The Phtoloysis of 3-diazo-4- phenylazopyrazole Derivatives in Different Solvents

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Abstract: The Photochemistry of 3-diazo-4-Phenylazopyrazoles (1a-c) has been investigated. The Photolysis of the title compound in the presence of different reagents (namely formic acid, acetic acid, Propanoic acid, Pyridine and nitrobenzene) at room temperature with a high pressure mercury lamp (300w, $\lambda \geq 320$nm) through a pyrex filter under argon gave 3-substituted pyrazole derivatives (3a-l) via carbene intermediate. The structures assigned to the new compounds that were supported by microanalysis, infrared, ^{1}H-NMR, and mass spectral data. [Journal of American Science 2010; 6(9):893-896]. (ISSN: 1545-1003).

Keywords: Photochemistry, Amine, Carbene, pyrazole, substitution.

1. Introduction

The Photochemistry of heteroaryl-diazo compounds is interesting for synthetic new derivatives from the parent compound [1]. A generalized photoreaction pattern involves extrusion of nitrogen and formation of a carbene-type intermediate from white products is formed through its singlet or triplet chemistry [2]. However, several parameters play an important role in developing this key species, and among these one should at first consider the nature of heteroaryl ring and constitutes on it. Also, the photoreaction medium and the presence of reagents also play a significant role in determining the final products. Pyrazoles and their substituted derivatives are interesting as potential pharmaceuticals and intermediates in dye industry [3-5]. In view of the above and in continuation of our programme directed towards the synthesis of new pyrazole derivatives [6–8], we report here the photolysis of the diazopyrazole (1a-c) in different reagents, to make new compounds for biological testing.

2. Experimental

Melting points were determined by a Büchi 510 apparatus and are reported uncorrected. IR spectra were recorded on potassium bromide disks using a Perkin–Elmer 383 spectrophotometer. ^{1}H-NMR was obtained on a Bruker Ac 200F instrument.

Mass spectra were obtained at 70 eV by using an AEI MS 30 mass spectrometer. The photoreaction was carried out in a pyrex immersion apparatus equipped with a 300w high pressure mercury lamp at room temperature.

General procedure for the photochemical reaction. A sample of compound (1a-c) in the appropriative anhydrous solvent reagent was irradiated until the starting material disappeared. After removing the solvent under reduced pressure, the residue was recrystallised from an appropriate solvent.

Irradiation of compound (1a) (0.43g, 2mmol) in formic acid (300ml) for 2h gave 5-hydroxyl-4-phenylazopyrazol-3-yl-carboxylate (4a) (0.25g, 54%), m.p. 210 (from diethylether). IR (cm^{-1}): 3521 (OH), 3435 (NH), 3040 (CH-aromatic), 1799 (C=O), 1660 (C=N), 1595, 1491, 1245, 1169. ^{1}H-NMR ($CDCl_3$); 6.2 (br, 1H, OH), 7.5-8.0 (m, 5H, ph), 10.2 (s, 1H, COOH), 11.5 (s, 1H, NH).

Irradiation of compound (1a) (0.43g, 2mmal) in acetic acid (300ml) for 2h gave 5-hydroxyl-4-phenylazopyrazole-3-yl (4b) (0.32g 71%), m.p.: 170^{o}C (from petroleum ether). IR (cm^{-1}) 3550 (OH), 3435 (NH), 3060 (CH–aromatic), 1751 (C=O), 1624 (C=N), 1596, 1545, 1369, 1250, 1161. MS m/z: 246 (M^+, 39%), 239 (32%), 210, 175 and 97[100%].

Irradiation of compound (1a) (0.43g, 2mml) in propanoic acid (300ml) for 3hr gave 5-hydroxyl-4-phenylazopyrazole-3-yl-propanate (4c) (0.28g 54%) m.p.: 216^{o}C (from ethanol). IR (cm^{-1}): 3568 (OH), 3420 (NH), 3040 (CH–aromatic), 1799 (C=O), 1660 (C=N), 1595, 1491, 1245, 1169. ^{1}H-NMR ($CDCL_3$): 1.29 (t, 3H, CH_3), 2.5 (q, 2H, CH_2), 7.50-8.0 (m, 6H, Ph and OH protons), 12.0 (s, 1H, NH).

