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Photoinduced Alcoholysis of Trihaloacetyl Group

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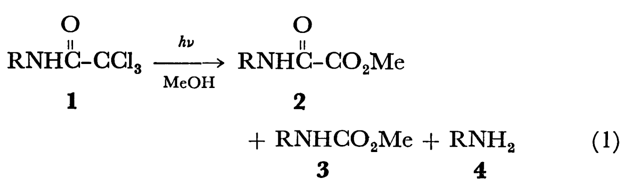
Synopsis. Photolysis of trichloroacetamide in non-degassed methanol gave methyl oxanilate (13—44%), along with carbamate (3—20%) and amine (4—12%). Similar irradiation of other trichloroacetyl derivatives of aliphatic ketone, aldehyde, and acetate afforded only radical product. The results are interpreted in terms of the mechanism involving electron transfer of the radical pair.

There has been increasing interest paid recently to photolysis of alkyl and alkenyl halides,[1-4] because, contrary to the earlier belief that only radical intermediates are involved, it becomes clear that cationic, as well as free radical, intermediates play an important role in the solution-phase photochemistry of these halides. During an effort[5-7] to generate α-oxo carbonium ion we found[8,9] that photolysis of α,α,α-trihaloacetophenone in alcohols gave a new photoalcoholysis product, benzoylformate, which was apparently derived from nucleophilic trapping of ionic species. Since thermal (dark) nucleophilic attack of alcohol on trihaloacetyl group is known to occur exclusively at carbonyl function to give benzoate (haloform reaction), the present photoalcoholysis is quite important not only from the standpoint of the reaction mechanism but also from synthetic viewpoints. Thus we have examined the photolysis of other trihaloacetyl compounds in alcohol.

Results and Discussion

Irradiation of a non-degassed solution of trichloroacetoanilide (**1a**) in methanol through a Pyrex filter for 4 h afforded methyl oxanilate (**2a**, 25.9%), along with methyl phenylcarbamate (**3a**, 12.5%) and aniline (**4a**, 12.3%). The similar reactions were found to occur with other trichloroacetoanilides as summarized in Table 1. The photoalcoholysis was also applicable to trichloroacetamide (**1e**, **f**). This is in marked contrast with that observed for trihalo-ketone where only aromatic ketone derivatives undergo photoalcoholysis to give formate (*vide infra*). Oxanilate **2** and carbamate **3** were apparently formed *via* nucleophilic trapping by methanol of cationic species resulting from C–Cl and C–CO bond fission in heterolytic way, respectively. Amine **4** was derived from radical species since trichloroacetaldehyde was detected in the reaction mixture.



$$\underset{\textbf{1}}{\mathrm{RNH\overset{O}{\overset{\|}{C}}\text{-}CCl_3}} \xrightarrow[\mathrm{MeOH}]{h\nu} \underset{\textbf{2}}{\mathrm{RNH\overset{O}{\overset{\|}{C}}\text{-}CO_2Me}} + \underset{\textbf{3}}{\mathrm{RNHCO_2Me}} + \underset{\textbf{4}}{\mathrm{RNH_2}} \qquad (1)$$

a: R=C_6H_5, **b**: R=*p*-$MeOC_6H_4$, **c**: R=*p*-MeC_6H_4
d: R=*p*-ClC_6H_4, **e**: R=$PhCH_2$, **f**: R=

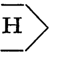
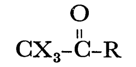


Table 1. Photoreaction of **1** in methanol[a)]

1	(R)	Irradiation time	Yield/%[b)]		
		h	**2**	**3**	**4**
1a	(C_6H_5)	4	28.9	12.5	12.3
1b	(*p*-$MeOC_6H_4$)	5	43.7	15.8	10.3
1c	(*p*-MeC_6H_4)	4	36.9	13.4	11.9
1d	(*p*-ClC_6H_4)	18	21.1	14.8	10.2
1e	($PhCH_2$)	20	28.5	20.2	3.5
1f	(*c*-C_6H_{11})	20	13.0	3.1	8.2

a) Irradiations were carried out in a Pyrex tube until all starting amide was consumed. b) Isolated yield.

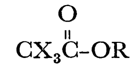
Irradiation of hexachloroacetone (**5a**) in methanol did not result in the formation of expected alcoholysis product, *i.e.*, methyl trichloroacetate or trichloropyruvate. Tribromoacetaldehyde (**5b**) also did not lead to the alcoholysis upon irradiation in methanol. The main product in these photolyses was reduction (radical) product. For example, dibromoacetaldehyde was obtained in more than 90% yield in the photolysis of **5b**. Irradiation of methyl trihaloacetate (**6a**, **d**) in methanol through quartz resulted in the formation of the reduction product *i.e.*, dihaloacetate. GC analysis showed that neither dimethyl oxalate nor carbonate was detected in the reaction mixtures. When aryl ester (**6b**, **c**) was similarly irradiated, phenol was isolated as a main product (70—80%), but no photoalcoholysis product was detected.



