

**PHOTOCHEMISTRY OF α -HALOCYCLOALKANONES AND
 α,α -DIHALOCYCLOALKANONES. IONIC AND RADICAL
PHOTOCHEMICAL CARBON-HALOGEN BOND CLEAVAGE**

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The nature of the photochemical carbon-halogen bond cleavage in α -halo cycloalkanones depends on the halogen atom bonded and on the ring size of the cycloalkanone. In the 2-halo-1-indanone series the amount of radical products increased from iodine to chlorine, while in the case of 2-halo-3,4-dihydro-1(2*H*)-naphthalenone 43% for iodo, 32% for bromo, and 53% for the chloro derivative were found. On the other hand, photochemical carbon-chlorine bond cleavage in 2,2-dichloro-1-indanone led to only radical products, while the formation of both radical and ionic products in the ratio 1 : 1 was observed in the case of 2,2-dibromo-1-indanone. In the 2,2-dihalo-3,4-dihydro-1(2*H*)-naphthalenone series, the ratio of the radical to ionic products formed strongly depended on the halogen atom bonded: preferential formation of the radical product in the case of the chloro derivative (92%), in contrast to 94% of the ionic products in the case of the bromo derivative, was observed.

The phototransformation of ketones substituted with heteroatoms on the α -carbon atom, such as α -halo^{1,2}, α -tosyloxy³, α -mesyloxy⁴, α -acetoxy⁵, and α -alkoxy⁶ derivatives results in a photoreduced loss of these substituents. Each of these substituents has an influence on the $n-\pi^*$ transition of the carbonyl⁷, thus controlling the chemistry of the excited states.

The photochemistry of α -halo cycloalkanones includes different types of photo-processes, such as α -cleavage⁸, photoelimination^{1,2}, hydrogen abstraction by α -keto radicals^{1,2,9}, and rearrangement¹⁰, which seem to depend upon the nature of α -halogen atom, the ring size of the ketone and the presence of other functional groups.

EXPERIMENTAL

Irradiation was carried out in a Rayonet Photochemical Reactor Model RPR-100, with eight 254 nm lamps. IR spectra (KBr disc) were recorded using a Perkin-Elmer 257 spectrometer. ¹H NMR spectra were determined by a Jeol JNM-PS-100 and Varian EM 360 L in CCl₄ or CDCl₃ solution with tetramethylsilane as an internal standard. Mass spectra were performed on a CEC 21-110 spectrometer. Gas-liquid chromatography was carried out on a Varian-Aerograph, Model 3 700: column length 1.5 m; 10% OV — Chromosorb AW at 180 or 190°C (unless

stated otherwise), with He as a carrier gas, flow rate 30 ml/min. Preparative TLC were run on Merck-PSC-Fertigplatten, Kieselgel F 254, with benzene as eluent. Melting points were determined on a Kofler apparatus and are uncorrected.

2-Chloro-1-indanone¹¹, 2-bromo-1-indanone¹², 2-chloro-3,4-dihydro-1(2*H*)-naphthalenone¹¹, 2-bromo-3,4-dihydro-1(2*H*)-naphthalenone¹², 2,2-dichloro-1-indanone¹³, 2,2-dibromo-1-indanone¹⁴, 2,2-dichloro-3,4-dihydro-1(2*H*)-naphthalenone¹⁵, 2,2-dibromo-3,4-dihydro-1(2*H*)-naphthalenone¹⁶, 3-bromo-1-indanone^{17,18}, *trans* 2,3-dibromo-1-indanone¹⁸, 2-indene-1-one¹⁷, 2-bromo-2-indene-1-one¹⁹, 2-chloro-1-naphthol¹⁵, and 2-bromo-1-naphthol²⁰ were prepared by published methods. 2-Iodo-1-indanone and 2-iodo-3,4-dihydro-1(2*H*)-naphthalenone⁹ were prepared by iodination of 1-indanone and 3,4-dihydro-1(2*H*)-naphthalenone in acetic acid using copolymer (styrene — 4-vinyl(pyridinium dichloroiodate(I))).

