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PHOTOCHEMISTRY OF HALOKETONES—I

REACTIONS OF SOME α-HALOCYCLOHEXANONES†

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Abstract—α-Halocyclohexanones **1–4** on irradiation in cyclohexane have been found to involve competing radical and ionic photo-behaviour. The principal photoprocess observed in α-chloro-, α-bromo- and α-iodo-cyclohexanones was homolytic β-cleavage of carbon–halogen bond to afford radical products. These were usually accompanied by ionic products such as cyclohexenones, but in much lower proportions. Photo-Favorskii type ring contraction reported recently for α-chlorocyclobutanones was found to be completely absent. Sensitisation and quenching studies indicate that radical cleavage occurs from n-π^* triplet states whereas ionic cleavage could be a singlet derived reaction; thus providing for the first time experimental support to the proposed Wagner-model for the cleavage of carbon–halogen bond in α-haloketones.

The photochemistry of cycloalkanones have been extensively studied and has been the subject of several recent reviews.[1] However, little attention has been paid to a similar study of α-substituted cycloalkanones. Ketones substituted with heteroatoms on α-carbon including α-halo,[2] α-tosyloxy,[3] α-mesyloxy,[4] α-acetoxy[5] and α-alkoxy[6] are known to undergo photoinduced loss of these substituents. Each of these substituents is known to affect the n-π^* transitions of the carbonyl[7] and thus controlling the chemistry of excited states. It is therefore conceivable that the nature of the substituent could eventually be used to effect selective transformations in excellent preparative yields.

There are a few reports on the study of the photochemistry of α-halocycloalkanones involving different types of photoprocesses. These include α-cleavage,[8] photoelimination[2] and rearrangement[9] mainly involving α-ketocarbonium ions which seem to depend upon α-halogen atom, ring size of ketone and other functional groups present in the molecule.

These reports indicate that the photochemistry of α-halocycloalkanones in particular has been accorded limited attention and a coherent picture is lacking. Accordingly, we decided to undertake a systematic investigation into the photochemistry of most commonly occurring ring size ketones, i.e. some α-halocyclohexanones **1–4** as model compounds.

As yet, the nature of the excited states involved in the photolysis of this class of compounds is not conclusive. Schaffner *et al.*[4] investigated the photochemistry of some α-mesyloxyketones and concluded that radical and ionic modes selectively originate from the singlet and triplet states respectively. On the other hand recently Wagner[10] has proposed that ionic cleavage occurs only from the excited singlets, whereas radical cleavage could be a triplet reaction. However, there is no experimental support for this model. We now wish to report for the first time, results which clearly support the Wagner-model. Jones and McDonell[11] have reported photo-Favorskii type rearrangement of α-halocyclobutanones. Our results show that this rearrangement is absent in α-halocyclohexanones.

RESULTS

α-Haloketones **1–4** required were prepared by standard procedures and found to be sufficiently pure. Since halogen-acids are expected to be liberated on irradiation of the present substrates, it was necessary to use acid-scavangers to prevent any side reaction due to the high acidity of the medium. Furthermore, it was essential to carry out control experiments in order to rule out the possibility of dark reactions. In polar solvents, ketones **1–4** were found to be highly susceptible to solvolytic reactions particularly in the presence of corresponding halogen-acids.[12] The use of acid-scavangers particularly in polar media was found to cause known thermal reactions such as reduction and elimination and hence the use of polar solvent was abandoned. In a non-polar solvent like cyclohexane or benzene containing acid-scavangers, the present substrates were recovered completely unchanged even after considerable period of time at room temperature. In view of the above facts, the present photochemical studies were carried out mostly in cyclohexane using mainly Zn wool[13] as acid-scavanger.

α-Haloketones **1–4** have n-π^* transitions with λ_{max} around 310–320 nm. It was therefore found convenient to conduct irradiations with a pyrex filtered light. Individual ketone in cyclohexane containing zinc wool was irradiated and the reaction was worked up to furnish reaction product in ~80% yield. Each component from the reaction product was isolated by preparative glc and characterised on the basis of their spectral properties and through comparison with authentic samples. The results obtained are summarised in Table 1 and Scheme A.

In the absence of Zn wool, the medium became highly acidic in **1**, **2** and **3**, while in **4**, it remained neutral and the liberation of free I was noticed. However, there was no significant difference in the product composition with or without Zn wool present in the photolysis of **4**.

