Tetrahedron. Vol. 29, pp. 529 to 532. Pergamon Press 1973. Printed in Great Britain

STUDIES OF HETEROAROMATICITY—LXVI[1]

PHOTOCHEMICAL AND THERMAL BEHAVIOURS OF HETEROCYCLES INVOLVING AZIDO-KETONE MOIETY

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(*Received in Japan* 16 *October* 1972; *Received in the UK for publication* 30 *October* 1972)

Abstract—The photolyses and thermolyses of compounds 1 and 2 in a nucleophilic solvent such as alcohol and diethylamine have been studied and form 4,5-disubstituted amino and alkoxy or dialkylamino groups. The mechanism for the formation of the products are proposed and discussed.

The chemistry of heteroaromatic nitrenes has been received little attention compared with arylnitrenes.[2,3]

Following on the thermal and photochemical behaviour of tetrazolo-azido polyazine derivatives,[4] we report similar reactions of azidopyridazinones which were carried out to obtain further evidence that a hetarylnitrene is involved, because of the presence of a powerful activating azido function adjacent to a CO group in the heterocyclic systems.

RESULTS

1,2-Dimethyl-4-azido-pyridazine-3,6-dione (1) was prepared by a modified method of Hassner *et al.*[5] Heating 3,5-dichloropyridazine-6-one with equimolar sodium azide gave 1-phenyl-3-chloro-5-azido-pyridazine-6-one (2).

The photolyses of 1 and 2 were performed using a 300W high pressure mercury lamp under nitrogen at room temperature. The thermolyses of 1 and 2 were carried out in solvents such as methanol, ethanol and diethylamine as a nitrene trapping agent, in a sealed tube at 120–130°. These results are summarized in Table 1.

Irradiation of 1 in methanol gave 1,2-dimethyl-4-*gem*-dimethoxy-5-amino-4,5-dihydropyridazine-3,6-dione (3) and 1,2-dimethyl-4-methoxy-5-amino-pyridazine-3,6-dione (4) together with a small amount of 1,2-dimethyl-4-cyanoimidazolidine-3,5-dione (5). In the case of the thermolysis of 1 in methanol, compounds (4) and (6) were isolated. On the other hand, photolysis and thermolysis of 1 in diethylamine afforded only 8 in 30 and 81% yields, respectively. When 2 was irradiated in alcohol, 9* was obtained, which was also prepared by heating 2 at 120°. In the case of 2 in diethylamine both by photolysis and thermolysis, only 10 was obtained in high yield instead of the expected 11. Structural elucidation of these products was based on the spectral data and the elemental analyses (Experimental). In contrast to the photochemical and thermal behaviour, compound 1 was very stable in a strong acid even at 100°, probably because of the ready protonation of the CO groups.

2-Azido-1,4-benzoquinone derivatives have been shown to rearrange in a strong acid to γ-cyanoalkylidine-$\delta^{\alpha,\beta}$-butenolides, whereas the

Table 1. Product distributions of photolyses and thermolyses of 1 and 2

Compound No.	Solvent	Reaction conditions Time (hr)		Product yield (%)	
1	MeOH	2	hν	3(44)	4(20) 5(5)
	MeOH	7·5	130°		4(25) 6(10)
	$HN(Et)_2$	3·5	hν	8(30)	
		3	120°	8(81)	
2	MeOH	1·3	hν	9a(46)	
	MeOH	4	120°	9a(40)	
	EtOH	2·7	hν	9b(56)	
	EtOH	4	120°	9b(54)	
	$HN(Et)_2$	2	hν	10(70)	
	$HN(Et)_2$	2	120°	10(75)	

