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# EFFECT OF STRUCTURE ON PHOTOALCOHOLYSIS OF AROMATIC α-HALOKETONES

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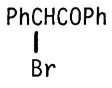
Desyl halide, α-bromophenylacetate, and 2,5-dimethoxy-α-bromoacetophenones undergo smooth photomethanolysis, whereas simple α-bromoacetophenone undergoes photoreduction to give acetophenone.

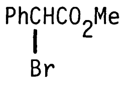
Contrary to the earlier belief that only radical intermediates are involved, it has been demonstrated that, cationic, as well as free radical intermediates may play an important role in the solution-phase photochemistry of benzyl,1) alkyl,2) and cycloalkyl halides.3) The photolytic generation of cationic species is especially interesting in that it is successfully applied to generate functionalized cationic species, e.g., vinyl and keto cations, as well; some vinyl halides4) and α-haloketones5-8) undergo competing ionic and radical reactions upon irradiation in the presence of nucleophiles. Thus, we found7) that photolysis of α,α,α-tribromoacetophenone in alcohols gives benzoylformate and that the formate is formed via initial photoalcoholysis of the bromoketone to the corresponding α-keto ether followed by its subsequent degradations. Thermal reaction of α-haloketone with alkoxide in dark generally does not lead to α-keto ether: the nucleophile either attacks on carbonyl carbon to give oxirane or abstracts α-proton to lead to the Favorskii rearrangement.9) Therefore, we investigated the photolysis of α-monohaloketone in alcohols in order to know the scope and limit of the present photolytic method to generate a keto cation.

Irradiation of a methanol solution of desyl bromide (**1**) in a Pyrex tube with a 300-W high-pressure Hg lamp resulted in a rapid disappearance of the starting bromide and concurrent appearance of benzoin methyl ether (**2**, 22%) along with deoxybenzoin (**3**, 13%), benzaldehyde (**4**, 15%), benzil (**5**, $\approx$1%), methyl benzoate (**6**, 6%), and pinacol dimethyl ether (**7**, $\approx$1%). Control experiments showed that the accompanying products (**4-7**) were not the primary photoproducts, but formed via a rapid photodecomposition of the benzoin ether in the presence of oxygen.10) Similar irradiation of methyl α-bromophenylacetate (**8**) also underwent smooth methanolysis to give α-methoxyphenylacetate (**9**) in about 80% yield. In a marked contrast, photolysis of monobromoacetophenone (**10a**) in methanol afforded acetophenone (**11a**, 41%) as a sole isolable products: no products arising from an ionic species e.g., α-methoxyacetophenone and methyl phenylacetate were isolated. Introduction of p-methoxyl group on phenyl ring and/or methyl group on the halide carbon atom (**10b-f**) did not result in significant change in the photochemical behaviors; irradiation of **10b-f** in methanol also gave the corresponding ketones (30-40%) as only volatile products.

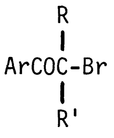
These results clearly indicate that the phenyl group attached on the halide carbon plays an important role in the generation of ionic species. In their interesting work on photosolvolysis of alkyl iodide, Kropp et al2) have proposed that ionic intermediates are not produced directly from the photoexcited state, but that the photoexcited state decays by homolysis to a radical


$\mathrm{Ph}\underset{\mathrm{Br}}{\underset{|}{\mathrm{C}}}\mathrm{HCOPh}$

**1**


$\mathrm{Ph}\underset{\mathrm{Br}}{\underset{|}{\mathrm{C}}}\mathrm{HCO_2Me}$

**8**


$\mathrm{ArCO}\overset{\mathrm{R}}{\underset{|}{\overset{|}{\underset{\mathrm{R'}}{\mathrm{C}}}}}\text{-}\mathrm{Br}$

**10**

**a**: Ar=$C_6H_5$, R=R'=H

**b**: Ar=$C_6H_5$, R=H, R'=Me

**c**: Ar=$C_6H_5$, R=R'=Me

**d**: Ar=p-$MeOC_6H_4$-, R=R'=H

**e**: Ar=p-$MeOC_6H_4$-, R=H, R'=Me

**f**: Ar=p-$MeOC_6H_4$-, R=R'=Me

pair, which may undergo radical reactions or electron transfer to afford an ion pair. Assuming that similar mechanism can be applied to explain the generation of the ketocation, the origin of the effect of phenyl group is due at least in part to an extended lifetime of the radical pair, which permits electron transfer to compete with diffusion of the radical components. Moreover, the phenyl group also stabilizes the keto cation which is otherwise very unfavorable.

