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PHOTOCHEMICAL AND THERMAL REACTIONS OF 2-ARYLOXYBENZOHYDROXAMIC ACIDS

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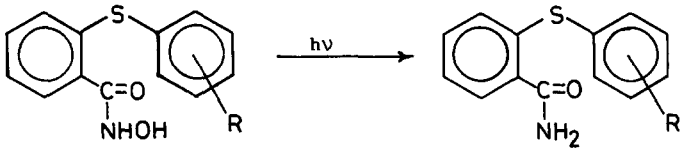
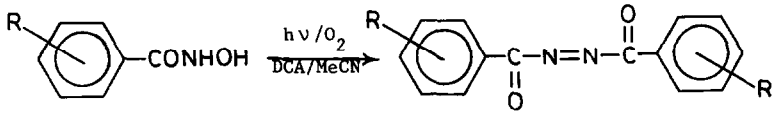
Abstract - 2-Aryloxybenzohydroxamic acids 1-7 were subjected to photolysis in benzene or methanol. In each case corresponding N-arylsalicylamides 8-10 were obtained in good yields. Compounds 1-7 on thermolysis in decaline also produced 8-10.

We have recently reported photodeoxygenation of 2-(arylthio)benzohydroxamic acids to 2-(arylthio)benzamides (eq. 1).[1,2] While searching for possible intermediates we have demonstrated formation of diacyldiazenes (eq. 2)[2] from simple benzohydroxamic acids. We have also shown that O-alkyl substituted benzohydroxamic acids under photolytic conditions provide same products as those observed in parent benzohydroxamic acids. These results pointed to an amidyl radical as a possible intermediate. No attempt was however made to characterise the radical intermediates, if any, by ESR.

Equation 1



Equation 2



In a related study we had an opportunity to compare the behaviour of 2-(aryloxy)benzohydroxamicacids and 2-(arylthio)benzohydroxamicacids in acid catalysed reactions. Whereas 2-(aryloxy)benzohydroxamicacids in PPA (polyphosphoric acid) lead to desired lactams,[3] 2-(arylthio)benzohydroxamic acids under identical conditions undergo novel facile oxygen transfer leading to 2-(arylsulfinyl)benzamides.[4-6] The observed difference in behaviour was attributed, amongst other things, to extended conjugation across S-bridge of protonated form of 2-(arylthio)benzohydroxamic acids.

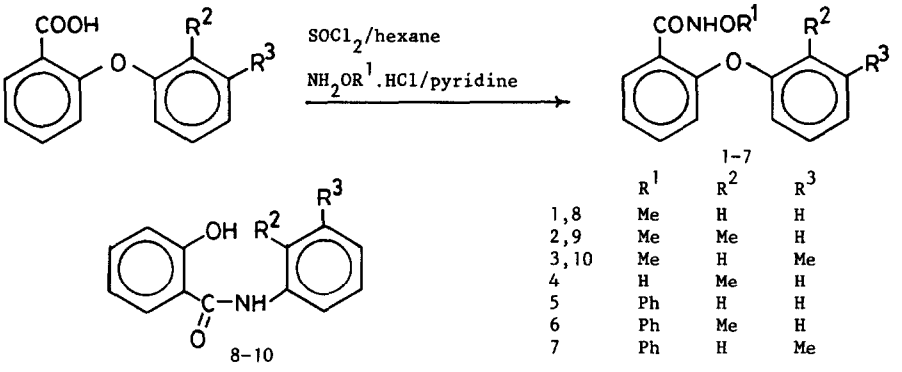
Hence it was thought worthwhile to investigate photochemistry of 2-(aryloxy)benzohydroxmic acids. Since we were unable to obtain direct evidence of radical formation in our earlier studies,[1,2] we have also investigated thermal reactions of 2-(aryloxy)benzohydroxamic acids. The results of this study, which are described in this paper, point to common processes in

photolysis and thermolysis of title compounds, thereby indicating involvement of radical intermediates.

Synthesis of 2-(aryloxy)benzohydroxamic acids (1-7) (Scheme - 1)

2-(Aryloxy)benzoic acids[7,8] were converted to the corresponding acid chlorides. The acid chlorides were reacted, without further purification, with corresponding hydroxylamine derivatives viz. O-methylhydroxylamine hydrochloride,[9] O-phenylhydroxylamine hydrochloride[10] to give 1-7 in 60-62% yield.

