

N. A. Al-Jalal

Chemistry Department, Kuwait University,
P. O. Box 5969, 13060 Safat, Kuwait
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Methoxy-, methyl-, and chloro-substituted benzonitriles undergo photocycloaddition to phenol to give substituted 1,2-dihydroazocin-2-ones **III**, by initial attack of the cyano group on the aromatic ring of the phenol. The efficiency of the photocycloaddition reaction varied with the position of the substituents, with the *para*-substituted ones giving the largest amount of photoproduct.

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Introduction.

In a previous report we have shown that nitrile groups undergo photocycloaddition to benzene rings in a manner analogous to that of acetylenes [1] to give azocines [2]. This facile direct access to the azacyclooctatetraene skeleton is of appreciable interest since such compounds are known to have hypnotic and anticonvulsive action [3] and to stimulate the central nervous system [4]. And more recently we have shown that not only benzenes substituted with both electron donor and electron acceptor substituents in a *para*-relationship produces azocines, but also phenol and certain substituted phenols readily undergo 1,2-addition of the nitrile group and thus yield 1,2-dihydroazocin-2-ones [5]. This process is also of considerable photochemical interest since the cycloaddition reactions involving phenols have been previously limited to the formation of a tricyclo-[5.2.1.0^{2,6}]dec-7-en-10-one [6] from cyclopentene and phenol, and the addition of acrylonitrile to 2-naphthol giving the cyclobutanol **IV** [7].

In our attempt to enhance our understanding about the factors controlling this type of addition we have investigated the photochemical reactions of various substituted benzonitriles with phenol. We have studied the following: benzonitrile, *o*-, *m*- and *p*-hydroxybenzonitrile, *o*-, *m*- and *p*-methoxybenzonitrile, *o*-, *m*- and *p*-methylbenzonitrile, *o*-, *m*- and *p*-aminobenzonitrile, *o*-, *m*- and *p*-nitrobenzonitrile and *o*-, *m*- and *p*-chlorobenzonitrile. We have observed that the photolabilities of these arenes in the presence of phenol vary appreciably and we now report details of these results.

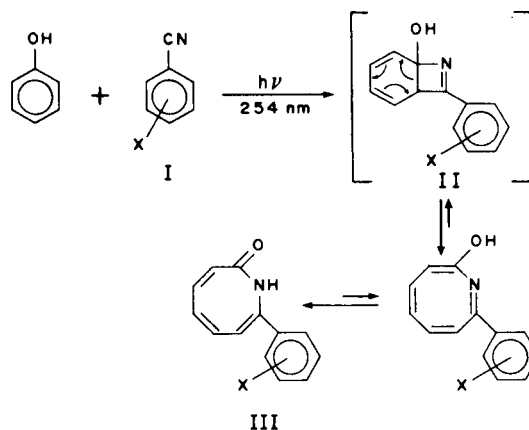
Results and Discussion.

Irradiation of phenol (0.1 *M*) and the substituted benzonitriles **I**_{a-m} (1.0 *M*) in acetonitrile solution, produced only one major photoproduct in each system, except for benzonitriles **I**_b, **I**_i and **I**_m, where no photochemical reaction was observed. All photoproducts were yellow in colour and were separated with >99% purity (gc) by flash chromatography. The 300 MHz ¹H nmr spectra of these photoproducts **III**_a and **III**_{c-k} showed the presence of only ethenyl

(5H, δ 6.70-7.20), aromatic (4H, δ 7.25-7.55) and amide protons (1H, δ 9.25); plus methoxy or methyl protons in the case of adducts **III**_{c-h}. From the various spectroscopic properties of these adducts (See Experimental Section), the substituted 8-phenyl-1,2-dihydroazocin-2-ones **III**_a and **III**_{c-h} were assigned.

The formation of the azocine photoproducts is accounted for by the reaction sequence presented in (Scheme I) and involves initial 1,2-photocycloaddition of the nitrile group to the aromatic ring of the phenol followed by ring

Scheme I



(X)	% Yield
a - H	20
b - OH (o-, m- and p-)	—
c - OCH ₃ (o-)	8
d - OCH ₃ (m-)	10
e - OCH ₃ (p-)	16
f - CH ₃ (o-)	8
g - CH ₃ (m-)	10
h - CH ₃ (p-)	13
i - Cl (o-)	8
j - Cl (m-)	10
k - Cl (p-)	16
l - NH ₂ (o-, m- and p-)	—
m - NO ₂ (o-, m- and p-)	—

Table 1

The Infrared, Electronic and Nuclear Magnetic Resonance Spectral Data of Compounds III_{c-h}.

