Photochemical Reactions of *N*-Acyl-2,3-dihydrobenzoxazol-2-ones

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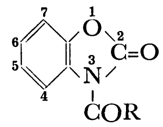
Photo-Fries rearrangements of *N*-acyl-2,3-dihydrobenzoxazol-2-ones are described. Irradiation of *N*-acyl-2,3-dihydrobenzoxazol-2-ones in acetonitrile afforded a mixture of 2-acyl-2,3-dihydrobenzoxazol-2-one and 6-acyl-2,3-dihydrobenzoxazol-2-one together with other minor products. However, 2,3-dihydrobenzoxazol-2-one and *N*-methyl-2,3-dihydrobenzoxazol-2-one were very photostable. The reaction scheme involving Norrish type I dissociation has been discussed.

The photochemical reactions of carbonyl compounds have been extensively studied; among them the photo-Fries rearrangement has been studied in detail for various aryl esters and *N*-arylamides.[1] In the photochemical reactions of acetoanilide[2] and its related compounds,[3] it has been shown that, in the liquid phase, the photo-Fries rearrangement originates from the lowest excited singlet state $S_1(\pi\pi^*)$ forming pair radicals which efficiently recombine in a solvent cage into the original substance, ortho- and para-isomers. The photo-Fries rearrangements of some heteroaromatic compounds, such as aryloxy-1,3,5-triazines,[4] 2-aryloxybenzazoles,[5] and *N*-acetylcarbazole[6] have been reported. The photochemical reactions of imides have been the subject of numerous recent studies; photochemical rearrangements of *N*-alkylphthalimides, which involve ring expansion *via* the Norrish type II process, have been reported by Kanaoka *et al.*,[7] and Mazzocchi *et al.*[8]

This paper will report on the photochemistry of *N*-acyl-2,3-dihydrobenzoxazol-2-ones (**1**) having a semicyclic imide skeleton. The photochemical behavior of these compounds is of interest to ascertain where dissociation occurs upon irradiation and what the photoproducts are.



(**1**)

Results and Discussion

Photo-Fries Rearrangement of N-*Acyl-2,3-dihydrobenzoxazol-2-ones.* *N*-Acyl-2,3-dihydrobenzoxazol-2-ones have been prepared by treating 2,3-dihydrobenzoxazol-2-one with acyl halide in pyridine, the details of which are listed in Table 1.

When the substituent at the 3-position is H (**1a**) or CH_3 (**1b**), no photochemical reaction was observed even after prolonged irradiation; this is particularly interesting because ordinary arylamides and arylesters are known to undergo photoreaction involving bond cleavage at -N-CO-[2d] and -O-CO-.[9]

When the substituent is an acyl group, a regular spectral change was observed upon irradiation in every case, a typical example of a spectral change being shown in Fig. 1 for the *N*-benzoyl derivative (**1g**).

In the case of the *N*-benzoyl compound (**1g**), a clean photo-chemical reaction took place to afford five photoproducts (**2g**, **3g**, **4**, **5**, **6**). The two products (**2g** and **3g**) were found to be positional isomers of the starting material (**1g**) which gave aminohydroxybenzophenones on treatment with hydrochloric acid. Spectral data showed that the compounds are benzene-ring-benzoylated products resulting from N→C migration of the benzoyl group, *i.e.* the reaction was a photo-Fries rearrangement. In the ordinary photo-Fries rearrangement of *N*-arylamides, the acyl group migrates to the ortho and para positions relative to the amino group. Therefore, the two isomeric products obtained have been assumed to be the ortho and para benzoylated products.

Table 1. 3-Substituted 2,3-dihydrobenzoxazol-2-ones

No.	3-Substituent	Mp (°C) (Lit)	Solvent for recrystallization	Found (%)		Calcd (%)	
				C	H	C	H
1a	H	139—140 (137—138)[a]	Benzene	—	—	—	—
1b	CH_3	84.5—85.5	Cyclohexane	64.31	4.65	64.42	4.73
1c	$COCH_3$	94—95 (95)[b]	Petroleum ether	—	—	—	—
1d	COC_2H_5	92—93	Cyclohexane	62.39	4.71	62.82	4.75
1e	COC_3H_7	82—83	Hexane	64.32	5.38	64.38	5.40
1f	$COCH(CH_3)_2$	47.5—48.5	Petroleum ether	64.61	5.47	64.38	5.40
1g	COC_6H_5	169—170 (174)[c]	Benzene	—	—	—	—
1h	COC_6H_4-(*p*)-CH_3	182.5—183	Benzene	71.35	4.37	71.14	4.37