Scheme 1



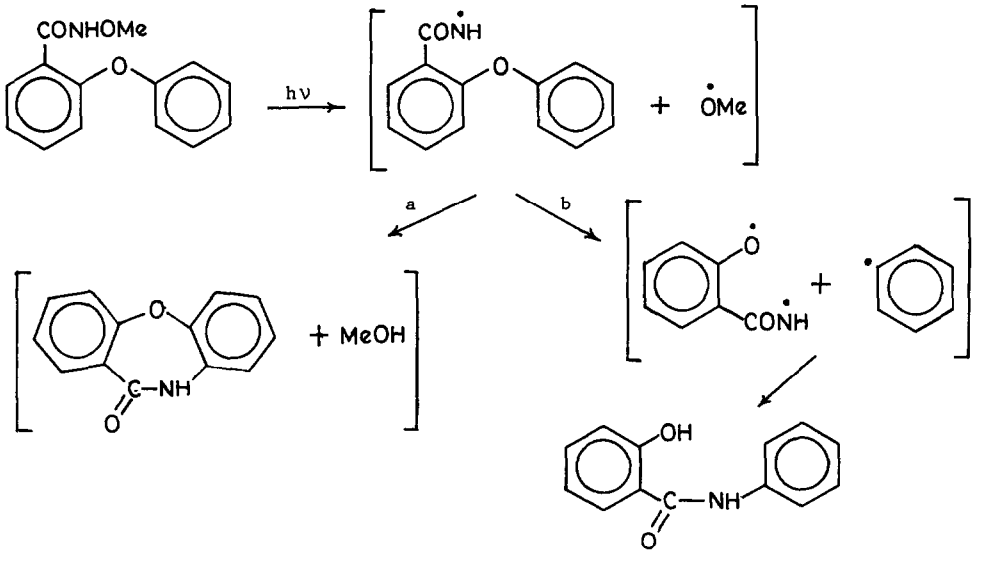
	R^1	R^2	R^3
1,8	Me	H	H
2,9	Me	Me	H
3,10	Me	H	Me
4	H	Me	H
5	Ph	H	H
6	Ph	Me	H
7	Ph	H	Me

N-arylsalicylamide 8-10[11] were prepared from methyl salicylate and corresponding aniline derivatives (eq. 3).

Photolysis of 2-(aryloxy)benzohydroxamic acids 1-7 (Table - 1)

O-methyl-2-phenoxybenzhydroxamic acid (1) was irradiated in benzene/methanol as described in experimental section. The product isolated after the usual work-up provided N-phenylsalicylamide (8). The formation of 8 is rather unusual and more than one pathway can be postulated (Scheme-2). Path 'a' involving cyclic lactam intermediate and path 'b' involving recombination of radical fragments. These can be easily differentiated in case of substituted 2-(aryloxy)-benzohydroxamic acids, wherein substitution pattern of product arising from path 'a' and path 'b' would be distinctly different.

Scheme 2



For this purpose O-methyl-(2-methylphenoxy)benzohydroxamic acid (2) and O-methyl-(3-methylphenoxy)benzohydroxamic acid (3) were irradiated under identical conditions. They afforded corresponding N-arylsalicylamides 9 and 10. It is evident from the position of methyl group in 9 and 10 that amide linkage is formed at the same carbon which had aryl ether linkage in

compounds 2 and 3. This eliminates mechanism involving path 'a' which would result in different substitution pattern.

If formation of amidyl radical is indeed the first step same results would be obtained irrespective of substitution on hydroxyl oxygen. For this purpose, the reaction was extended to compounds 4-7. In each case the expected N-arylsalicylamide 8-10 was formed.

Thermolysis of 2-(aryloxy)benzohydroxamic acids 1-7 (Table 1)

2-(Aryloxy)benzohydroxamic acids (1-7) were thermolysed in decalin at reflux temperature as described in experimental section. In each case coresponding N-arylsalicylamide was produced albeit in lower yields.

In conclusion it can be stated that photolysis and thermolysis of 2-(aryloxy)benzohydroxamic acids (1-7) produce identical results indicating a common radical process. Though exact mechanism of formation of N-arylsalicylamide is uncertain, it seems to involve amidyl radical formation as first step as evident from the fact that O-substituted 2-(aryloxy)benzohydroxamicacids lead to same product irrespective of nature of substitution of hydroxyl oxygen.

EXPERIMENTAL

All the melting points reported are uncorrected. IR spectra were recorded on Hilger-Watts infracord model H-900 and Beckman spectrophotometer model IR-4250. Mass spectra were recorded on Varian Mat CH-7 and Mat-6 spectrometers. NMR spectra (δ, ppm) were scanned on Varian EM-360 at room temperature using TMS as an internal standard and $CDCl_3$ as a solvent. Photoirradiations were carried out using high pressure Hg-lamp USHIO-UM-452 (450 watts). An induction period of 10 minutes was given to lamp prior to photolysis. Spectral data of some of compounds are given in Table 2. All new compounds gave satisfactory elemental analyses.

Preparation of 2-(aryloxy)benzohydroxamic acids 1-7

2-(Aryloxy)benzoic acid(0.01 mole), hexane (50 ml) and thionyl chloride (1 ml) were refluxed on steam bath for 4 hrs. The reaction mixture was filtered and filtrate was concentrated. Fresh hexane (50 ml) was added and solvent was distilled off again. The oily residue of acid chloride was used as such for the next step.