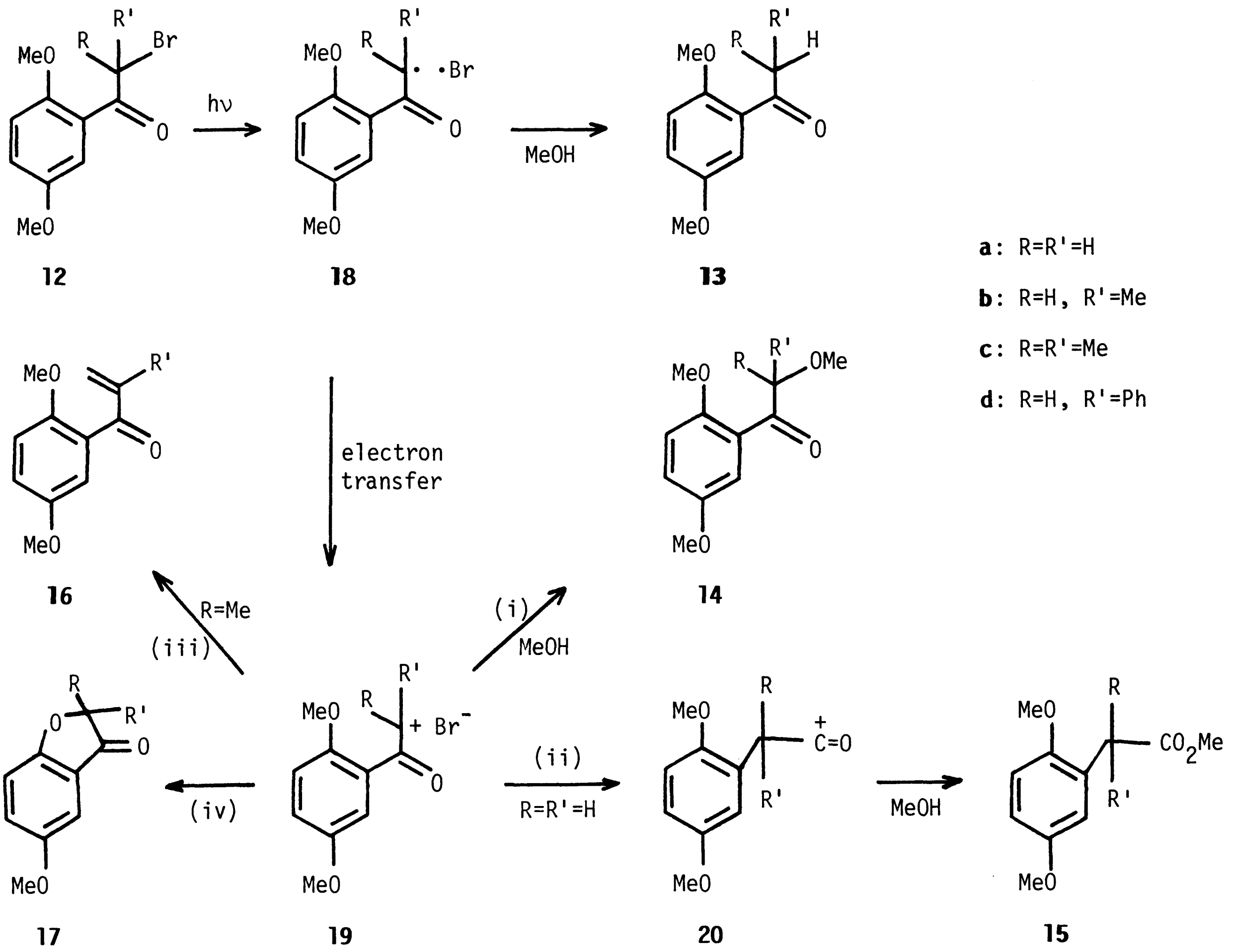
Introduction of MeO group on ortho position of α-bromoacetophenones (**10**) caused a dramatic change in their photochemical course. Thus, irradiation of 2,5-dimethoxy-α-bromoacetophenone (**12a**) in methanol afforded α-methoxyacetophenone (**14a**) and methyl phenylacetate (**15a**) along with acetophenone (**13a**). Similar irradiation of the bromides of propio- (**12b**) and isobutyrophenone (**12c**) in methanol afforded vinyl ketone (**16**) and coumaranone (**17**) in addition to **13-14**, while **12d** gave only keto ether (**14d**) upon irradiation in methanol. The reaction path leading to each products is explained as outlined in the following Scheme 1. The radical pair (**18**) formed by homolysis of the C-Br bond either abstracts hydrogen to give the ketone (**13**) or undergoes electron transfer to afford keto cation (**19**), which in turn collapses via four competing reaction pathways: (i) nucleophilic trapping by the solvent to give the keto ether (**14**), (ii) nucleophilic attack of aromatic π-electrons, followed by methanolysis to lead to the acetate (**15**), (iii) deprotonation to the vinyl ketone (**16**), and (iv) intramolecular cyclization to the coumaranone (**17**).