a) Ref. 12. b) H. Zinner, H. Herbig, and H. Wigert, *Chem. Ber.*, **89**, 2135 (1956).
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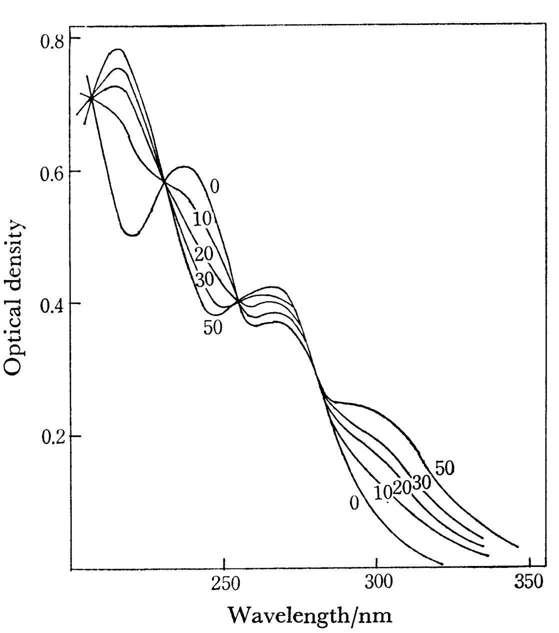
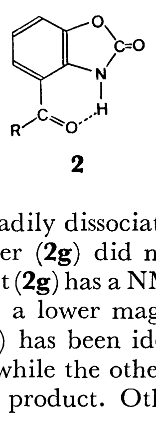


Fig. 1. Spectral change of an ethanol solution of 3-benzoyl-2,3-dihydrobenzoxazol-2-one by irradiation with a low-pressure mercury lamp. Numbers refer to time at a measurement in seconds.

In the ortho rearranged product, the formation of an intramolecular hydrogen bond as shown (**2**) may be possible:



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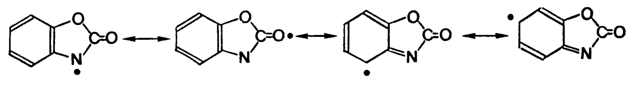
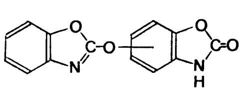
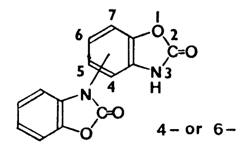
One product (**3g**) readily dissociated in the presence of alkali, while the other (**2g**) did not. In addition, the weaker acidic product (**2g**) has a NMR band attributable to an NH proton at a lower magnetic field. On this basis the isomer (**2g**) has been identified as the ortho-rearranged product while the other (**3g**) corresponds to the para-benzoylated product. Other products obtained were benzoic acid (**4**) and 2,3-dihydrobenzoxazol-2-ones (**5**). At the same time a derivative of 2,3-dihydrobenzoxazol-2-one which does not contain benzoyl group was obtained in a low yield. This compound was also obtained in the case of other *N*-acyl derivatives (**1c, 1h**), and was shown to be a dimer (**6**) of benzoxazolin-2-one. It appears that the dimer resulted from the coupling of two benzoxazolonyl radicals. This radical have four reactive positions, *viz*:





(**6a**)

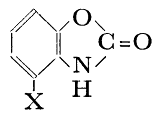
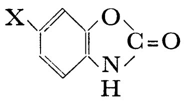
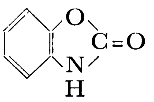


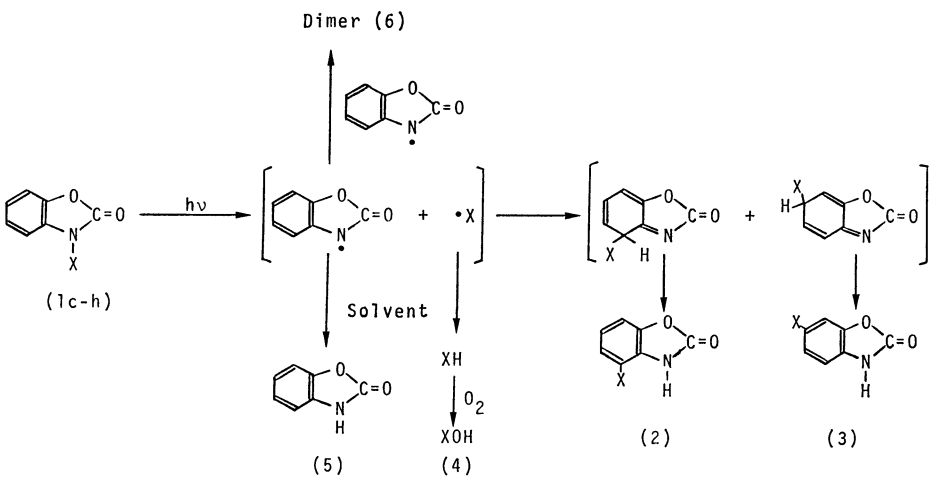
(**6b**)

