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PHOTOLYSIS OF 1,3,4-OXADIAZOLES IN ALCOHOLS[1)]

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Irradiation of 2,5-diphenyl-1,3,4-oxadiazole in alcohols induces a heterolytic addition of alcohols to the C=N bond of the oxadiazole, followed by cycloelimination to yield benzoic acid ester and benzonitrile imine. The latter reacts with the oxadiazole to form 4-benzamido-3,5-diphenyl-1,2,4-triazole which is photochemically transformed into benzamide and 3,5-diphenyl-1,2,4-triazole. Upon irradiation of 2-phenyl-1,3,4-oxadiazole in methyl alcohol, the 1:1 adduct is obtained.

Previously, we reported the unique photochemical additions of furan[2)], indene[3)], and benzo[b]-thiophenes[4)] to the C=N bond of 2,5-diaryl-1,3,4-oxadiazole. We report here the novel photolysis of 1,3,4-oxadiazoles in alcohols which provided unambiguous evidence supporting heterolytic addition of alcohols to the C=N bond of 1,3,4-oxadiazoles.

When a solution of 1.11 g (5×10^{-3} mol) of 2,5-diphenyl-1,3,4-oxadiazole (1a) in 250 ml of methyl alcohol was irradiated, benzamide, methyl benzoate, and 3,5-diphenyl-1,2,4-triazole (2a) were obtained, together with recovery of 1a. Neither reductive nor alkylated products were formed, although the

Table 1. Photolysis of 2,5-Diaryl-1,3,4-oxadiazoles (1) in Alcohols[a)]

1	ROH	Products, %			Recovery of 1, %
		$ArCONH_2$	$ArCO_2R$	2	
1a	MeOH	42	19	31	34
〃	EtOH	40	13	30	37
〃	i-PrOH	54	10	15	38
〃	t-BuOH[b)]	5	2	1	84
1b	MeOH	16	4	3	74
〃	i-PrOH	22	trace	1	78

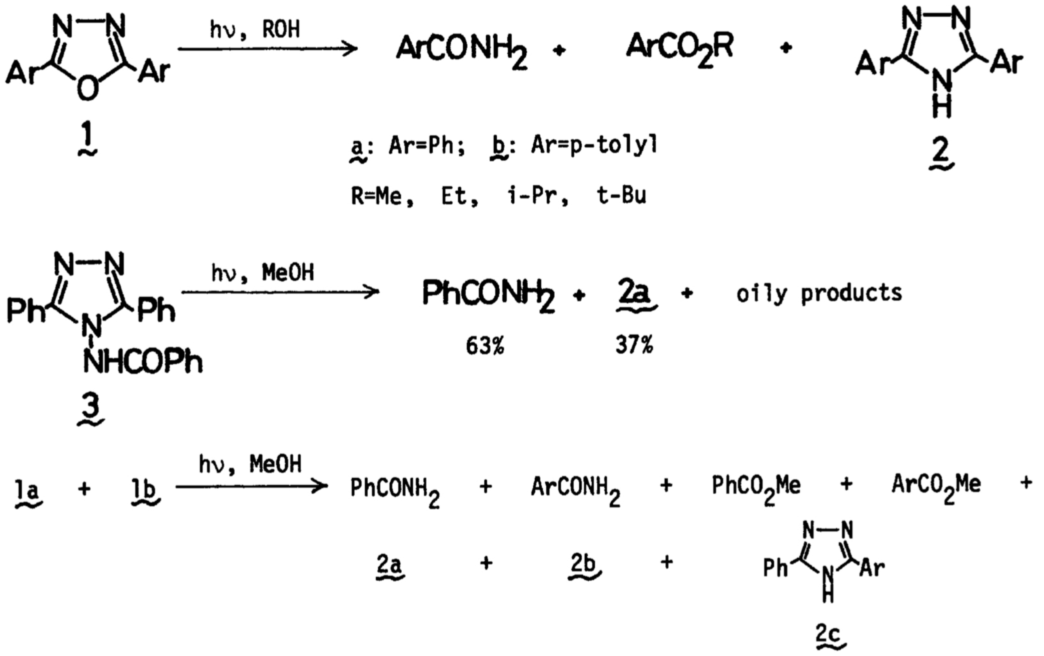
a) Irradiation was performed with Pyrex-filtered light from a 300-W high pressure mercury lamp (taika HLV-B) below 20°C for 20 hr, in a nitrogen atmosphere.