Compound	Infrared Spectra (potassium bromide)		Electronic Spectra (Acetonitrile)		NMR (Deuteriochloroform)	
	Cm ⁻¹	ν	λ_{\max} (nm)	ϵ	δ (ppm)	Assignment (No. of protons)
III _c	1600 (m)	C=C	324	1680	3.90 (s)	(3) OCH ₃
	1670 (s)	C=O	420	418	6.70 (m)	(1) H-5
	3450 (br)	NH			6.95 (m)	(3) Ar-H, H-4
					7.22 (dd)	(1) H-7
					7.32 (m)	(1) H-6
					7.51 (m)	(2) Ar-H
					7.75 (dd)	(1) H-3
					9.25 (s)	(1) N-H
III _d	1600 (m)	C=C	295	1778	3.85 (s)	(3) OCH ₃
	1660 (s)	C=O	345	1415	6.72 (m)	(1) H-5
	3400 (br)	NH			7.0-7.3 (m)	(6) Ar-H, H-4, H-7
					7.35 (m)	(1) H-6
					7.73 (dd)	(1) H-3
					9.20 (s)	(1) N-H
III _f	1620 (m)	C=C	292	1221	2.20 (s)	(3) CH ₃
	1680 (s)	C=O	320	1816	6.72 (m)	(1) H-5
	3400 (br)	NH			6.92 (m)	(1) H-4
					7.2-7.6 (m)	(6) Ar-H, H-6, H-7
					7.70 (dd)	(1) H-3
					9.20 (s)	(1) NH
III _g	1600 (m)	C=C	272	2300	2.22 (s)	(3) CH ₃
	1670 (s)	C=O	335	1750	6.73 (m)	(1) H-5
	3400 (br)	NH			7.02 (m)	(1) H-4
					7.22 (dd)	(1) H-7
					7.35 (m)	(5) Ar-H, H-6
					7.70 (dd)	(1) H-3
					9.20 (s)	(1) NH
III _h	1600 (m)	C=C	275	2001	2.20 (s)	(3) CH ₃
	1660 (s)	C=O	331	1163	6.70 (m)	(1) H-5
	3400 (br)	NH			6.95 (m)	(1) H-4
					7.22 (m)	(3) Ar-H, H-7
					7.35 (m)	(1) H-6
					7.55 (d)	(2) Ar-H
					7.72 (dd)	(1) H-3
					9.25 (s)	(1) NH

Table 1 contd....

The Infrared, Electronic and Nuclear Magnetic Resonance Spectral Data of Compounds III_{c-k}.

Compound	Infrared Spectra (potassium bromide)		Electronic Spectra (Acetonitrile)		NMR (Deuteriochloroform)	
	Cm ⁻¹	ν	λ_{\max} (nm)	ϵ	δ (ppm)	Assignment (No. of protons)
III _i	1620 (m)	C=C	290	2100	6.72 (m)	(1) H-5
	1670 (s)	C=O	310	1650	7.02 (m)	(1) H-4
	3400 (br)	NH			7.22 (dd)	(1) H-7
					7.3-7.8 (m)	(6) Ar-H, H-3, H-6
					9.25 (s)	(1) NH
III _j	1620 (m)	C=C	285	2450	6.73 (m)	(1) H-5
	1670 (s)	C=O	315	1780	6.95 (m)	(1) H-4
	3400 (br)	NH			7.20 (dd)	(1) H-7
					7.32 (m)	(1) H-6
					7.4-7.7 (m)	(5) Ar-H, H-3
				9.25 (s)	(1) NH	
III _k	1620 (m)	C=C	284	4744	6.70 (m)	(1) H-5
	1660 (s)	C=O	308	6304	6.95 (m)	(1) H-4
	3400 (br)	NH			7.22 (dd)	(1) H-7
					7.33 (m)	(1) H-6
					7.42 (d)	(2) Ar-H
					7.63 (d)	(2) Ar-H
					7.72 (dd)	(1) H-3
				9.25 (s)	(1) NH	

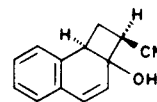
opening and tautomerization. Attempts were made to isolate the intermediate *ortho*-cycloadduct **II** by refluxing the crude reaction mixture after irradiation with *N*-phenylmaleimide in ethanol for 3 hours, and by the addition of tetracyanoethylene after irradiation (or during photolysis) at low temperature (-10°). However, no adduct was obtained.

Solvent polarity studies have shown that the azocine photoproduct formation is doubled upon change of solvent from cyclohexane to acetonitrile, but the effect is only evident for nitrogen degassed solutions (See Experimental Section). In a preparative experiment, irradiation of phenol (0.3 *M*) and 4-methoxybenzonitrile (3.0 *M*) in 20 ml acetonitrile solution with a 16-watt low pressure mercury arc-lamp for 48 hours gave 0.3 g (not optimized) of the azocine photoproduct, following flash chromatography.

