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Photolysis of 2-Aza-3-aryl-1,4-naphthoquinones in the Presence of Hydrogen Donors

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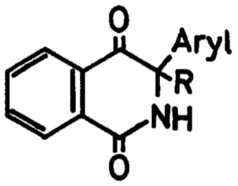
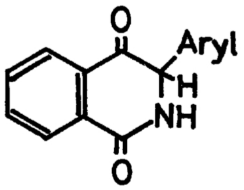
Photochemical reaction of 2-aza-3-phenyl-1,4-naphthoquinone and two derivatives **4** with a variety of hydrogen donors was investigated. Depending on the nature of hydrogen donors, (i) addition products **1** of hydrogen donor to the carbon-nitrogen double bond, (ii) hydrogenation products **2** of the >C=N- double bond, and (iii) ring contracted addition products **3** were obtained, but their yields are not of satisfactory.

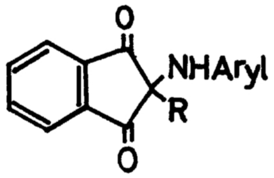
Recently A. Padwa published a comprehensive review on the photochemical reaction of compounds containing carbon-nitrogen double bond.[1] However, little is described in the review on the photochemical reaction of azaquinones. To our knowledge no photochemical reaction of azaquinones has been published. We now wish to report the photochemical reaction of azaquinones with a variety of hydrogen donors.



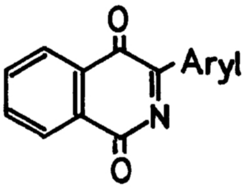
1a~c



2a~c



3a~c



4a~c

a:Aryl=C_6H_5 , b:Aryl=p-ClC_6H_4 , C:Aryl=p-$CH_3C_6H_4$

2-Aza-3-aryl-1,4-naphthoquinones **4** a-c,[3] prepared by the method of H.W Moore,[2] exhibits a characteristic absorption at about 540 nm region, which corresponds to the lowest excited state. The absorption band shifts to a shorter wave-length region in a solvent of higher polarity; λ_{max}=527 nm in CH_3CN, 535 nm in CH_2Cl_2, and 555 nm in hexane, ε=200. The effect of the solvents on λ_{max} indicates that the lowest excited state of **4** is of a character of n,π^* excitation.

Upon irradiation of an acetonitrile solution (30 ml) of **4** (1.3 mmol) and a hydrogen donor (2.2 mmol) in a Pyrex vessel using a 300W high pressure Hg lamp for 20-25 h at room temperature aralkyl benzenes as hydrogen donors afforded products **1**, whereas ethereal hydrogen donors gave both of products **2** and **3**. As Table shows yields of isolated products are poor, in general. After chromatographic separation of products on Silica gel a large amount of intractable matters was remained on the adsorbent. This is partly due to photochemical and/or thermal instability of the products.

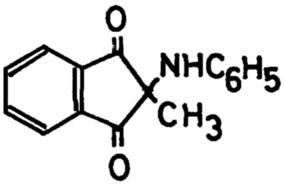
Table YIELDS OF PRODUCTS[6,f]

Azaquinones	H-Donors(R-H) R-	Products[a]		
		1	**2**	**3**
4 a (109-10)	9-Xanthenyl	60%(204.5-5.5)	$<$5%[b]	–[c]
	$C_6H_5CH_2$-	15%(227-9)	$<$5%[b]	–[c]
	p-$CH_3C_6H_4CH_2$-	18%(255-6)	$<$5%[b]	–[c]
	3,5-$(CH_3)_2C_6H_3CH_2$-	18%(225-6)	$<$5%[b]	–[c]
	α-Tetrahydrofuryl	–[c]	14%[d]	15%(206-8)[e]
	α-1,4-Dioxanyl	–[c]	$<$5%[b]	13%(201-2.5)
	α-Tetrahydropyranyl	–[c]	30%[d]	5%(202-3)
	$C_2H_5OCH(CH_3)$-	–[c]	$<$5%[b]	7%(132-3.5)
4 b (90-2)	9-Xanthenyl	22%(167-9)	$<$5%[b]	–[c]
	α-Tetrahydrofuryl	–[c]	$<$5%[b]	12%(194-5)
4 c (152-4)	9-Xanthenyl	29%(159-60.5)	$<$5%[b]	–[c]
	α-Tetrahydrofuryl	–[c]	$<$5%[b]	15%(203-4)