Table 1. Photolysis[a] of the α-bromoketone (12)

| 12 | Solvent | Yield/%[b] | | | | |
|---|---|---|---|---|---|---|
| | | **13** | **14** | **15** | **16** | **17** |
| **12a** | MeOH | 1 | 10 | 29 | — | 0 |
| **12b** | MeOH | c | 28 | 0 | c | 13 |
| | MeCN | c | — | — | 10 | 66 |
| | $CCl_4$ | c | — | — | 57 | 2 |
| | PhH | c | — | — | 34 | 5 |
| **12c** | MeOH | c | 7 | 0 | 41 | 12 |
| | MeCN | c | — | — | 27 | 15 |
| | $CCl_4$ | c | — | — | 54 | c |
| **12d** | MeOH | c | 72.7 | 0 | — | 0 |
| | MeCN | c | — | — | — | 20 |

a) Irradiations were carried out on a 40 mM solution of **12** containing pyridine as a buffer in Pyrex tubes at 10 °C.

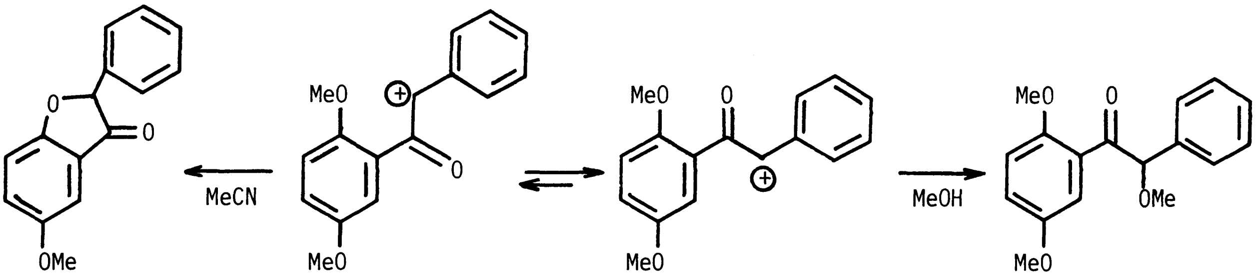
b) Determined by GC based on the bromoketone used. c) Trace.



Scheme 1.

The contrasting differences in the photochemical behaviors between **10** and **12** can be attributed to the stabilization of cationic species by ring substituents. Since the keto cations usually have planar geometry with the phenyl ring, the vacant p orbital of keto cation **19** is in the molecular plane and in close vicinity to the lone pair on the oxygen atom of the o-methoxyphenyl group.11) Consequently, **19** can be stabilized significantly by the non-bonding interaction, which facilitates the electron transfer process to generate the keto cation. The formation of coumaranone therefore serves as evidence for the intervention of the keto cation. Moreover, the finding that irradiation of 2,5-dimethyl-α-bromoacetophenone in methanol did not afford the products arising from cationic species also supports the above explanation.

The effect of structure on the product distribution in the photomethanolysis of **12** is noteworthy. Thus, phenylacetate (**15**) was formed only from the keto cation **19a** (R=R'=H), while the formation of coumaranone (**17**) was important pathway for **19b**, **c** (R=H, R'=Me; R=R'=Me). The cation **19d** (R=H, R'=Ph), on the other hand, did not undergo the intramolecular reaction in methanol but was trapped only by the solvent. Presumably, the less sterically hindered and more reactive keto cation **19a** can be attacked even by aromatic π-electrons, while such attack becomes unfavorable to the more sterically hindered and more stabilized cations **19b, c** which are in turn attacked by the more basic and closer lone pair on the oxygen atom of o-MeO group. The cation **19d** should adopt a sterically more favoravle conformation (**19d'**), which can not undergo intramolecular attack. Although, in the conformer **19d'**, stabilization of the cationic center by o-MeO group is not attained, this cation is intrinsically stabilized by the adjacent Ph group. In acetonitrile, **19d'** has nothing to do but rotates to **19d**, which undergoes cyclization to coumaranone (**17d**).



**17d** **19d** **19d'** **14d**

The keto cation can be generated even in non-hydroxylic solvents since irradiation of the bromoketones in MeCN, $CCl_4$, and PhH also resulted in the formation of the vinyl ketone (**16**) and coumaranone (**17**) (Table 1). The product ratios are somewhat sensitive to the solvent employed: cyclyzation to coumaranone is favored in polar solvent while deprotonation is favored in non-polar solvent. An explanation of these observations must include at least in part the change in the reactivity of keto cation due to solvation.

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11) Similar interaction has been reported4) in the vinyl cation bearing o-methoxyphenyl group at β-position.

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