b) In this case, 4-benzamido-3,5-diphenyl-1,2,4-triazole (3) was isolated in 1% yield.

processes which have been observed for the photochemistry of imine systems in alcohols are photoreduction and photoalkylation. Irradiations of 1a and 2,5-di(p-tolyl)-1,3,4-oxadiazole (1b) in several alcohols were performed under similar conditions, and the results are summarized in Table 1.

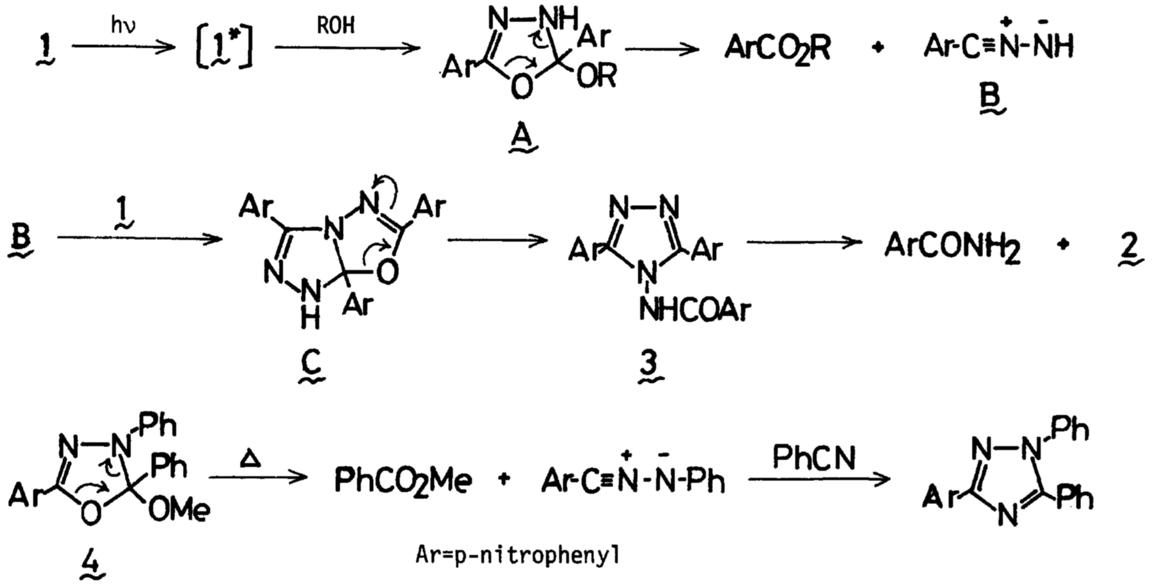
2a: Mp 194-195°C (lit.[5]) mp 189°C), IR 3200-2800 cm^{-1} (NH), MS m/e 221 (M^+), 193 (M^+ - N_2), 118 (M^+ - PhCN), 103, 91, 77. 3,5-Di(p-tolyl)-1,2,4-triazole (2b): Mp 255-257°C, IR 3200-2800 cm^{-1} (NH), MS m/e 249 (M^+), 221 (M^+ - N_2), 132 (M^+ - MeC_6H_4CN), 117, 105, 103, 91.