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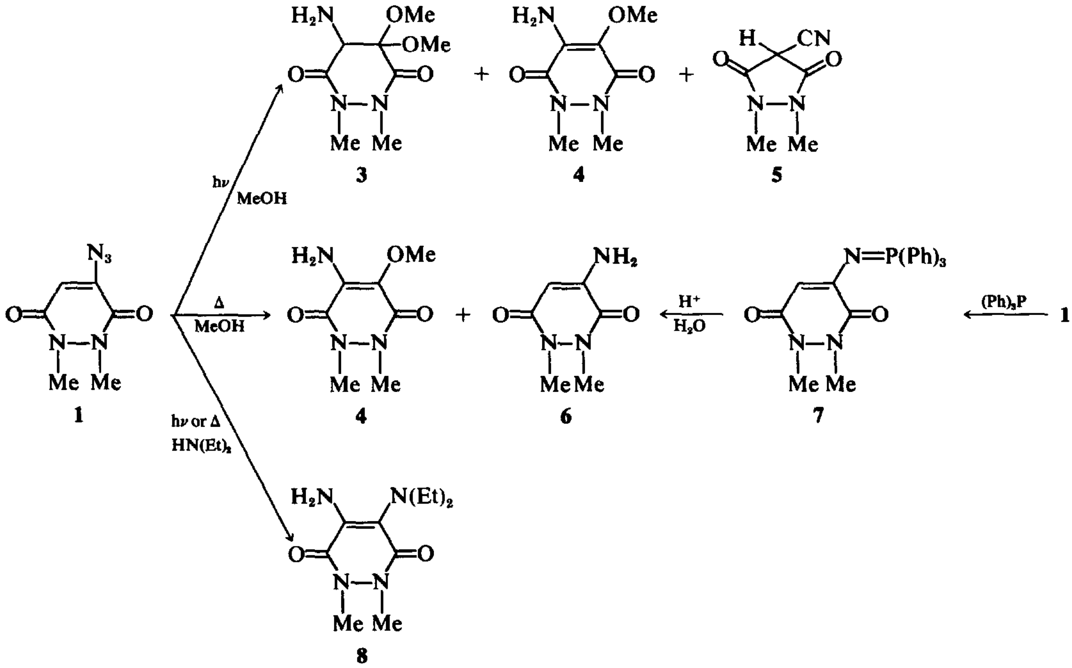
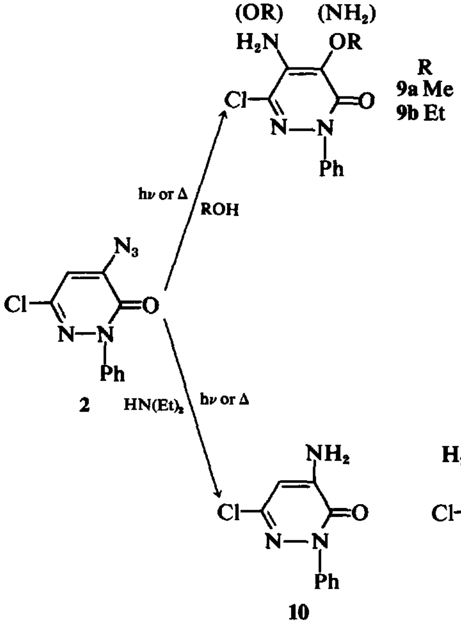
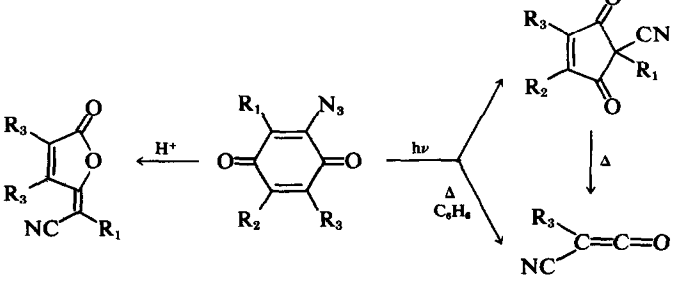
*The positions of amino and alkoxy groups are uncertain.


