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# Photolysis of Aromatic Oxime Esters. Finding of Aromatic Substitution by Diphenylmethyleneimino Radicals

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**Synopsis.** Diphenylmethyleneimino radicals, $Ph_2C=N\cdot$, generated from photolysis of benzophenoxime benzoates undergo aromatic substitution on benzene as well as dimerization into azine. On the other hand, phenylmethyleneimino radicals, $PhCH=N\cdot$, generated from photolysis of benzaldoxime benzoate are oxidized to benzonitrile in preference to dimerization.

Recently increasing interest has been paid to photochemical behaviour of carbon-nitrogen double bond.[1] Our interest in free radicals containing carbon-nitrogen double bond moiety[2] led us to investigate generation and behaviours of imino radicals by conducting photolysis of aromatic oxime esters in benzene. Previously, Okada, Kawanisi and Nozaki reported that irradiation of aromatic ketoxime benzoates afforded the corresponding ketazines probably through combination of the intermediate ketimino radicals but benzaldoxime benzoate did not afford benzaldazine.[3] Vermes and Beugelmans reported that the irradiation of steroidal oxime esters gave their parent oximes and ketones.[4] We now add new findings to photochemistry of benzophenoxime benzoates and benzaldoxime benzoate in benzene to show that the ketimino radicals undergo, in addition to their dimerization into the ketazine, nuclear substitution on benzene, whereas the aldimino radicals are oxidized to benzonitrile in preference to their dimerization into benzaldazine.

## Results and Discussion

Benzophenoxime benzoate (Ia), *p*-methoxybenzoate (Ib), *p*-chlorobenzoate(Ic) and benzaldoxime benzoate(II) were photolyzed in benzene with a 400 W high pressure mercury lamp through Pyrex wall under nitrogen or oxygen without any added sensitizer or with benzophenone or naphthalene. The volatile products were determined as summarized in Table 1.

Photolysis of Ia gave, along with benzophenone azine(III) (20%), benzophenone, biphenyl, phenyl benzoate, benzoic acid and *N*-(diphenylmethylene)-aniline(IVa). The presence of oxygen in the photolysis remarkably increased the yields of benzophenone and phenyl benzoate accompanied by decrease of the yields of IVa and biphenyl. These products are understood to arise from diphenylmethyleneimino radicals (V) or benzoxyl radicals generated by photochemical homolysis of nitrogen-oxygen linkage of Ia.

$$Ph_2C=NOCOAr\ (I) \xrightarrow{h\nu} Ph_2C=N\cdot\ (V) + ArCO_2\cdot$$

$$Ar:\ a,\ C_6H_5;\ b,\ p\text{-}CH_3OC_6H_4;\ c,\ p\text{-}ClC_6H_4$$

The resulting benzoxyl radicals undergo the established reactions. Thus, they undergo aromatic substitution induced by oxygen to afford phenyl benzoate[5] or decarboxylation into phenyl radicals which substitute

TABLE 1. VOLATILE PRODUCTS FROM THE IRRADIATION OF BENZOPHENOXIME BENZOATE(Ia), *p*-METHOXYBENZOATE(Ib), *p*-CHLOROBENZOATE(Ic) AND BENZALDOXIME BENZOATE(II) IN BENZENE AT ROOM TEMPERATURE WITH A HIGH PRESSURE MERCURY LAMP

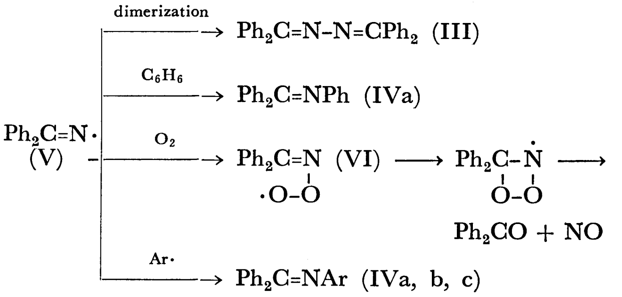
| Ester[a] | Products (%) | | | | | |
|---|---|---|---|---|---|---|
| | $Ph_2CO$ | ArPh[e] | $ArCO_2Ph$[e] | $PhCO_2H$ | PhCR=NPh[f] | PhCN |
| Ia | 27 | 14 | 10 | g | 6.4 | |
| Ia[b] | 89 | 1.2 | 60 | g | 0.6 | |
| Ia[c] | g | 22 | 15 | g | 16 | |
| Ia[d] | 21 | 14 | 10 | g | 6.5 | |
| Ib | 14 | 16 | 3 | g | 9 | |
| Ib[c] | g | 22 | 3 | g | 23 | |
| Ic | g | 13 | g | g | 8 | |
| Ic[c] | g | 20 | g | g | 25 | |
| Ic[d] | g | 14 | g | g | 5 | |
| II | | 9.7 | 3 | 23 | trace | 40 |
| II[b] | | 0.8 | 33 | 19 | g | 62 |
| II[c] | | 17 | g | g | g | 28 |
| II[d] | | 8 | 1 | 26 | 2 | 50 |