General Irradiation Procedure

Cyclohexane solution (0.028 mol l⁻¹; 18 ml) of the substrate (*Ia*, *Ib*, *VIa*, or *VIIb*) was irradiated in a quartz tube for 15 hours, the solvent was evaporated in vacuo and the crude reaction mixture was analyzed by ¹H NMR spectroscopy. The reaction mixtures were separated by TLC and GC.

2-Chloro-1-indanone (*Ia*). The product formed was isolated by preparative GC: *R_f* 3.16. On the basis of IR, NMR, and MS spectroscopic data and comparison of spectroscopic and GC data with the authentic sample, the product was identified as 1-indanone.

2-Bromo-1-indanone (*Ia*). The reaction mixture was separated by preparative GC and preparative TLC: 2-bromo-1-indanone¹² (*Ia*), 1-indanone (*IIIa*), 3-bromo-1-indanone^{17,18} (*V*), and *trans*-2,3-dibromo-1-indanone¹⁸ (*IV*) were isolated and identified on the basis of their IR, NMR, and MS spectroscopic data and their comparison to those of the authentic samples.

*2-Chloro-3,4-dihydro-1(2H)-naphthalenone*¹¹ (*Ib*). The reaction mixture was separated by preparative GC and 3,4-dihydro-1(2*H*)-naphthalenone (*IIIb*, *R_f* 2.55) and 1-naphthol (*IIB*, *R_f* 3.85) were isolated and identified on the basis of their IR, NMR, and MS spectroscopic data and by comparison of the spectroscopic and GC data to those of the authentic samples.

2-Bromo-3,4-dihydro-1(2H)-naphthalenone (*Ib*). The reaction mixture was separated by preparative GC and 3,4-dihydro-1(2*H*)-naphthalenone (*IIIb*, *R_f* 2.56) and 1-naphthol (*IIB*, *R_f* 3.87) were isolated and identified on the basis of their IR, NMR, and MS spectroscopic data, and by comparison of the spectroscopic and GC data to those of the authentic samples.

2,2-Dichloro-1-indanone (*VIa*). The reaction mixture was separated by preparative GC and 1-indanone (*R_f* 3.16), 2-chloro-2-indene-1-one (*R_f* 5.60), 2-chloro-1-indanone (*R_f* 7.07), and 2,2-dichloro-1-indanone (*R_f* 7.97) were isolated and identified on the basis of their IR, NMR, and MS spectroscopic and GC data, and in comparison with those of the authentic samples.

2,2-Dibromo-1-indanone (*VIa*). The reaction mixture was separated by preparative GC and TLC and *trans*-2,3-dibromo-1-indanone (*IV*), 2,2-dibromo-1-indanone (*VIIa*), and 2-bromo-2-indene-1-one (*VIIa*) were isolated and identified on the basis of IR, NMR, and MS spectroscopic data, and by comparison with the authentic samples.