The sensitisation and quenching experiments were restricted to **2** and **4**, since photodecomposition of **1** and **3** was found to be extremely slow. The sensitizers used include benzene, acetone, acetophenone, and ben-

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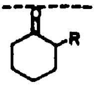
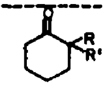
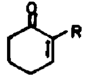
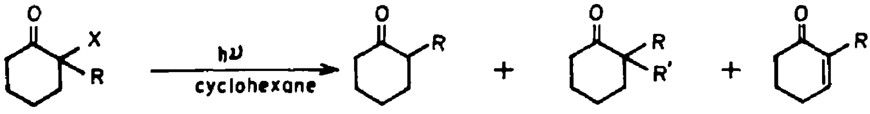
Table 1. Irradiation of α-halocyclohexanones[a] (1–4) in cyclohexane

Compound	Time (hrs)	Disappearance of starting (%)	Reaction products %[b]	1,3,4, R=H; 2 R=CH_3, R' = cyclohexyl[3]	
					
1	28	80	28	59	13
2	30	95	16	58	26
3	65	95	90	-	10
4	10	100	70	-	30
4[c]	9	100	76	-	24

a - Irradiations were carried out using (~0.5 to 0.7% solution) with Pyrex filter and in presence of Zn wool.

b - Determined by GLC

c - Irradiation without Zn wool.



1, X = Cl , R = H

2, X = Cl , R = CH_3

3, X = Br , R = H

4, X = I , R = H

5, R = H

7, R = CH_3

9, R = H
R' = Cyclohexyl

10, R = CH_3
R' Cyclohexyl

6, R = H

8, R = CH_3

Scheme A.

zophenone and the results are summarised in Table 2. Oxygen[14] and triethylamine[15] were used as triplet quenchers and the results are listed in Table 3.

DISCUSSION

From the above results it is seen that α-haloketones 1–4 afford principal photoproducts which are clearly derived from hydrogen abstraction by α-ketoradicals. These products are usually accompanied by the corresponding ionic (α,β-unsaturated ketones) products, however these were obtained in much lower proportions. These results reveal that, in general, α-ketoradical as well as α-ketocarbonium ion intermediates play an important role in the solution-phase photochemistry of α-halocyclohexanones, contrary to the photobehaviour observed previously in α-fluorocyclohexanone[8], α-chlorocyclobutanones[11] and other bicyclic α-halocycloalkanones.[9] Also Schaffner *et al.*[3] have obtained mostly ionic products together with some radical products in the photolysis of α-tosyloxycyclohexanone. This difference in photobehaviour could be attributed mostly to the nature of the α-substituent. About the photoreactivity, it is seen that **1**, **2** and **3** react slowly but the iodo analogue **4** was found to undergo the photodecomposition at much faster rate. In addition a slight preference for more of ionic product **6** is also seen from **4**. This photobehaviour of present α-haloketones 1–4 seems to have some resemblance with the photobehaviour of alkylhalides, wherein alkyliodides afford more of ionic products than alkylbromides.[13] In alkylhalides, the change in halosubstitution makes a marked change in product composition whereas in halocyclohexanones this change is not appreciable. Thus it is seen that the photochemistry of carbon–halogen bond is very much affected by the α-keto group which favours the expulsion of halogen atom rather than that of a halide anion; making the radical photobehaviour as the predominant process. In addition, the dual potentiality of n-π^* excited state involves contribution by structures 11 and 12. The latter seems to play a major role in nonpolar solvent like cyclohexane in deciding homolytic vs heterolytic fission of the carbon–halogen bond as proposed by Zimmermann[16] (Scheme B).

The incorporation of cyclohexane moiety in radical products of 9 and 10 has occurred only in chloroketones 1 and 2. This could be partly attributed to the fact that activation energy for hydrogen abstraction[17] by Cl radical is much less (~1 kcal/mole) as compared to Br (~14 kcal/mole), thus cyclohexyl radicals are generated at much faster rate. These combine with the α-keto radicals resulting in the formation of **9** and **10**. Similarly, on irradiation of **4**, I atom liberated on homolytic fission

Table 2. Irradiation (sensitized)[f] of α-iodocyclohexanone, 4 in cyclohexane[a]