hν MeOH
Δ MeOH
hν or Δ HN(Et)₂
H⁺ H₂O
(Ph)₃P
1
3
4
5
4
6
7
8


R
9a Me
9b Et
hν or Δ ROH
HN(Et)₂ hν or Δ
2
10
11


H⁺
hν
Δ C₆H₆
Δ

pyrolyses and photolyses of the quinone derivatives give the cyanoketenes and the 2-cyano-1,3-cyclopentadienone derivatives, respectively.[6]

DISCUSSION

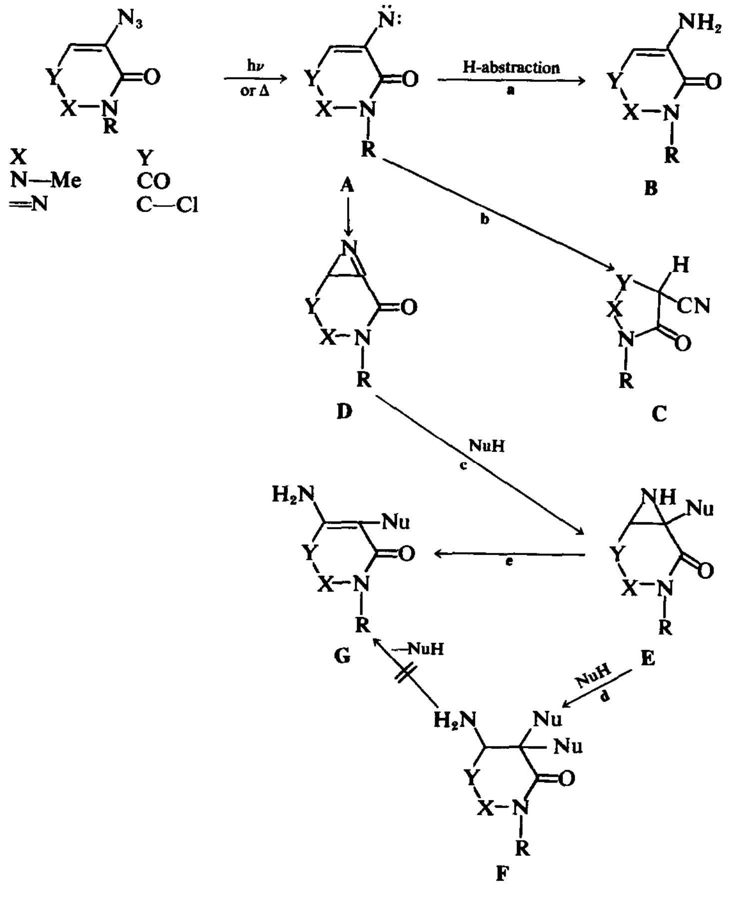
As described, the photochemical and thermal reactions of **1** and **2** in alcohol might proceed *via* the discrete nitrene intermediate. Thus, the mechanistic speculation leads to consideration of three reaction pathways; (a) Hydrogen abstraction of the nitrene (A) occurs in the case of both by photolyses and thermolyses of **1** and **2** in methanol and diethylamine. (b) Rearrangement into the ring contracted cyano derivative (C) is observed in the photolyses of **1** in methanol. (c) The azirine intermediate (D) could arise from the nitrene (A) by the Neber-like rearrangement, which proceeds subsequently by nucleophilic solvent such as alcohol or diethylamine to give the aziridine (E). The formation of G might be explained to proceed *via* F and/or the direction of ring opening of the intermediacy of (E). However, since an attempt to transform **3** to **4** under the conditions of the photolysis and the thermolysis was unsuccessful, routs **d** and **e** were concluded to be competitive. In the case of the photolysis and thermolysis of **2** in diethylamine, **10** was obtained, which indicates path **a**.

Our present method provides an efficient synthetic entry to the 4,5-disubstituents (amino and alkoxy or dialkylamino groups) on the pyridazinone moiety.