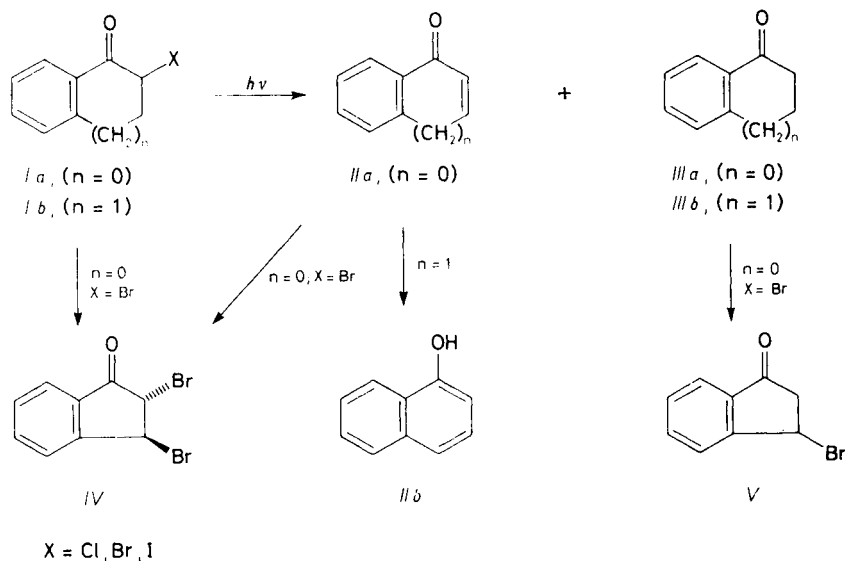
2,2-Dichloro-3,4-dihydro-1(2H)-naphthalenone (*VIIb*). The reaction mixture was separated by preparative GC and 3,4-dihydro-1(2*H*)-naphthalenone (*IIIb*, *R_f* 2.56), 2-chloro-1-naphthol (*VIIb*, *R_f* 3.88), 2-chloro-3,4-dihydro-1(2*H*)-naphthalenone (*Ib*, *R_f* 5.95), and 2,2-dichloro-3,4-dihydro-1(2*H*)-naphthalenone (*VIIb*, *R_f* 7.83) were isolated and identified on the basis of the IR, NMR, and MS spectroscopic data, and the comparison of spectroscopic and GC data to those of the authentic samples.

2,2-Dibromo-3,4-dihydro-1(2H)-naphthalenone (VIb), 1-Naphthol (IIb) and 2-bromo-1-naphthol (VIIb) were isolated from the reaction mixture by preparative GC (FFAP 10% on Chromosorb AW, t 170°C) and their GC and IR, NMR, and MS spectroscopic data were in agreement with those of the authentic samples.

RESULTS AND DISCUSSION

We have already found that UV irradiation of 2-iodo-1-indanone and 2-iodo-3,4-dihydro-1(2H)-naphthalenone results in competition between the radical and ionic photoprocesses, the nature of the photochemical carbon-iodine bond cleavage depending on the carbonyl group, the phenyl ring substitution and the ring size of the ketones. We found it instructive to study the influence of the halogen atom bonded, and thus 2-halo-1-indanone (*Ia*) and 2-halo-3,4-dihydro-1(2H)-naphthalenone (*Ib*) were chosen as model compounds.

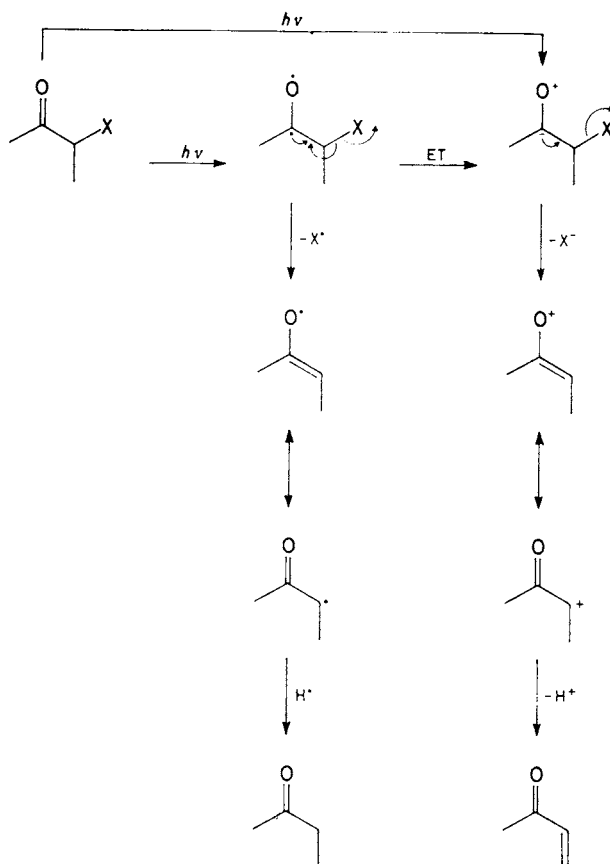
A 15-hour irradiation of 2-chloro-1-indanone¹¹ (*Ia*) in cyclohexane solution at 254 nm led to a complete conversion of the starting material, with only 1-indanone (*IIIa*) formation (Scheme 1, Table I). On the other hand, irradiation of 2-bromo-1-indanone¹² (*Ia*) under the same reaction conditions resulted in a reaction mixture containing the starting 2-bromo-1-indanone, 1-indanone (*IIIa*), 3-bromo-1-indanone^{17,18} (*V*), and *trans*-2,3-dibromo-1-indanone¹⁸ (*IV*, Scheme 1, Table I). The