Sensitizer	Triplet Energy E_T (KCal/Mole)	Time (hrs)	Disappearance of starting (%)	Reaction Products % [b]	
				5	6
Benzene[e]	85	4	100	80[c]	20
Acetone[e]	79	5	68	75[c]	25
Acetophenone	74	5	100	82[c]	18
Benzophenone	69	3	100	85[c]	15
Acetophenone	74	5	90	100[d]	-
Benzophenone	69	5	100	88[d]	12

a - Irradiation using (~ 0.5 to 0.7% solution) with Pyrex filter.

b - Determined by GLC

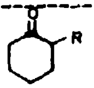
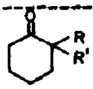
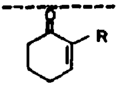
c - With Zinc wool

d - With triethylamine (1 mol. eq.)

e - Irradiations were carried out in benzene and acetone as a solvent with vycor filter.

f - With 3~4 Mole. eq. of sensitizer.

Table 3. Irradiation of α-halocyclohexanones[a] (1–4) in cyclohexane using triplet quenchers

Compound	Time (hr)	Disappearance of starting (%)	Reaction Products %	[b] 1,3,4,R=H; 2, $R=CH_3$ R' = Cyclohexyl	
					
1[c]	21	46	22	67	11
2[c]	16	60	15	55	30
3[c]	40	88	16	-	84
4[c]	12	100	11	-	89
2[d,e]	22	83	80	-	20
4[d]	6	100	26	-	74

a - Irradiations were carried out using (~ 0.5 to 0.6% soln.) with Pyrex filter.

b - Determined by GLC

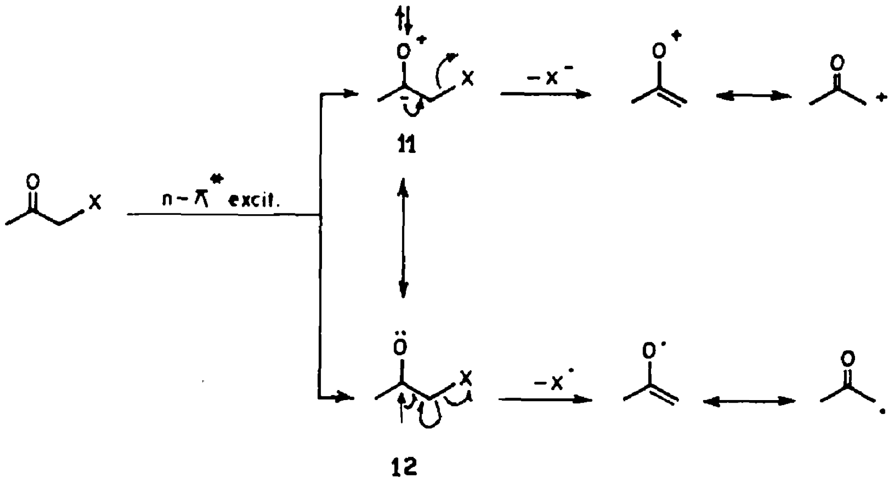
c - Triethylamine (2 Mole eq.)

d - Oxygen was bubbled throughout the irradiation

e - See Ref.20

of C–I bond, prefers to combine with another I atom rather than undergoing hydrogen abstraction which is known to be extremely slow.[17]

The excited states involved in the above competing radical vs ionic processes could be triplet and singlet respectively as suggested by Wagner[10] (Scheme B) or it could be vice versa as observed by Schaffner *et al.*[4] Therefore, in order to understand the nature of the excited states involved, we have carried out both sensitisation and quenching studies on 2 and 4. The results (Table 2) obtained on irradiation of 4 using different sensitisers reveal that in acetone, the product ratios of radical to ionic remained almost the same as in unsensitised reaction, while there is a slight increase in the radical products when acetophenone and benzophenone were used as sensitisers. However, the time required for



Scheme B.

sensitised reactions is almost half of that of unsensitised. These results, therefore, implicate that the photoprocess of 4 seems to have been sensitised and the major radical process may be occurring mostly through triplets while minor ionic process could be through singlet states as suggested by Wagner.[10] This was further supported by the quenching studies carried out using triethylamine and oxygen as triplet quenchers (Table 3). The former also served the purpose of scavanging the free halogen-acid liberated on irradiation. These results clearly show a marked change in the product composition of the products from 3 and 4 only while in the case of 1 and 2 it remained unaltered, indicated that triplet excited states involved in the radical photobehaviour of 3 and 4 were quenched, and favour the singlet derived ionic products. The photobehaviour of 1 and 2 seems to be different from 3 and 4 as similar quenching by both oxygen as well as triethylamine was not observed. The lack of quenching is mostly consistent with a view that this process could involve shortlived (unquenchable yet reactive) triplet states. This conclusion is further supported by the fact that the sensitised irradiation of 2 did not alter the product composition.