EXPERIMENTAL

M.ps were measured on a Yanagimoto micro mp apparatus and were uncorrected. The microanalyses were performed on a Perkin-Elmer 240 elemental analyser. The IR and UV spectra were obtained on JASCO Model IR-S and ORD/UV-5 spectrometers, respectively. The NMR spectra were recorded with a JEOL Model C-60-XL spectrometer with TMS as internal standard, the chemical shift values are expressed in δ values (ppm).

1,2-*Dimethyl*-4-*azido*-*pyridazine*-3,6-*dione* (**1**). A mixture of 1,2-dimethyl-4,5-dibromo-pyridazine-3,6-dione (9·0 g, 0·03 mol) and sodium azide (4·0 g, 0·062 mol) was stirred in DMF (70 ml, dried over molecular sieves) at room temp for 48 hr. The solvent was then evaporated at 70°, and the resulting mixture was dissolved in water–chloroform. The chloroform layer was washed with water and dried (Na_2SO_4). After removing the chloroform under reduced pressure, **1** was obtained as pale yellow crystals in 75–80% yield. It was recrystallized from EtOH, mp 113–115°; IR(KBr) 2140 cm^{-1}, NMR($CDCl_3$) δ 3·58, 3·64



(each 3H, s), 6·29 (1H, s), UV(EtOH) λ max 334 nm (ε 3300), 278(14700), 228(13300). (Found: C, 39·77; H, 3·91; N, 38·64. Calc for $C_6H_7N_5O_2$: C, 39·78; H, 3·89; N, 38·66%).

1,2-Dimethyl-4-triphenylideneamino-pyridazine-3,6-dione (**7**). A mixture of **1** (0·1 g) and triphenylphosphine (0·15 g) was dissolved in CH_2Cl_2 (10 ml). After standing for 1 hr, the solvent was removed and recrystallization of the ppt from EtOH gave **7** (0·2 g, 90%), mp 183–185°. (Found: C, 69·36; H, 5·29; N, 10·50. Calc for $C_{24}H_{22}N_3PO_2$: C, 69·39; H, 5·34; N, 10·12%).

1-Phenyl-3-chloro-5-azido-pyridazine-6-one (**2**). Compound **2** was prepared by treatment of 1-phenyl-3,5-dichloro-pyridazine-6-one with sodium azide by the method reported,[4] mp 117° (dec).

Photolysis of **1** *in methanol.* A soln of **1** (1·0 g) in MeOH (500 ml) was irradiated for 1 hr. After removing of MeOH *in vacuo*, a yellow residue was chromatographed on silica gel with elution of benzene–ethanol (6:1). The clear yellow material (0·54 g, 44%) as the first crop was recrystallized from light petroleum as colorless needles, mp 85–87°, and was identified as **3**; IR (KBr) 3440, 3380, 1678 cm^{-1}, NMR ($CDCl_3$) δ 1·70 (2H, s exchanged by D_2O), 3·30, 3·47 (each 6H), 3·96 (1H), UV(EtOH) λ max 249 nm (ε 4550), 225 (3400). (Found: C, 43·96; H, 6·91; N, 19·63. Calc for $C_8H_{15}N_3O_4$: C, 44·24; H, 6·91; N, 19·35%). Compound **4** (0·2 g, 20%) was obtained as the second crop and recrystallized from EtOH to give pale yellow needles, mp 158°; IR (KBr) 3380, 3280 cm^{-1}, NMR ($CDCl_3$) δ 3·55, 3·67 (each 3H, d), 3·91 (3H, d), 5·20 (2H, br s, exchanged by D_2O). Compound **5** (0·039 g, 5%) was isolated as the third crop, mp 122° (dec); IR (KBr) 2230, 1680 cm^{-1}, NMR ($CDCl_3$) δ 3·66, 3·43 (each 3H, d), 3·29 (1H, s). (Found: C, 47·41; H, 4·32; N, 27·10. Calc for $C_6H_7N_3O_2$: C, 47·05; H, 4·61; N, 27·44%).