a) Isolated yields, calculated on the basis of azaquione used. b) Detected by TLC. c) Not detected by TLC. d) mp 239-41 °C. e) Other products (4%) of unidentified structure were isolated. f) Values in parenthesis show melting points of the compounds (°C).

The structures of the products were determined on the basis of their spectral data. The IR spectra of **1** a-c showed the characteristic absorption of amide-NH, carbonyl, and C-C double bond. Their ^{1}H-NMR spectra were all compatible with the structures **1**a-c, which were substantiated by Mass and elemental analyses.[6] The structures of **1** a (in the case of R: p-$CH_3C_6H_4CH_2$-) and **2** were confirmed further by comparison with their authentic sample.[4] The structures of the products **3** were determined on the basis of their spectral data (^{1}H-NMR, IR) by comparing them with those of 2-anilino-2-methylindan-1,3-dione **5** prepared from 2-bromo-2-phenylindan-1,3-dione and aniline.[5]

An investigation of the above reactions by CIDNP technique revealed unambiguously a contribution of radicals in the reaction paths; the products **1** were produced via radical species, for polarlized signals corresponding to **1** could be observed.[7] However, the mechanism of the formation of the ring contracted products **3** remains still to be clarified.[8]



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References and Notes

1) A. Padwa, Chem. Rev., 77 , 37 (1977)

2) H. W. Moore and D. S. Pearce, Tetrahedron Lett., 1971 , 1621

3) The compounds **4** b and **4** c were synthesized first by the present authors.

4) H. W. Moore, Chem. Soc. Rev., 2 , 415 (1973)
I. Felner and k. Schenker , Helv. Chim. Acta, 52, 1810 (1969)

5) D. T. Nowry , E. L. Ringwald, and M. Renoll, J. Am. Chem. Soc., 71, 120 (1949)

6) The spectral data of the representatives of products are as follows;
3-phenyl-3-(9-xanthenyl)-1,2,3,4-tetrahydroisoquinoline-1,4-dione **1** a(R: 9-Xanthenyl) mp 204-5.5 °C : ^{1}H-NMR($CDCl_3$) δ 5.35 (1H, s), 6.42 (1H, bs), 6.31 (2H,d), 6.5-8.1 (15H, m) ; IR(KBr) 3310, 3090, 2930, 2880 (NH,CH), 1670 (C=O), 1600, 1580 (C=C) cm^{-1}. 2-Anilino-2-(2-tetrahydrofuryl)indan-1,3-dione **3**a (R: α-Tetrahydrofuryl) mp 206-8 °C : ^{1}H-NMR($CDCl_3$) δ 1.6-2.4 (4H,m), 3.7 (2H, t, J=5 Hz), 4.30 (1H, t, J=7 Hz), 4.52 (1H, bs), 6.40 (2H, d, J=8 Hz), 6.74 (1H, t, J=8 Hz), 7.02 (2H, t, J=8 Hz), 8.00 (4H,m) ; IR (KBr) 3320 (NH), 1745, 1705 (C=O), 1600 (C=C).

7) For example, in the reaction of **4**a with xanthene a ^{1}H-NMR absorption polarized signal due to $9'$-proton of xanthenyl moiety of **1** a (R: 9-Xanthenyl) was clearly observed during irradiation.

8) In the reaction of **4**a with ethereal hydrogen donors strong ^{1}H-CIDNP signals due to olefins, which were produced via dehydrogenation of the hydrogen donors, were observed without exception. The resulting olefins were confirmed by comparisons of their ^{1}H-NMR signals with those of the authentic samples.

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