Photosensitised irradiations with acetophenone and benzophenone were also conducted using triethylamine and the results are included in Table 2. These results are highly significant because the product composition has been completely shifted mostly to radical products against the ionic products which were obtained on direct irradiation conducted in the presence of triethylamine. In this unusual combination[18] of sensitiser and quencher it is possible that triethylamine might have quenched selectively sensitiser triplets or the quenching of triplets of 4 was not effective due to the large population of these triplets accumulated because of sensitisation. In the present haloketones, a heavy atom effect[19] was supposed to induce rapid intersystem crossing in the order of Cl < Br < I thus furnishing more of triplet derived radical products in the same order. In fact, the observed product composition (Table 1) is in the opposite order and hence heavy atom effect is not effective in the present cases.

Further studies are in progress on the photochemistry of some more α-haloketones with fixed stereochemistries in order to check the generality of the present results as well as the stereochemical outcome of the photoprocess.

EXPERIMENTAL

General. All b.ps are uncorrected. The following instruments were used for spectral data: Perkin–Elmer Infracord model 137E (IR); Varian Associates A-60 spectrometer (PMR); CEC Mass spectrometer, model 21-110B (Mass; 70 eV, direct inlet system); "Aerograph" model A-350-B (glc; A; Silicon QF1, 300 cm × 0.6 cm. Al columns packed with silicon QF1 5% on chromosorb W of 60-80 mesh; B: FFAP, 180 cm × 0.6 cm Al columns packed with 20% FFAP on chromosorb W of 60–80 mesh. C: Preparative Silicon QF1, 300 cm × 0.6 cm. Al columns packed with 30% silicon QF1 on chromosorb W of 60–80 mesh. D: Preparative FFAP, 300 cm × 1 cm Al columns packed with 30% FFAP on chromosorb W of 30–60 mesh; H_2 as carrier gas. All IR taken as neat samples. All PMR spectra were taken in CCl_4 with TMS as internal standard; signals are reported in ppm (δ). While citing the PMR data the following abbreviations have been used: s, singlet; d, doublet; t, triplet; q, quartet; bm, broad multiplet; m, multiplet. To summarize the mass spectral data only the molecular ion and the most abundant ions are given with their relative intensities.

Photoirradiations were conducted with the Hanovia 200 Watt high pressure mercury lamp placed into an Ace double walled, water cooled, quartz immersion well using pyrex filter sleeve which was fitted in a pyrex reaction vessel equipped with a magnetic bar, condenser and N_2 inlet tube. Except where otherwise indicated a minute steady flow of O_2-free N_2 was passed through the mixture for 15–20 min prior to irradiation; where indicated finely cut Zn wool used as a scavenger for liberated I and HBr and HCl.

Benzene and cyclohexane were prepared for use as photolysis solvents by conventional treatment with H_2SO_4, extractive workup and distillation over Na. Acetone was refluxed with successive small quantities of $KMnO_4$ until the violet colour persists, dried over K_2CO_3, filtered and fractionated. After the irradiation had been completed solvent removed at 45–50° with the aid of water aspirator.

α-Chlorocyclohexanone (1)

(*A*) *Preparation.* α-Chlorocyclohexanone 1 was prepared by a known method.[21] Yield (61%), b.p. 120–21° (40 mm), Lit.[21,22] b.p. 90–91° (14–15 mm); λ_{max} (EtOH) 306 nm (ε 21), (cyclohexane) 313 nm (ε 32). IR: 810, 975, 1068, 1126, 1437, 1451, 1723, 2852 cm^{-1}. PMR: α-H (1 H, bm 4.17–4.33 ppm).