Thermolysis of **1** *in methanol.* A soln of **1** (0·6 g) in MeOH (60 ml) was heated for 4 hr at 130°. Compounds **4** (0·15 g, 25%) and **6** (0·065 g, 10%) were separated by chromatography on silica gel with elution of chloroform–ethanol (5:1). Recrystallization of **6** from EtOH gave colorless needles, mp 205–207°. Compound **6** was also obtained by treatment of **7** with HCl aq in quantitative yield: IR (KBr) 3380, 3220, 1605 cm^{-1}, NMR ($CDCl_3$) δ 3·57 (6H, d), 5·07 (2H, br s, exchanged by D_2O), 5·82 (1H, s). (Found: C, 46·55; H, 5·93; N, 27·28. Calc for $C_6H_9N_3O_2$: C, 46·45; H, 5·85; N, 27·08%).

Photolysis of **1** *in diethylamine (DEA).* A soln of **1** (1·0 g) in DEA (500 ml) was photolyzed for 4 hr under N_2. Evaporation of DEA afforded the residue which was chromatographed on alumina with elution of benzene; **8** (0·375 g, 30%) was obtained, mp 135–138°; IR (KBr) 3500, 3310, 1650, 1620 cm^{-1}; NMR ($CDCl_3$) δ 1·00 (6H, t), 3·06 (4H, q), 3·52, 3·62 (each 3H, d), 5·27 (2H, br s, exchanged by D_2O). (Found: C, 53·24; H, 8·14; N, 24·69. Calc for $C_{10}H_{18}N_4O_2$: C, 53·08; H, 8·02; N, 24·76%).

Thermolysis of **1** *in DEA.* A soln of **1** (0·2 g) in DEA (10 ml) was heated at 120° for 3 hr in a sealed tube. Evaporation of DEA afforded a residue, which was chromatographed on silica gel. Elution of chloroform gave **8** (0·203 g, 81%).

Photolysis of **2** *in methanol or ethanol.* A soln of **2** (0·01 mol) in MeOH or EtOH (500 ml) was irradiated until the disappearance of starting material by TLC. Concentration of the solns gave an oil which was subjected to column chromatography on silica gel. Elution with chloroform gave **9a** (46%) and **9b** (56%), respectively.

9a: mp 142–144°, IR (KBr) 3500, 3380, 1648, 1618 cm^{-1}, NMR ($CDCl_3$) δ 4·10 (3H, s), 4·54 (2H, br s, exchanged by D_2O), 7·72–7·30 (5H, m). (Found: C, 52·61; H, 4·06; N, 16·32. Calc for $C_{11}H_{10}N_3O_2Cl$: C, 52·49; H, 3·97; N, 16·69%).

9b: mp 178–180°, IR (KBr) 3480, 3320, 1620 cm^{-1}, NMR ($CDCl_3$) δ 1·37 (3H, t), 4·42 (2H, q), 4·55 (2H, br s, exchanged by D_2O), 7·66–7·23 (5H, m).

Thermolyses of **2** *in methanol or ethanol.* A soln of **2** (0·001 mol) in MeOH or EtOH (15 ml) was heated at 120° for 4 hr in a sealed tube. Chromatography techniques gave **9a** (40%) and **9b** (54%), respectively.

Photolysis of **2** *in DEA.* A soln of **2** (0·7 g) in DEA (250 ml) was irradiated for 2 hr. The yellow soln was evaporated *in vacuo*, and the resulting residue was chromatographed on silica gel. Elution with chloroform gave **10** (0·44 g, 70%), mp 198–200°, as identified with an authentic sample.[7]

Thermolysis of **2** *in DEA.* A soln of **2** (0·4 g) in DEA (16 ml) was heated at 120° for 2 hr in a sealed tube. Similar work-up gave **10** (0·264 g, 75%).

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