Irradiation of compound (1b) (0.43g, 2mml) in form acid (300ml) for 2h gave 5-amino-4-phenylazopyrazale-3-yl-carboxylate (4d) (0.3, 65%), m.p. 200^{o}C. IR 3550-3435 (NH_2), 3090 (CH–aromatic), 1690 (C=O), 1620 (C=N), 1596, 1440, 1250, 1190. ^{1}HNMR (DMSO); 7.30–8.0 (m, 7H, ph

and NH_2 protons), 10.2 (s, 1H, O=C–H), 12.0 (s, 1H, NH).

Irradiation of compound (1b) (0.43g, 2mml) in an acid (300ml) for 2h gave 5-amino-4-phenylazo-*1H*-pyrazole-3-yl-acetate (4e) (0.28g, 57%) m.p. 230°C (from benzene). IR (cm^{-1}): 3598–3435 (NH_2, NH), 3050 (CH–aromatic), 1775 (C=O), 1624 (C=N), 1569, 1545 (C=C).

Irradiation of compound (1b) (0.43g, 2mml) in propanoic acid (300ml) for 3h gave 5-amino-4-phenylazo-*1H*-pyrazole-*1H*-pyrazole-3-yl-propanate (4f) (0.26, 50%) m.p. 233°C (from ethyl acetate). IR (cm^{-1}): 3450–3230 (NH_2, NH), 3050 (CH–aromatic), 1775 (C=O), 1640 (C=N), 1550, 1448 (C=C).

Irradiation of compound (1c) (0.28g, 1mml) in formic acid (300ml) for 2h gave 4-phenylazo-*1H*-pyrazole-3,5-yl-dicarboxylate (4g) (0.20g, 77%), m.p. 120°C (from toluene). IR (cm^{-1}): 3435 (NH), 3050 (CH–aromatic), 1775 (C=O), 1665 (C=N), 1593, 1547, 1445. ^{1}H-NMR ($CDCL_3$): 7.3–8.1 (m, 5H, ph), 10.0 (s, 2H, O=C-H), 13.1 (1H, NH).

Irradiation of compound (1c) (0.28g, 1mml) in acetic acid (300ml) for 2h gave 4-phenylazo-*1H*-pyrazole-3,5-yl-diacetate (4h) (0.21g, 72%), m.p. 360°C (from benzene), IR (cm^{-1}): 3435 (NH), 3050 (CH–aromatic), 1730–1775 (C=O), 1627 (C=N), 1594 (C=C). ^{1}H–NMR ($CDCL_3$): 1.29 (s, 6H, $2CH_3$), 7.30 (m, 11H, ph), 12.7 (s, 1H, NH).

Irradiation of compound (1c) (0.28g, 1mml) in propanoic acid (300ml) for 3h gave 4-phenylazo-*1H*-pyrazale-3,5-yl-dipropanate (4k) (0.15, 47%), m.p. 145°C (from xylene); IR (cm^{-1}): 3435 (NH), 3053 (CH–aromatic), 1750, 1738 (C=O), 1630 (C=N), 1590, 1450. MS m/z: 316 [(M^+) 34%], 264 [100%], 197 [93%], 154 [100%], 68 [87%], 57 [45%].

Irradiation of compound (1b) (0.43g, 2mml) in pyridine (200ml) for 2h gave 2-[5-amino-4-phenylazo-*1H*-Pyrazol-3-yl] Pyridine (6) (0.21g, 40%), m.p. 340°C (from diethyl ether). IR (cm^{-1}): 3419 (NH_2), 3090 (H-aromatic), 1677 (C=N), 1535 (C=C).

Irradiation of compound (1a) (0.45, 2mml) in nitrobenzene (300ml) for 3h gave 5-hydroxyl-3-(3-nitrophenyl)-4-phenylazopyrazole (10) (0.32g, 52%), m.p. 155°C (from methanol); IR (cm^{-1}), 3520 (OH), 3367 (NH), 3060 (CH-aromatic), 1678 C=N), 1590, 1520, 1480. MS m/z: 308 [(M^+ (45%)], 238 (49%), 209 (19%), 105 (100%).