$$\mathrm{CX_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}R}$$

5

a: X=Cl, R=CCl_3,
b: X=Br, R=H



$$\mathrm{CX_3\overset{O}{\overset{\|}{C}}\text{-}OR}$$

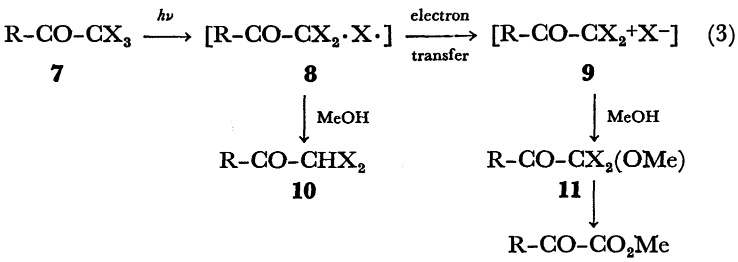
6

a: X=Cl, R=Me,
b: X=Cl, R=C_6H_5,
c: X=Cl, R=*p*-MeC_6H_4,
d: X=Br, R=Me

The results indicated that the photoalcoholysis of $COCX_3$ to $COCO_2R$ is applicable to trihaloacetamide group, but not to aliphatic trihalo-ketone, -aldehyde, and trihaloacetate. This is in contrast with that observed for photoalcoholysis of simple halides, where not only arylalkyl halide, *e.g.*, benzyl halide,[1,3] but also more simple alkyl and cycloalkyl halides[2] efficiently undergo photoalcoholysis to give ether and/or olefins along with radical products. In their interesting work on photosolvolysis of alkyl iodide Kropp *et al.*[2] have proposed that ionic intermediates are not produced directly from the photoexcited state, but that the photoexcited state decays by homolysis to a radical pair, which may undergo radical reactions or electron transfer to afford an ion pair as shown in Eq. 2. We

$$\mathrm{R\text{-}X} \xrightarrow{h\nu} [\mathrm{R\cdot X\cdot}] \xrightarrow[\text{transfer}]{\text{electron}} [\mathrm{R^+X^-}] \qquad (2)$$

have also suggested [8,9] that photoalcoholysis and photoreduction of trihaloacetophenone (**7**) are coupled through the common intermediacy of the radical pair (**8**) and that benzoylformate is formed *via* spontaneous (dark) alcoholysis of initial photoalcoholysis product, *i.e.*, α-alkoxy-α,α-dihaloacetophenone (**11**). The ratio of heterolytic products to the radical (reduction) products is then influenced by lifetime of the radical pair **8**, since the radical pair must have a lifetime to permit electron transfer to compete with diffusion of the radical components from the caged pair. The present results then suggest that only radical pair generated from trihaloacetophenone and trihaloacetamide has sufficient lifetime for electron transfer to occur, while that derived from aliphatic trihalo derivatives undergoes predominant hydrogen abstraction before electron transfer occurs. Alternatively, an α-oxo dihalo carbonium ion generated from trihaloacetophenone and trihaloamide may be stabilized by non-bonded interaction of phenyl and amide nitrogen. This will facilitate electron transfer process to generate the α-oxo dihalo carbonium ion which may be otherwise very unfavorable.



$$\begin{tikzcd}
\text{R-CO-CX}_3 \arrow[r, "h\nu"] & {[\text{R-CO-CX}_2\cdot\text{X}\cdot]} \arrow[r, "\text{electron}", "\text{transfer}"'] \arrow[d, "\text{MeOH}"] & {[\text{R-CO-CX}_2{}^+\text{X}^-]} \arrow[d, "\text{MeOH}"] & (3) \\
\textbf{7} & \textbf{8} & \textbf{9} & \\
& \text{R-CO-CHX}_2 & \text{R-CO-CX}_2\text{(OMe)} \arrow[d, "\textbf{11}"'] & \\
& \textbf{10} & \text{R-CO-CO}_2\text{Me} &
\end{tikzcd}$$

Experimental

Materials. α,α,α-Trichloroacetamide **1a**—**f** was prepared by the reaction of hexachloroacetone with amine according to the literature procedure.[10] Tribromoacetaldehyde **5b** was obtained by treatment[11] of paraldehyde with excess bromine. Aryl trichloroacetate **6b**, **6c** was synthesized by the Schotten-Baumann reaction of trichloroacetyl chloride with phenol. Methyl tribromoacetate **6d** was obtained by esterification of the corresponding acid. All other trihalo compounds were obtained from commercial source. Oxanilate **2** and carbamate **3** were prepared by the reaction of amine with dimethyl oxalate[12] and methyl chloroformate,[13] respectively.

Irradiation of Trichloroacetamide in Methanol. In a typical run, a solution of trichloroacetamide (1 mmole) in methanol (200 ml) was placed in a Pyrex tube and irradiated with a high-pressure, 300W, Hg lamp with a water-cooled jacket. The progress of the reaction was monitored by TLC. The irradiated mixtures were concentrated on a rotary evaporator and extracted with ether–water. Acidification of the aqueous layer, followed by ether extraction gave amine. The ethereal solutions were concentrated and chromatographed on 2.0 cm × 30 cm silica gel (Woelm, Activity III) column with $CHCl_3$ as eluant to give oxanilate **2** and carbamate **3**, all of which showed the same NMR spectra and GC retention time as authentic samples.

Irradiation of Other Trihaloacetyl Compounds in Methanol. Irradiations were carried out as outlined above. Identifications of photoproducts were done either by GC comparison with authentic samples or by isolation followed by spectroscopic determination.

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