Pyridazine derivatives and related compounds. Part 14[1]. Photolysis of 3-diazo-4,5-diphenylpyrazolo[3,4-*c*]pyridazine

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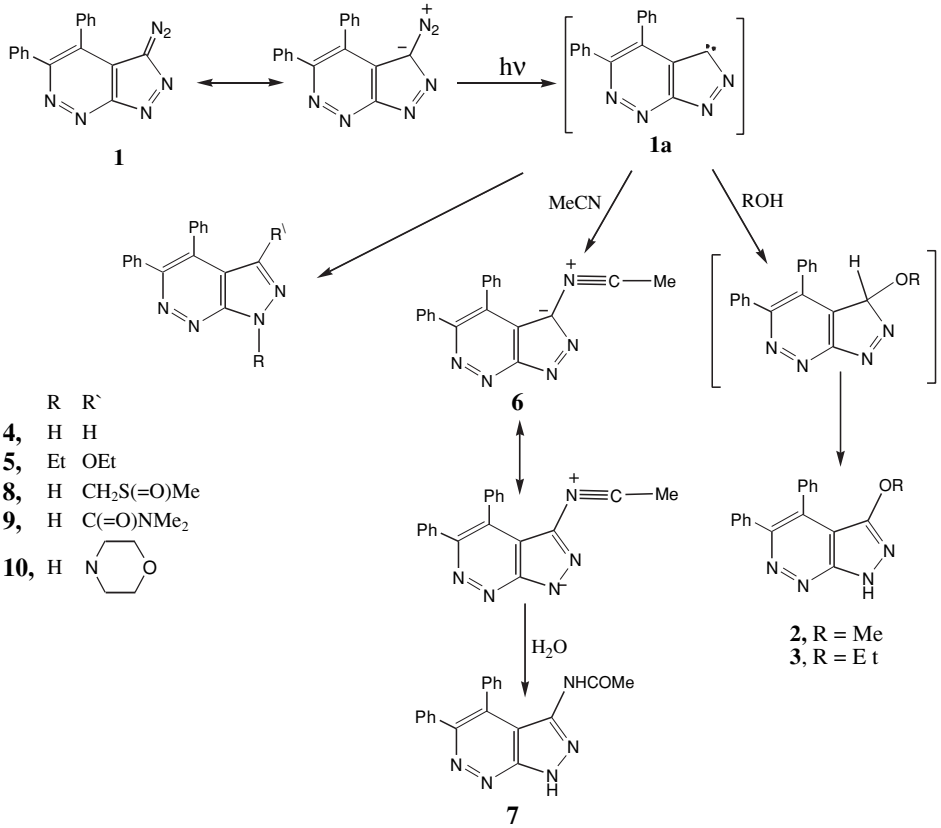
The photochemistry of 3-diazopyrazolopyridazine has been investigated. The irradiation of 3-diazo-4,5-diphenylpyrazolo[3,4-*c*]pyridazine in various solvents forms a carbene intermediate, which transforms into 3-substituted derivatives. For photolysis in the presence of acetylacetone or ethyl acetoacetate the coupling reactions which occur at the methylene group are faster than carbene formation, and can lead to direct cyclisation into condensed 1,2,4-triazines. Photolysis in the presence of diethyl malonate forms an acyclic hydrazone.

Keywords: pyridazine derivatives, photolysis, 3-diazo-4,5-diphenylpyrazolo[3,4-*c*]pyridazine

The photochemistry of heteroaryl diazo compounds has received attention from not only theoretical and mechanistic but synthetic points of view.[3] A generalised photoreaction pattern involves extrusion of nitrogen and formation of a carbene-type intermediate from which reaction products are formed through its singlet or triplet chemistry.[4] However, several parameters play an important role in developing this key species, and among these one should at first consider the nature of the heteroaryl ring (and substituents on it) which affects reactivity and even the reaction pathway. Also, the photoreaction medium and the presence of reagents also play a significant role in determining the final products. Pyridazine derivatives and heterocyclic annelated pyridazines continue to attract considerable attention for their applications in agriculture and in particular for their biological activity for use as potential drugs.[5,6] In view of the above and in continuation of our programme directed towards the synthesis of new pyridazine derivatives, we report here the photolysis of the title compound in the presence of different reagents. In a previous paper[7] we presented the thermolysis of 3-diazo-4,5-diphenylpyrazolo[3,4-*c*]pyridazine **1** in the presence of different reagents. The present paper reports the photolysis of the diazo derivative in the presence of different reagents at room temperature with a high-pressure mercury lamp (300 w, $\lambda \geq 320$ nm) through a Pyrex filter under argon.