3. Results and Discussion

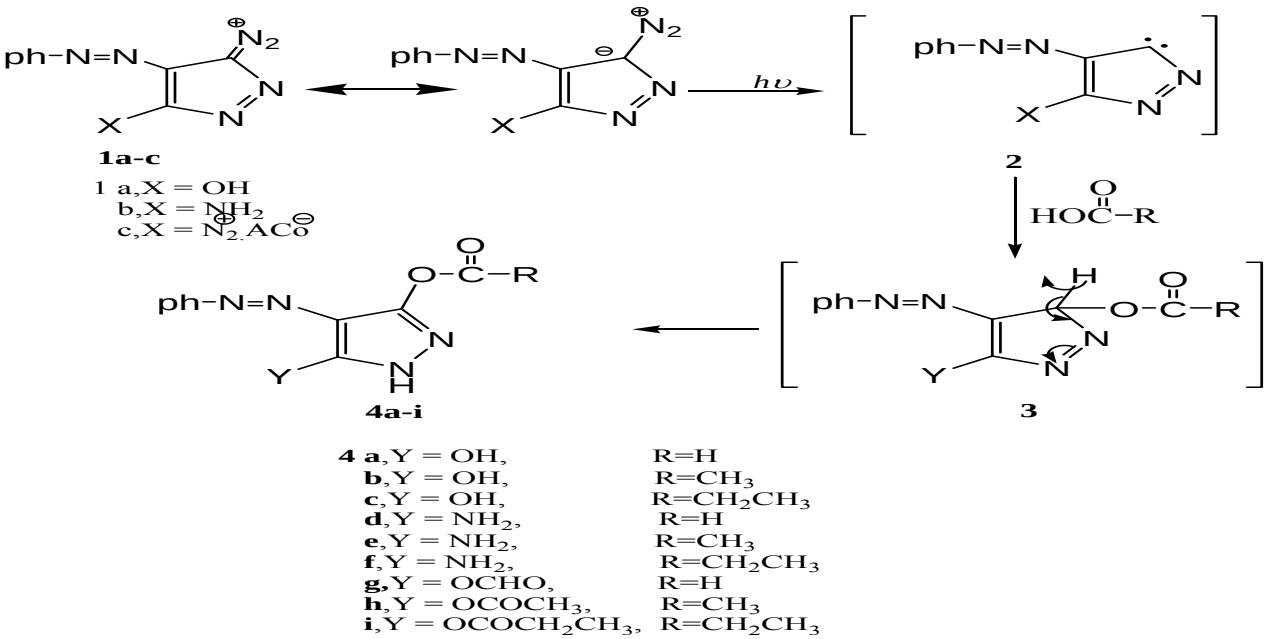
The present paper reports the photolysis of the 3-diazo-4-phenylazopyrazole derivatives (1a-c) in the presence of different reagents at room temperature with a high–pressure mercury lamp (300w, $\lambda \geq 320$nm) through a pyrex filter under argon. 3-diazopyrazole (1a–c) was prepared for the corresponding 3–amino–pyrazole derivatives as reported previously.[9] Irradiation of the 3-diazo-4-phenylazopyrazole derivative (1a–c) in formic acid, acetic acid and/or propanoic acid essentially gave 4-phenyl-azo-*1H*-pyrazol-3-yl-formate, 4-phenylazo-*1H*-pyrazol-3-yl-acetate and/or 4-phenyl-azo-*1H*-pyrazol-3-propanate derivatives (4 a–i) respectively.

To explain the formation of these compounds is by assuming the initial formation of the highly electrophilic carbene is by loss of nitrogen. The carbene is directly inserted into the OH bond of the reagent to produce an intermediate 3, which after rearrangement gives the final products (4 a–i) as shown in scheme 1.

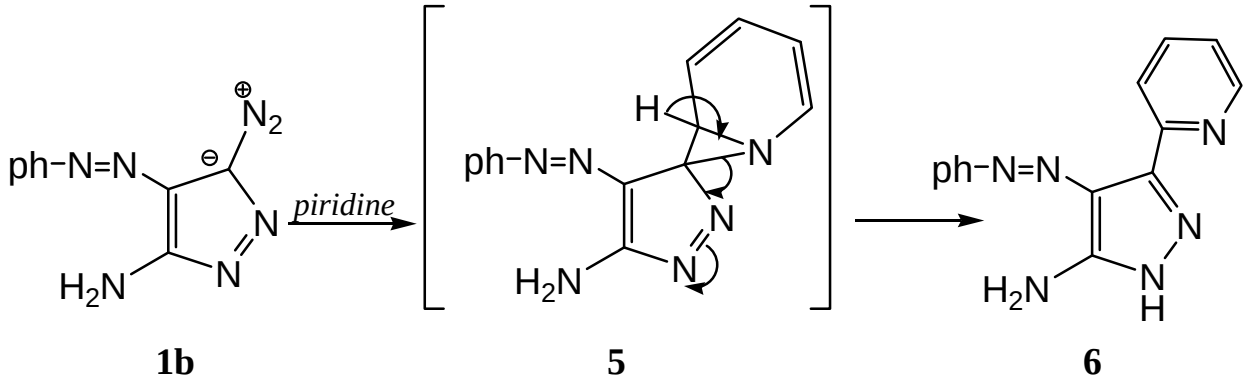
In the Photolysis of 5-amino-3-diazo-4-phenyl-azo-pyrazole (1b) in pyridine gave 2-[5-amino-4-phenyl-azo-*1H*-pyrazol-3-yl] pyridine.