SCHEME 1

products were isolated by preparative TLC and GC and the structures were determined on the basis of their spectroscopic data, which were in agreement with those

of the authentic samples. The formation of 1-indanone (*IIIa*) can be explained by hydrogen abstraction by the α -keto radical, formed by homolytic carbon–bromine bond cleavage, while 3-bromo-1-indanone (*V*) formation corresponds to the radical bromination of 1-indanone (Scheme 2); the same product was also observed by the



SCHEME 2

radical bromination of 1-indanone with N-bromosuccinimide. *Trans*-2,3-dibromo-1-indanone (*IV*) could be formed either by radical bromination of the starting 2-bromo-1-indanone or by the addition of bromine to 2-indene-1-one^{17,18} (*IIa*), which was formed via the ionic pathway from the corresponding α -keto carbonium ion, by elimination of a proton. The *trans* isomer of 2,3-dibromo-1-indanone was also obtained by radical bromination of 2-bromo-1-indanone, with N-bromosuccinimide as brominating agent. Irradiation of a cyclohexane solution of 2-iodo-1-indanone

resulted in the formation of 1-indanone as the radical product and 2-indene-1-one as the ionic product in the ratio⁹ of 2:1 : 1.

In order to determine the influence of the ring size of the cycloketone on the nature of the photochemical carbon-halogen bond fission, we studied the photo-transformation of 2-halo-3,4-dihydro-1(2*H*)-naphthalenone (*Ib*); UV irradiation of a cyclohexane solution of the 2-chloroderivative¹¹ led to the complete conversion of the starting ketone, with 3,4-dihydro-1(2*H*)-naphthalenone (*IIIb*) and 1-naphthol (*Iib*) formation in the ratio 1:12 : 1 (Scheme 1, Table I). The formation of the reduction product corresponds to the radical reaction pathway, while 1-naphthol formation can be explained as a tautomeric form of the initial ionic product. The complete conversion of the starting ketone was also observed by irradiation of 2-bromo-3,4-dihydro-1(2*H*)-naphthalenone¹² under the same reaction conditions and a mixture of 3,4-dihydro-1(2*H*)-naphthalenone as radical and 1-naphthol as ionic product in the ratio 1 : 2:1 was obtained (Scheme 1, Table I).

From the above results, as well as those of our previous study on the photochemical behaviour of 2-iodo-1-indanone and 2-iodo-3,4-dihydro-1(2*H*)-naphthalenone⁹, it can be concluded that cationic as well as radical intermediates play the major role in the solution-phase photochemistry of α -halo cycloketones (Scheme 2). The nature of the intermediates formed depends upon the halogen atom bonded and the ring size of the cycloketone, radical intermediates being favoured in the case of the five membered ketone, while for the six membered ring both radical and ionic intermediates were observed. This can be explained by the geometry of the excited state, since the partially negative charge on the carbon atom is more stabilized in the conformation of the six-membered ring²¹ than in the nearly planar five-membered²²