2-(Aryloxy)benzoyl chloride (0.01 mole), O-substituted hydroxylamine hydrochloride (0.91 mole) and pyridine (5 ml) were heated on steam bath for 30 minutes. The reaction mixture was cooled and diluted with dry benzene. White precipitate of pyridine hydrochloride was filtered off. The benzene layer was washed successively with saturated sodium bicarbonate (2 x 25 ml) and alkali (10%, 2 x 25 ml). The alkali extract on neutralization afforded 2-(aryloxy)benzohydroxamic acid (1-7) in 60-62% yield.

Photolysis of 2-(aryloxy)benzohydroxamic acids 1-7

2-(Aryloxy)benzohydroxamic acid (0.0003 mole) was dissolved in 100 ml of solvent irradiated with high pressure Hg-lamp for 5 hours. The solvent was removed by flash evaporation. The semisolid thus obtained was passed through column of silica gel (12 cm, 8.0 mm, E. Merck, 6.0 g). Elution with benzene 250 ml afforded corresponding N-arylsalicylamide which was found identical with the samples (8-10) prepared as described below (mmp, co-IR, co-TLC).

Thermolysis of 2-(aryloxy)benzohydroxami acids 1-7

2-(Aryloxy)benzohydroxamicacid (0.0016 mole) was dissolved in decalin (50 ml) and refluxed under Nitrogen atmosphere. On cooling it afforded solid which was crystallised from benzene:petroleum ether (60-80°) to give N-arylsalicylamide found identical with the authentic samples (8-10) prepared as described below (mmp, co-IR, co-TLC).

Preparation of authentic samples of N-arylsalicylamides 8-10[11]

A mixture of methylsalicylate (1.52 g, 0.01 mole) and aniline derivative (0.01 mole) was refluxed for 3 hours. The reaction was cooled, treated with crushed ice and extracted with chloroform (2 x 30 ml). The chloroform extract was washed with hydrochloric acid (1:1, 2 x 35 ml) and water. The dried chloroform extract on evaporation gave a solid which was crystallised from benzene-petroleum ether (60-80°) to give N-arylsalicylamide.

Table 1

Starting compound	Product	hν/MeOH % yield	hν/C_6H_6 % yield	Δ / Decalin % yield
1	8	71	65	-
2	9	72	66	44
4	9	56	44	33
3	10	72	61	-
5	8	70	65	44
6	9	71	65	37
7	10	72	66	39

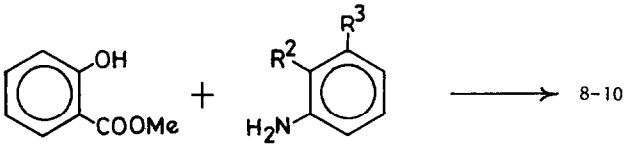


Table 2

Cpd.	m.p. °C	I.R. (KBr) cm^{-1}	NMR ($CDCl_3$) ppm	m/z	Molecular formula	Elemental Analysis	C	H	N
1	68	3280,2900,1660, 1600	-	-	$C_{14}H_{13}NO_3$	Calc.	69.13	5.34	5.76
						Found	69.45	5.58	5.92
2	93	3340,3200,2900, 1660,1590	2.26 (s,3H), 3.95 (s,3H), 6.56-8.34 (m, 8H), 10.26 (s, 1H).	-	$C_{15}H_{15}NO_3$		-	-	-
3	Oil	3340,3200,2900, 1650	-	-	$C_{15}H_{15}NO_3$		-	-	-
4	155	3360,3100,2840, 1616,1590	-	-	$C_{14}H_{13}NO_3$		-	-	-
5	114	3120,2920,1650	6.54-8.58 (m,14H), 10.26 (s,1H)	305(M^+)	$C_{19}H_{15}NO_3$	Calc.	74.15	4.91	4.59
						Found	74.27	5.35	4.51
6	108	3120,2920,1650	2.26 (s,3H), 6.56-8.40 (m,13H), 10.31 (s,1H)	319(M^+)	$C_{20}H_{17}NO_3$	Calc.	75.23	5.32	4.38
						Found	75.06	5.62	4.32
7	120	3140,2960,1655	-	-	$C_{20}H_{17}NO_3$	Calc.	75.23	5.32	4.38
						Found	75.12	5.21	4.26
8[11]	135	3320,3050,1610	-	-	$C_{13}H_{11}NO_2$	Calc.	73.23	5.16	6.57
						Found	73.29	5.34	6.12
9[11]	145	3300,3100,1625	2.39 (s,3H), 6.86-7.8 (m,9H), 12.04 (s,1H)	-	$C_{14}H_{13}NO_2$	Calc.	74.00	5.72	6.16
						Found	73.45	5.18	6.35
10[11]	135	3300,2900,1615	-	-	$C_{14}H_{13}NO_2$	Calc.	74.00	5.72	6.16
						Found	74.11	5.35	6.07

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