The transformation of alcohols into the respective benzoates involves a fission of polar O-H bond rather than homolytically weaker α-C-H bond of alcohols. This is strongly supported by the formation of t-butyl benzoate upon irradiation of 1a in t-butyl alcohol having no α-hydrogen atom. In addition, 4-benzamido-3,5-diphenyl-1,2,4-triazole (3) among the photolysates of 1a in t-butyl alcohol was isolated. 3: Mp 239-240°C (lit.[5]) mp 240°C); IR 3200-2800 (NH), 1680 cm^{-1} (CO); MS m/e 340 (M^+), 312 (M^+ - N_2), 221 (M^+ - PhNCO), 119, 105, 89, 77. Irradiation of 3 in methyl alcohol gave benzamide and 2a, besides unidentified oily products. Therefore benzamide and 2a shown in Table 1 may be interpreted as secondary products arising via photolysis of 3. When a mixture of 1a and 1b in methyl alcohol was irradiated, a mixture of three triazoles, 2a, 2b, and 3-phenyl-5-p-tolyl-1,2,4-triazole (2c) was formed together with the respective benzamides and benzoates.[6]



Scheme 1

On the above observations, the reaction would proceed via initial formation of 2-alkoxy-2,5-diaryl-1,3,4-oxadiazoline A by the reaction of an excited state of 1 with the alcohol. This is followed by cycloelimination of A to yield benzoic acid ester and nitrile imine B, and subsequent 1,3-dipolar

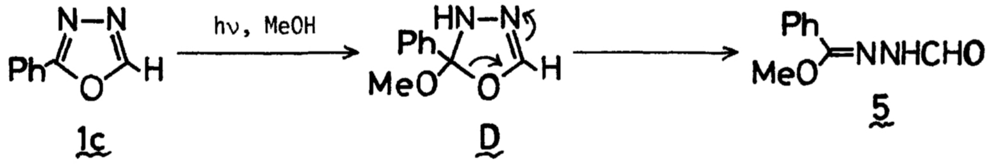


Ar=p-nitrophenyl

Scheme 2

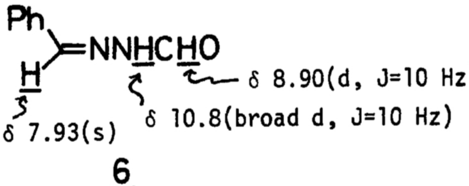
cycloaddition of **B** to the C=N bond of **1** yields cycloadduct **C**. Ring opening of **C** with the concurrent hydrogen shift affords **3** which upon irradiation in alcohol is transformed into benzamide and **2**. The process of the formation of benzoic acid ester and **B** from **A** is analogous to that of thermolysis of 2-methoxy-2,3,5-triaryl-1,3,4-oxadiazoline (**4**) in benzonitrile[7] (Scheme 2).

Upon irradiation in methyl alcohol for 5 hr, however, 2-phenyl-1,3,4-oxadiazole (**1c**) gave 1-(α-methoxybenzylidene)-2-formylhydrazine (**5**) in 7% yield, together with 53% recovery of **1c**. Structural elucidation of **5** was accomplished on the basis of spectral data.



Scheme 3

5: Mp 120-121°C; IR 3200 (NH), 1740 cm^{-1} (CO); NMR ($CDCl_3$) δ 3.80 (3H, s, OCH_3), 7.3-7.8 (5H, m, ArH), 8.76 (1H, d, CHO, J=11 Hz, changed to a singlet when treated with D_2O), 10.0 (1H, broad d, NH, J=11 Hz, exchanged with D_2O); MS m/e 178 (M^+), 177, 149 (M^+ - CHO), 147 (M^+ - OMe), 134 (M^+ - NHCHO), 105, 104, 103, 91, 77. The NH and formyl proton NMR signals of **5** are comparable to those of benzaldehyde formylhydrazone (**6**), mp 137-138°C.



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It is interpreted that **5** is formed via 2-methoxy-2-phenyl-1,3,4-oxadiazoline **D** as depicted in Scheme 3. The formation of

5 definitely shows a heterolytic addition of methyl alcohol to the C=N bond of **1c**. The mode of fission of intermediary adduct **D** is different from that of **A**; this seems to be somewhat analogous to the observation which the mode of thermolysis of 2-ethoxy-3,5-diaryl-1,3,4-oxadiazoline[8] differs from that of **4**.

References and Notes

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6) Photoproducts were isolated by chromatography on silica gel using chloroform as an eluent. The IR spectrum of the mixture of triazoles was very similar to those of triazoles **2a** and **2b**, and its MS showed parent ions at m/e 249 (**2b**$^+$), 235 (**2c**$^+$), and 221 (**2a**$^+$).

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