TABLE I

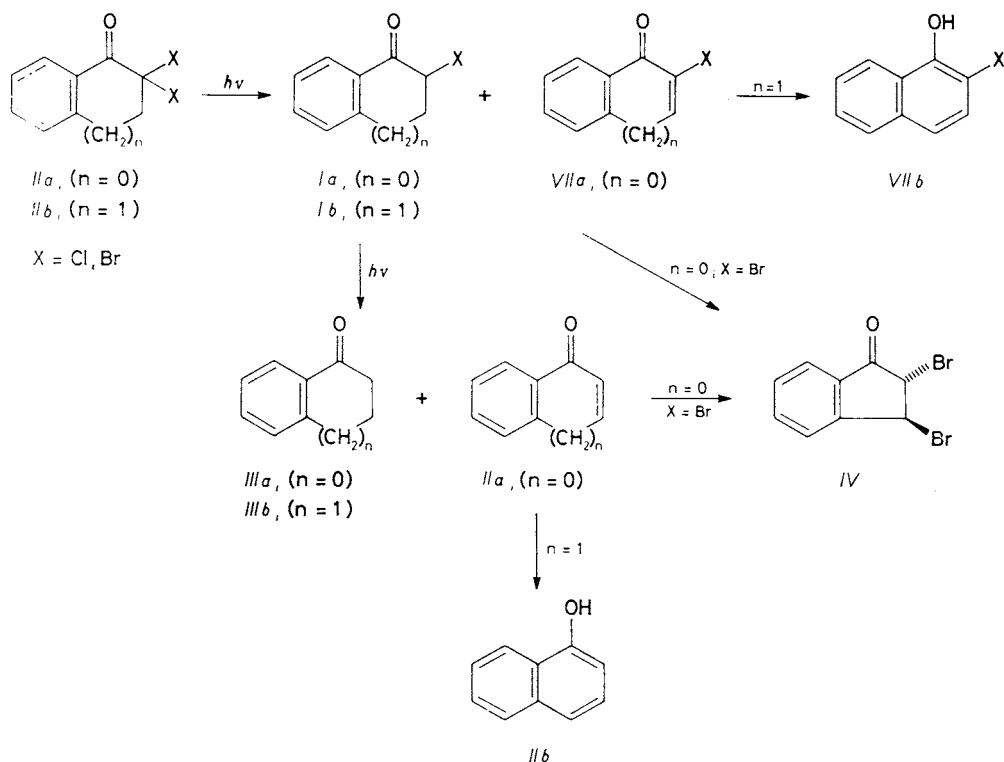
The effect of the ring size and the halogen atom on the nature of the photochemical carbon-halogen bond cleavage in ketones *I*

Ketone <i>I</i>		Relative yields				Conversion %	Products ratio ^a
X	n	<i>II</i>	<i>III</i>	<i>IV</i>	<i>V</i>		
Cl	0	—	100	—	—	100	1
Cl	1	47	53	—	—	100	0.53
Br	0	—	22	22	56	46	0.78 or 1
Br	1	68	32	—	—	100	0.32
I	0	32	68	—	—	83	0.68
I	1	57	43	—	—	100	0.43

^a Radical vs radical and ionic.

system in 1-indanone. In the case of 2-chloro-3,4-dihydro-1(2*H*)-naphthalenone, the radical product was predominantly formed, while in the case of bromo and iodo derivatives the ionic reaction pathway was the principal one (Table I).

We have further studied the influence of introducing another α -halogen atom into α -halo cycloketones on the nature of the carbon-halogen bond cleavage. For this purpose, the following substrates were chosen: 2,2-dichloro-1-indanone¹³, 2,2-dibromo-1-indanone¹⁴, 2,2-dichloro-3,4-dihydro-1(2*H*)-naphthalenone¹⁵, and 2,2-dibromo-3,4-dihydro-1(2*H*)-naphthalenone¹⁶. Irradiation of a 0.028M cyclohexane solution of 2,2-dichloro-1-indanone (*VIa*) in a quartz tube with ultraviolet light of 254 nm led to a 56% conversion of the starting ketone, with 2-chloro-1-indanone (*Ia*) and 1-indanone (*IIIa*) formation (Scheme 3), in the relative yields of 91% and 9%, respectively (Table II). The formation of both products could be explained by the radical reaction pathway, with 2-chloro-1-indanone (*Ia*) formed as the primary radical product, reacting further to 1-indanone.



