involving photoionization of the C-Cl bond followed by ring contraction to acylium ions which got trapped by solvent molecules is suggested. The lack of diene quenching of cycloelimination or of ring contraction-solvent capture suggests that the products are singlet derived. Another example of the above rearrangement is the conversion of

Chart-20 (147-154)

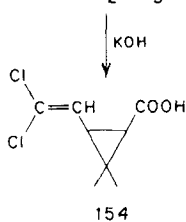
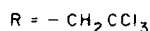
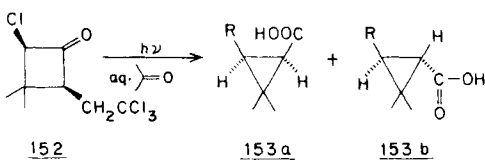
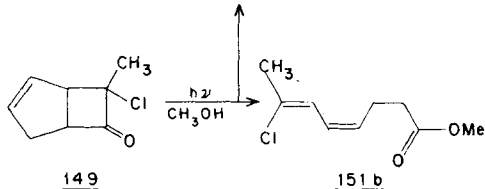
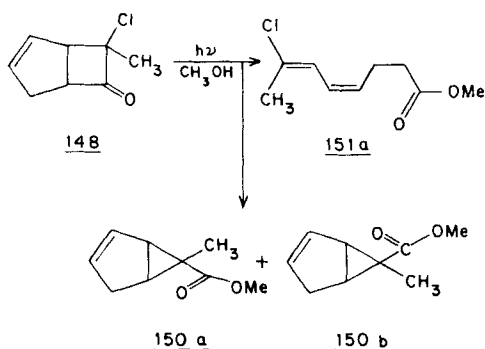
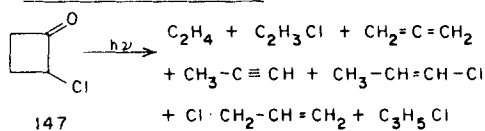


Chart 20.

Chart-21 (155-165)

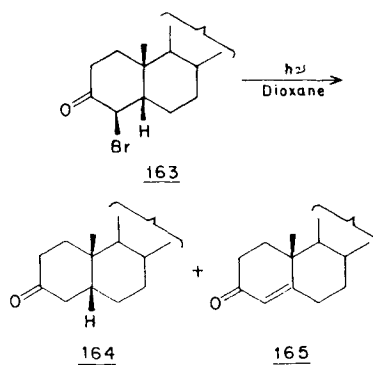
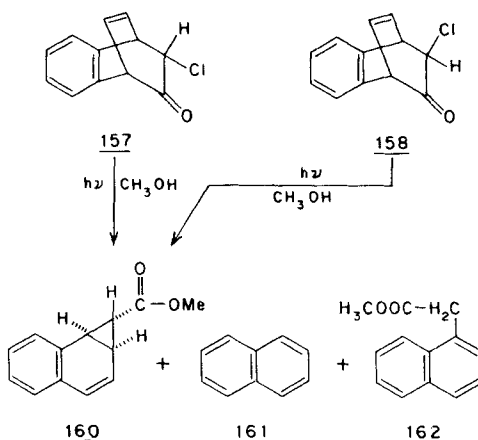
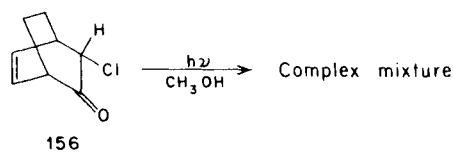
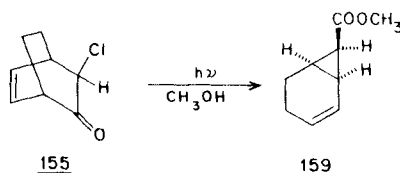


Chart 21.

152 into the intermediates 153 *a, b* (98 %, 1 : 2 of *a* and *b*) which on treatment with alkali furnish the acid 154, a highly useful compound in the synthesis of pyrethroids (Martin *et al* 1979).

The photochemistry of β, γ -unsaturated α -chloroketones 155–158 has been investigated by Givens and Streckowski (1975). The exo-chloroketone 155 furnished 159 (55%) while the irradiation of the endo-isomer 156 under similar conditions gave a complex product mixture. Photolysis of the endo- and exo-chloroketones 157 and 158 resulted in the same products 160–162 in different proportions (exo- 160, 60%; 161, 10%; 162, 30%; endo- 160, 34%; 161, 10%; 162 26%).

The photolysis of the steroidal α -bromoketone 163 in dioxane led to the radical and ionic products 164 and 165, respectively, in a 1 : 1 proportion (Huppi *et al* 1966).

A systematic study of the photochemistry of some α -halocycloalkanones 166 *a–d* carried out recently (Purohit and Sonawane 1981) revealed the occurrence of competing radical and ionic photobehaviour. Sensitization and quenching studies indicated that the radical products (167 *a–d* (*a*, 28%; *b*, 16%; *c*, 90%; *d*, 70%)) arise from the $n\pi^*$ triplet states whereas the ionic products 168 *a–d* (*a*, 13%; *b*, 26%; *c*, 10%; *d*, 30%) originate from the $n\pi^*$ singlet excited states, thus providing, for the first time, experimental support to the Wagner model (Wagner 1976) for the cleavage of the C–X bond in α -haloketones.

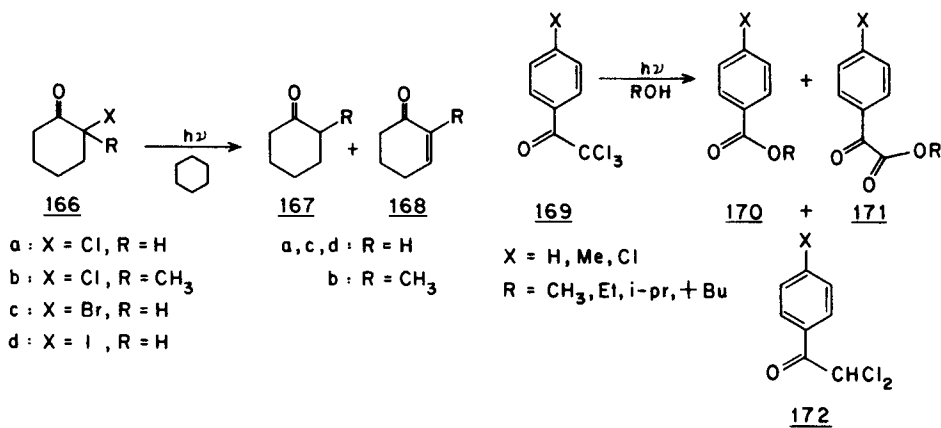


Chart 22.

Izawa *et al* (1980) have obtained the products 170 (23%), 171 (5%) and 172 (60%) from the photoinduced alcoholysis of substituted α, α, α -trichloroacetophenones 169. It is interesting to note that sensitization and quenching studies revealed that 170 and 171 arise from two different triplet excited states.

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