The results, which are summarized in (Scheme I), clearly indicate that the formation of the azocine photopro-

ducts depend on the type and position of the substituents. In general, all substituted benzonitriles are less productive than benzonitrile itself. The *para*-substituted compounds give the largest amount of photoproduct of the substituted benzonitriles.

These results indicate that the addend requirements for this novel addition process are still not clear. But evidently, polar factors are important since the rate of the reaction in all cases is markedly increased with increase in solvent polarity. These observations strengthen our earlier suggestion [5], in which we have stated that the reaction may proceed by photo-induced electron transfer from the phenol to the cyano compound and the radical-ion species thus formed either undergo addition or react with oxygen.



IV

Table 2

Melting Points and Element Analysis of Compounds III_{c-k}

Compound No.	MP °C	Formula	Calcd. %				Found			
			C	H	N	Cl	C	H	N	Cl
III _c	68-70	C ₁₄ H ₁₃ NO ₂	74.0	5.72	6.16		74.2	5.83	6.08	
III _d	70-72	C ₁₄ H ₁₃ NO ₂	74.0	5.72	6.17		74.15	5.63	6.03	
III _f	65-67	C ₁₄ H ₁₃ NO	79.62	6.16	6.64		79.25	6.05	6.53	
III _g	63-65	C ₁₄ H ₁₃ NO	79.62	6.16	6.64		79.52	6.03	6.51	
III _h	68-70	C ₁₄ H ₁₃ NO	79.62	6.16	6.64		79.48	6.01	6.56	
III _i	92-94	C ₁₃ H ₁₀ ClNO	67.39	4.32	6.05	15.33	67.23	4.18	5.92	15.13
III _j	90-92	C ₁₃ H ₁₀ ClNO	67.39	4.32	6.05	15.33	67.18	4.22	5.96	15.22
III _k	95-97	C ₁₃ H ₁₀ ClNO	67.39	4.32	6.05	15.33	67.21	4.19	5.95	15.18

EXPERIMENTAL

An annular photoreactor model APQ40 (Applied Photophysics Limited) fitted with a 16-Watt low pressure mercury arc-lamp was used for the comparative irradiations of phenol (0.1 M) and the substituted benzonitriles (1.0 M) in quartz cells. The ¹H nmr spectra were obtained with a Bruker AM-300 MHz spectrometer. The chemical shifts are given as ppm (δ) and tetramethylsilane (δ = 0) was used as internal standard. Infrared and ultraviolet spectra were determined with a Perkin-Elmer 580 B and a Shimadzu UV-Visible recording spectrophotometer (UV 160), respectively. Mass spectra were recorded on a Ribermag R10-10C (Nermag). The gas chromatography (gc) was performed with a Varian 3300 instrument fitted with a flame ionization detector and an 8 m DB1-15W (OV 17) bonded phase capillary column. Melting points were taken on a Buchi 510 melting point apparatus. Microanalyses were done by H. Mallissa, Microanalytical Laboratory, West Germany.

The benzonitrile and all of the substituted benzonitriles were from Aldrich and were all used without further purification. Ethyl acetate and acetonitrile were purified by distillation before use. The photoproducts were isolated by flash chromatography using the method of Still *et al.* [8] using silica gel (E. Merck No. 9385, 40-60 μm) eluted with ethyl acetate-petroleum ether (40-60°) and using E. Merck TLC sheet No. 60 (silica gel) to monitor. The solutions were degassed by bubbling nitrogen for one hour before irradiation. The azocine photoproducts were identified from their spectroscopic data and by comparison with known azocines [2,5,9].

Photochemical Reaction of Phenol and the Substituted Benzonitriles.

Irradiation of phenol (0.1 M) and the substituted benzonitriles (1.0 M) in acetonitrile (20 ml) for 24 hours gave in each case where there is a photochemical reaction, an azocine photoproduct (yellow in colour) which was isolated in ~99% purity (gc, tlc one spot) by flash chromatography using 1:5 v/v mixture of ethyl acetate and petroleum ether (40-60°) as eluting solvent. In all cases, only 15% of the starting phenol was converted to the azocine products as indicated by gc. The results are reported in Tables 1 and 2, except for compounds III_a and III_e, since their spectroscopic properties have been published earlier [5].

Solvent Polarity Studies.

A "merry-go-round" apparatus fitted with a low pressure mercury arc-lamp was used for the solvent polarity studies using phenol (0.1 M) and all substituted benzonitriles (1.0 M) in four different solvents, acetonitrile, methanol, ethylacetate and cyclohexane in quartz tubes. The results, as checked by gc, showed that the amount of azocine photoproducts have doubled in going from cyclohexane to acetonitrile.

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