SCHEME 3

A 15-hour irradiation of a cyclohexane solution of 2,2-dibromo-1-indanone (*VIa*) resulted in the formation of *trans*-2,3-dibromo-1-indanone (*IV*) and 2-bromo-2-

-indene-1-one¹⁹ (*VIIa*) in the ratio 1 : 1, with 58% conversion of the starting ketone. The formation of enone *IV* corresponds to the radical bromination of 2-bromo-1-indanone (*Ia*) formed via the radical intermediate by hydrogen abstraction, or by the addition of bromine to 2-indene-1-one (*IIa*), resulting in both cases in only the *trans* isomer, while 2-bromo-2-indene-1-one (*VIIa*) was formed via the ionic reaction pathway, by elimination of a proton from α -keto carbocation (Schemes 2 and 3).

Irradiation of 2,2-dichloro-3,4-dihydro-1(2*H*)-naphthalenone (*VIb*) under the same reaction conditions resulted in 93% conversion and a complex reaction mixture containing 2-chloro-3,4-dihydro-1(2*H*)-naphthalenone (*Ib*), 3,4-dihydro-1(2*H*)-naphthalenone (*IIIb*) and 2-chloro-1-naphthol¹⁵ (*VIIb*) in the relative yields of 64%, 28% and 8%, respectively, was obtained. Hydrogen abstraction by α -keto radical resulted in the formation of product *Ib*, which could be transformed in the next radical step to *IIIb*, while the product *VIIb* was a tautomer of the initially formed ionic product.

The nature of the carbon-halogen bond cleavage became completely changed in the case of 2,2-dibromo-3,4-dihydro-1(2*H*)-naphthalenone (*VIb*) where 94% of the ionic product 2-bromo-1-naphthol²⁰ (*VIIb*) was formed (Scheme 3, Table II), as well as 1-naphthol in 6% relative yield, its formation being the result of further ionic transformation of the primary radical product 2-bromo-3,4-dihydro-1(2*H*)-naphthalenone (*Ib*). From the results obtained by irradiation of α,α -dihalo cycloketones we can conclude that the introduction of second halogen atom into the α -position to the carbonyl group changed the nature of the photochemical carbon-halogen bond cleavage, which is shown in Tables I and II: the ratio of the radical products to the total products formed was in the case of 2,2-dibromo-1-indanone higher than that obtained by irradiation of 2-bromo-1-indanone, while in the case of 2,2-dichloro-1-indanone only the formation of radical product was observed.

TABLE II

The effect of the halogen atom and the ring size on the nature of the photochemical carbon-halogen bond cleavage in ketones *VI*

Ketone <i>VI</i>		Relative yields					Conversion %	Products ratio ^a
X	n	<i>I</i>	<i>II</i>	<i>III</i>	<i>IV</i>	<i>VII</i>		
Cl	0	91	—	9	—	—	56	1.00
Cl	1	64	—	28	—	8	93	0.92
Br	0	—	—	—	50	50	58	0.5
Br	1	—	6	—	—	94	100	0.06

^a Radical vs radical and ionic.

By irradiation of a six membered analogue (2,2-dihalo-3,4-dihydro-1(2H)-naphthalenone) the introduction of the second chloro atom increased the expulsion of the halogen atom (53% of the radical products in the case of 2-chloro-3,4-dihydro-1(2H)-naphthalenone, compared to 92% in the case of 2,2-dichloro-3,4-dihydro-1(2H)-naphthalenone) while, on the other hand, the introduction of another bromo atom into 2-bromo-3,4-dihydro-1(2H)-naphthalenone increased the ionic reaction pathway, resulting in 94% formation of 2-bromo-1-naphthol.

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