a) Under nitrogen except b) in 0.025 M. b) Under oxygen atmosphere. c) Benzophenone was added (0.025 M). d) Naphthalene was added (0.025 M). e) Ar: $C_6H_5$, $p$-$CH_3OC_6H_4$, $p$-$ClC_6H_4$ and $C_6H_5$ for Ia, Ib, Ic and II, respectively. f) R: Ph and H for I and II, respectively. g) Not determined.

on benzene to give biphenyl and its yield is reduced under oxygen due to the consumption of phenyl radicals by oxygen.[6]

$$\mathrm{PhCO_2\cdot + C_6H_6 \rightleftharpoons PhCO_2C_6H_6\cdot \xrightarrow{O_2} PhCO_2C_6H_5}$$

On the other hand, the imino radicals, V, arising from I either dimerize into the azine, III, or substitute on benzene to afford IVa, or give benzophenone.



In view that vinylic radicals react with oxygen resulting in the oxidative cleavage of their unsaturated bonds,[7] it is reasonable to suppose that an imino radical combines with an oxygen molecule to give peroxy radical (VI), which would undergo intramolecular addition followed by decomposition to give benzophenone and nitric oxide, though detection of nitric oxide was not attempted.[8] Formation of benzophenone in the irradiation under nitrogen could be attributable to either reaction of the imino radical with oxygen eventually present or hydrolysis of the resulting benzophenone imine benzoate[3] with water adventitiously present or possible rearrangement of Ia into oxaziridine followed by its cleavage.[4]

Production of the imine, IVa, from Ia is mostly ascribed to substitution of the imino radical on benzene not to recombination between the imino and phenyl radicals both generated from Ia, since irradiation of Ib and Ic in benzene also gave IVa along with negligible amount of *N*-(*p*-methoxyphenyl)imine(IVb) and *N*-(*p*-chlorophenyl)imine(IVc), respectively. So, it is clear that the geminate reaction between the imino radical and aryl radical arisen from I does not effectively take place.

In the irradiation of I, the presence of naphthalene, which was attempted to be used as a sensitizer, did not affect the products formation. However, use of benzophenone remarkably increased the yield of IVa and moderately increased the yield of biphenyl; thus, aromatic substitutions by the imino radicals and phenyl radicals seem to be promoted by the presence of benzophenone. This fact is not attributable to the action of benzophenone molecules in their ground state on cyclohexadienyl-type radicals resulting from the addition of the imino radicals or phenyl radicals on benzene molecules, since a control experiment showed that the presence of benzophenone in thermal decomposition of dibenzoyl peroxide in benzene did not increase the yield of biphenyl. Therefore, benzophenone in the excited state seems to be responsible for this effect.

Irradiation of II is now shown to afford benzonitrile as a main product. Production of biphenyl, benzoic acid together with the effect of oxygen to increase the yield of phenyl benzoate shows that II is also photolyzed through N–O bond cleavage like I. An observed effect of oxygen to promote the production of benzonitrile suggests that benzonitrile results from phenylmethyleneimino radicals(VII) through their hydrogen atom transfer with other radicals or oxygen molecules.[9]

$$\mathrm{PhCH{=}N\cdot\ (VII) + R\cdot \longrightarrow PhCN + RH}$$

$$\mathrm{R\cdot : PhCO_2\cdot,\ Ph\cdot\ or\ O_2}\ etc.$$

A possibility that irradiation of II would give benzaldazine and its subsequent photolysis would give benzonitrile seems to be excluded on the basis that irradiation of II did not afford stilbene which would be produced from photolysis of benzaldazine.[9]

## Experimental

Benzophenoxime benzoate (Ia), *p*-methoxybenzoate (Ib), *p*-chlorobenzoate (Ic) and benzaldoxime benzoate (II) were prepared according to literature.[10,11] Irradiation was carried out for 0.025 M benzene solution (400 ml) with a 400 W Riko high pressure mercury lamp. The reaction mixture was shaken with aqueous sodium hydrogen carbonate to extract benzoic acid and the remaining solution was used for product analysis. In vpc analysis with a Hitachi K53 gas chromatograph, benzonitrile and benzaldehyde were determined with a 4 m series of columns of silicone and polyethyleneglycol sebaciate at 160 °C, and biphenyl, benzophenone, phenyl benzoate and IVa were determined with a 6 m or 4 m column of silicone at 240 °C. Production of benzophenone azine was confirmed by its separation through column chromatography over silica gel.

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