The mechanism due to selective electrophilic attack of the carbene (1b) on the π-system of the pyridine ring occurred to give the spiro-compound (5), followed by heterolytic rupture of the cycloazine ring to give the corresponding ring substitution product (6) as shown in scheme 2.

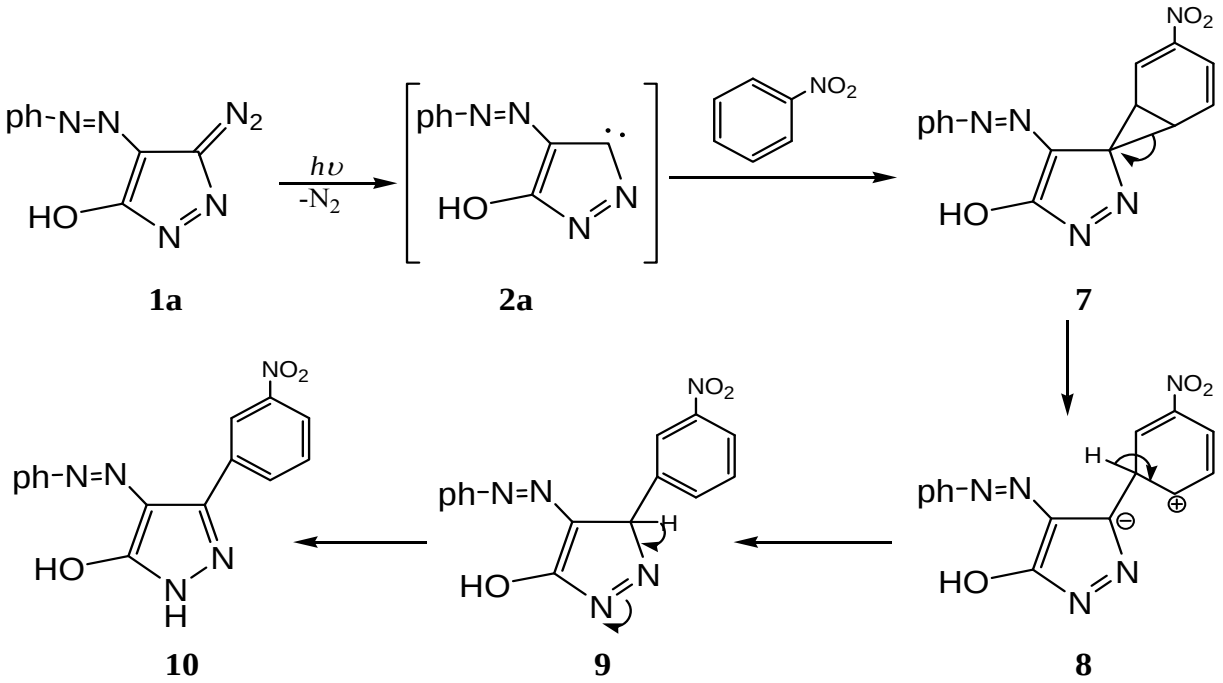
Irradiation of (1a) in nitrobenzene showed selective electrophilic attack of the carbene (2a) on the π-system of the benzene ring to give spiro-dodeca-diene. (7) which can heterolytic cleavage of the cycle propane to give 5-hydroxyl-3-(3-nitrophenyl)-4-phenylazopyrazole (10) as shown in scheme 3



Scheme 1



Scheme 2



Scheme 3

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8/5/2010