(*B*) *Photoproducts.* The material obtained (80%) on usual working was found to be mixture of three components having RRT of 1.0 (28%) and RRT of 2nd component 1.6 (13%) and RRT of 3rd component 9.6 (59%). These components were isolated in pure form by glc using column D, 1st component of RRT 1.0 was characterized as 5. IR: 750, 865, 908, 1120, 1232, 1312, 1455, 1715, 2850 cm^{-1}. PMR: α 2 CH_2 (4 H, bm 2.2 ppm). It has same RRT with authentic sample on both the columns A and B; 2,4-DNP derivative of **5** has m.p. 161° (Lit.[23] 162°). The component of RRT 1.6 was characterized as **6**; IR: 733, 765, 880, 940, 1120, 1208, 1380, 1420, 1680 cm^{-1}. λ_{max} (MeOH): 227 nm (ϵ 10,300). PMR: α H (1 H, m, 5.93 ppm), β H (1 H, m, 6.88 ppm). The component of RRT 9.6 was characterized as **9**. IR: 842, 898, 1141, 1474, 1710, 2852 cm^{-1}. PMR: $-CH_2-\overset{\overset{O}{\|}}{C}-$ (2 H, m, 2.2 ppm); MS: *m/e* 180 (M^+ 1%), 98 (20%), 41 (7%), 32 (26%), 28 (100%); (Found: C, 79.45; H, 10.92; O, 10.63. $C_{12}H_{20}O$ requires: C, 80.0; H, 11.11; O, 9.89%). α-Cyclohexylcyclohexanone was prepared employing the method of Rapson.[24] RRT and spectral data were identical with that of **9**.

α-Chloro α-methylcyclohexanone 2

(*A*) *Preparation.* Compound **2** was prepared by a known method,[25] Yield (85%) b.p. 82° (23 mm), Lit.[25] 94–96° (27 mm), λ_{max} (EtOH) 304 nm (ϵ 43); (cyclohexane) 310 nm (ϵ 36). IR: 730, 829, 880, 1095, 1137, 1334, 1353, 1725, 2845 cm^{-1}. PMR: α-Methyl (3 H, s, 1.63 ppm).

(*B*) *Photoproducts.* The material obtained (95%) on usual work up was found to be mixture of three components having RRT of 1.0 (16%) and RRT of 2nd component (1.7 (2.6%)) and RRT of 3rd component (15.0 (58%)). These components were isolated in pure form by glc using column D, 1st component of RRT 1.0 was characterized as **7**. IR: 728, 825, 872, 1126, 1147, 1216, 1310, 1449, 1710, 2848 cm^{-1}. PMR: α-Methyl (3 H, d, 1.0, $J = 6$ Hz). It has the same RRT with authentic sample on both the columns A and B. 2,4-DNP derivative of **7** has m.p. 136–38° (Lit.[23] 137°). The component of RRT 1.7 was found to be **8**. IR: 882, 903, 1105, 1357, 1675, 2852 cm^{-1}. PMR: vinylic H (1 H, bs, 6.54–6.82 ppm); vinylic Me (3 H, d; 1.69 ppm). α-Methylcyclohexenone was prepared by employing the method of Warnhoff.[26] RRT and spectal data were identical with that of **8**. The compound of RRT 15.0 was found to be **10**. IR: 908, 1382, 1450, 1710, 2850 cm^{-1}. PMR: -Methyl (3 H, bs; 1.03 ppm). MS: *m/e* 194 (M^+ 8%), 112 (82%), 111 (23%), 98 (100%), 83 (20%), 81 (18%), 67 (21%), 55 (40%), 43 (16%), 41 (35%), 3.9 (17%). α-Cyclohexyl-α-methylcyclohexanone was prepared by using the method of Rapson[24] and RRT and spectral data were identical with that of **10**.

α-Bromocyclohexanone 3

(*A*) *Preparation.* Compound **3** was prepared by oxidation of α-bromocyclohexanol[27] with chromic acid[28] b.p. 68° (2 mm), λ_{max} (EtOH) 311 nm (ϵ 67), (cyclohexane) 317 nm (ϵ 90), (Lit.[7] λ_{max} (EtOH) 308 nm (ϵ 70). IR: 826, 924, 1129, 1223, 1430, 1448, 1716, 2851 cm^{-1}. PMR: H (1 H, bm, 4.17-4.37 ppm).

α-Iodocyclohexanone 4

(*A*) *Preparation.* Compound **4** was prepared by oxidation of α-iodocyclohexanol[27,29] with chromic acid,[28] λ_{max} (EtOH) 317 nm (ϵ 290), (cyclohexane) 320 nm (ϵ 302) (lit.[30] λ_{max} (CCl_4) 316 nm (ϵ 180), IR: 818, 920, 1084, 1187, 1440, 1712, 2845 cm^{-1}. PMR: (1 H, bm, 4.37–4.6 ppm).

(*B*) *Photoproducts.* Photo products from **3** and **4** isolated (preparative glc Column C) were proved to be **5** and **6** from their spectral data.

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