Thus, between the two radicals various types of coupling may be expected resulting in the formation of various dimers. One dimer was however obtained, showing that the coupling was regiospecific. This regiospecific nature of benzoxazolonyl radicals may be ascribed in part to their high selectivity caused by the delocalization as shown above. NMR spectra show that the dimer has seven aromatic protons and one active hydrogen atom, consequently, two possible formulas (**6a** and **6b**) for the dimer have to be considered. However, since 2-aryloxybenzoxazoles readily rearrange to give 2-(2- and/or 4-hydroxyaryl)benzoxazoles upon irradiation,[5] (**6a**) seems less probable than (**6b**). Furthermore, the 6-(2-oxo-2,3-dihydrobenzoxazol-3-yl)-2,3-dihydrobenzoxazol-2-one derivative is preferable to the 4-isomer since there is less steric hindrance and the corresponding odd π-electron density is high at the 6-position.[10] The dimer formation is evidence that the reaction proceeds *via* Norrish type I dissociation in the liquid phase.[11]

Similar photoreactions have been observed for other *N*-acyl derivatives, the yields and products of which are listed in Table 2. Table 2 shows that the ratios of ortho and para rearranged products is about 1. The reaction

Table 2. Photochemical rearrangement of 3-substituted 2,3-dihydrobenzoxazol-2-ones in acetonitrile

Compound	Yield of product (%)			Other compds
	 (mp/°C)	 (mp/°C)		
1c [X: $COCH_3$]	18.8 (208—209)	17.4 (223—225)	19.0	Dimer (trace)
1d [X: COC_2H_5]	14.0 (148—149)	11.5 (203—204)	36.4	—
1e [X: COC_3H_7]	18.2 (136.5—137.5)	14.4 (151—152)	35.5	—
1f [X: $COCH(CH_3)_2$]	15.0 (121—122)	17.7 (192—193)	39.0	—
1g [X: COC_6H_5]	18.4 (197—198)	20.4 (147—148)	28.9	Dimer (6.3), Benzoic acid (17.2)
1h [X: COC_6H_4-(*p*)-CH_3]	19.0 (206—207)	21.5 (203—204)	29.2	Dimer (4.8), *p*-Toluic acid (20.0)



Scheme 1.

appears to proceed *via* the following Scheme *i.e.*, i) a Norrish type I fission of the N–COR bond which may originate from the lowest excited singlet state $S_1(\pi\pi^*)$[2,3] to give benzoxazolonyl and acyl radicals, ii) the attack by the acyl radical upon the 4 and 6 positions in a solvent cage yielding the corresponding products, and iii) the escape of the radicals from the solvent cage reacting differently depending upon the nature of radicals. A part of the benzoxazolonyl radical abstracts hydrogen atoms from the solvent (acetonitrile) resulting in the formation of 2,3-dihydrobenzoxazol-2-one. A part of the benzoxazolonyl radical couples to each other to give the dimer. While the acyl radical gave the corresponding acid, presumably *via* oxidation of the intermediary aldehyde resulted from the hydrogen abstruction of acyl radical from the solvent.

In the photo-Fries rearrangement of aryloxy-1,3,5-triazines,[7a] the viscosity of solvent scarcely affected the ortho-rearrangement, but considerably affected the para-rearrangement. The viscosity dependence of the solvent upon the photochemical rearrangements has been examined in a EtOH–glycerol mixture. In the photolysis of **4f**, the para/ortho (6-/4-) ratios decreased with an increase in the glycerol contents; the ratios were 1.22, 0.88, and 0.55 in zero, 30, 60 glycerol volume percent respectively. This indicates that the dependence of the 6-rearrangement on the stiffness of the solvent cage is larger than that of the 4-rearrangement because the 6-position is separated by a longer path.

In summary, it has been shown that, in *N*-acyl-2, 3-dihydroxybenzoxazol-2-ones, Norrish type I fission takes place at the 3–8 bond to give photo-Fries rearrangement products, demonstrating that the 2,3-dihydrobenzoxazol-2-one skeleton is very photostable. This apparent photostability of 2,3-dihydrobenzoxazol-2-one may be interpreted as follows. If the fission of the 1–2 or 2–3 bond takes place upon irradiation, the free migration of the acyl radical to positions where odd π electron densities are large is hindered by the bond to the benzene nucleus through the hetero atom. Consequently the rate of back reaction to give the starting material would dominate other reactions. The lifetime and fluorescence quantum yield of this molecule **1a** is about 2 ns and $5(\pm 2)\times 10^{-2}$ in ethanol at room temperature respectively, indicating that the radiationless processes in the excited state of **1a**, other than the reaction predominant. The fluorescence quantum yield of **1f** was very small (approx. 10^2 less than that of **1a**), and the lifetime was unobservable.

Experimental

All melting points are uncorrected.

Materials. 2,3-Dihydrobenzoxazol-2-one was prepared according to the literature method.[12] *N*-Methyl-2,3-dihydrobenzoxazol-2-one was prepared by the alkylation of 2,3-dihydrobenzoxazol-2-one with dimethylsulfate, and *N*-acyl-2,3-dihydrobenzoxazol-2-ones by treatment of 2,3-dihydrobenzoxazol-2-one with acyl halide. A typical preparation is shown in the case of *N*-isobutyryl-2,3-dihydrobenzoxazol-2-one (**1f**). Isobutryl chloride (7.46 g, 0.07 mol) was added dropwise into a cold solution of 2,3-dihydrobenzoxazol-2-one (6.76 g, 0.05 mol) in pyridine (50 ml). After stirring for 1 h at room temperature, the mixture was poured into ice water and the resulting precipitate filtered and dried. Recrystallization from petroleum ether gave a pure sample (yield, 90%).

Irradiation. All irradiations were conducted with a low-pressure mercury lamp (30 W×2) and a typical reaction is shown in the case of *N*-benzoyl-2,3-dihydrobenzoxazol-2-one: A solution containing *N*-benzoyl-2,3-dihydrobenzoxazol-2-one (2.00 g, 8.36 mmol) in acetonitrile (100 ml) was irradiated for 48 h and the photochemical reaction monitored by TLC. After removal of the solvent, the residue was chromatographed on a silica gel column using a benzene–acetone mixture (10: 1, v/v) as an eluent and gave the following products: a) starting material (0.30 g, 1.26 mmol) which was identified by a mixed-melting point test with an authentic sample. b) 6-Benzoyl-2,3-dihydrobenzoxazol-2-one (recrystallized from benzene): yield, 0.31 g (18%); MS *m/e* 239 (M^+); PMR ($CDCl_3$), δ 6.93—7.88 (m, 8H), 10.70, (broad, 1H); IR (KBr), 3200 (-NH), 1780 (C=O, ring), 1640 cm^{-1} (C=O). Found: C, 69.92; H, 3.78; N, 5.66%. Calcd for $C_{14}H_9NO_3$: C, 70.29; H, 3.79; N, 5.86%. This compound was decomposed in refluxing hydrochloric acid (20 wt %) for 40 h to give crude 4-amino-3-hydroxybenzophenone. Recrystallization from benzene gave a pure sample: yield, 0.33 g (88%); mp 134—135 °C; MS *m/e* 213 (M^+);

IR (KBr), 3480, 3360 (OH), 3150 cm^{-1} (NH_2). Found: C, 73.35; H, 5.21; N, 6.80%. Calcd for $C_{13}H_{11}NO_2$: C, 73.22; H, 5.20; N, 6.57%. c) 4-Benzoyl-2,3-dihydrobenzoxazol-2-one (recrystallized from benzene): yield, 0.35 g (21%); MS *m/e* 239 (M^+); PMR ($CDCl_3$), δ 6.97—7.85 (m, 8H), 10.00 (broad, 1H); IR (KBr), 3120, 3040 (NH), 1850 (C=O, ring), 1640 cm^{-1} (C=O). Found: C, 70.14; H, 3.83; N, 5.96%. Calcd for $C_{14}H_9NO_3$: C, 70.29; H, 3.79; N, 5.86%. This compound was decomposed in refluxing hydrochloric acid for 10 h to give 2-amino-3-hydroxybenzophenone. Yield, 0.30 g (68%); mp 129.5—130.5 °C; MS *m/e* 213 (M^+). Found: C, 73.29; H, 5.28; N, 6.72%. Calcd for $C_{13}H_{11}NO_2$: C, 73.22; H, 5.20; N, 6.57%. d) Dimer (recrystallized from methanol): yield, 0.069 g (6%); mp 258—259 °C; MS *m/e* 268 (M^+); PMR (*p*-dioxane), δ 7.0—8.0 (m, 7H), 9.97 (broad, 1H); IR (KBr), 3250 (NH), 1780, 1760 cm^{-1} (C=O, ring). Found: C, 62.91; H, 3.11; N, 10.33%. Calcd for $C_{14}H_8N_2O_4$: C, 62.91: H, 3.11; N, 10.45%. e) Benzoic acid (sublimed under reduced pressure) which was identified by a mixed-melting point test with an authentic sample: yield, 0.15 g (17%).

Measurements of the Isomer Ratios. After irradiation in a given solvent, the products were seperated by silica gel TLC using a mixture of benzene and acetone (20: 1 in volume) as the developing solvent. From the chromatogram each isomer was extracted and diluted with ethanol to a fixed volume and the extinction measured spectrophotometrically.

Measurements of Fluorescence Lifetime. The experimental procedure is reported elsewhere.[13]

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