Irradiation of the diazopyrazolopyridazine **1** in methanol and in ethanol essentially gave the 3-methoxy-and 3-ethoxy-4,5-diphenyl-1*H*-pyrazolo[3,4-*c*]pyridazines **2** and **3**. No reduced pyrazolopyridazine **4** was detected. It is reasonable to explain the formation of these compounds by assuming the initial formation of the highly electrophilic carbene by loss of nitrogen. The carbene is directly inserted into the OH bond of the reagent to produce an intermediate followed by prototropic rearrangement to give the final products (Scheme 1).



Scheme 1

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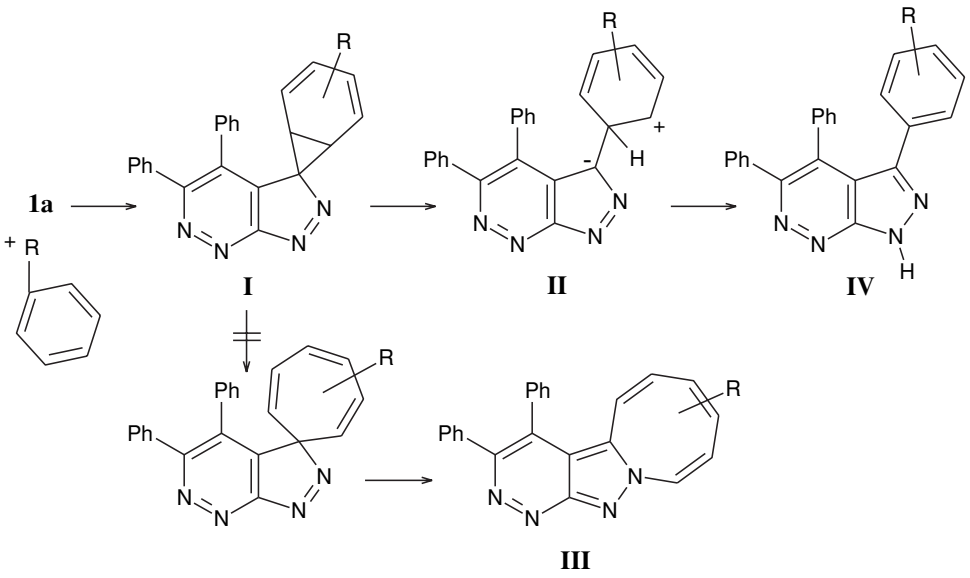


The IR spectra of these compounds indicated the absence of the diazo absorption band which appeared as a sharp band at 2180 cm^{-1} in the spectrum of compound **1** and supplementary evidence for the assigned structures has been gained from the MS and ^1H NMR data. For compound **3** the MS spectrum showed ion peaks at *m/z* 316 [M^+, 57.3%], 287 [M^+–Et, 100%] and 271 [M^+–OEt, 30.6%]. The ^1H NMR spectrum revealed the presence of the typical pattern of the ethoxy group at δ 1.34 (t, 3H, CH_3) and 4.23 (q, 2H, CH_2), a multiplet centred at δ 7.20 (m, 10H, 2Ph) and a singlet at δ 9.8 (s, 1H) attributed to the NH proton.

When compound **1** was irradiated in propan-1-ol, propan-2-ol or aqueous acetone a single product was formed which was shown to be product **4** also obtained from dediazonation with hypophosphorous acid,[7] not the expected 3-substituted pyrazolo[3,4-*c*]pyridazines. This was confirmed by the analytical and spectroscopic data.

Compound **4** showed a signal at δ = 8.21 ppm in the ^1H NMR spectrum that was assigned to the H-3 proton. Its MS showed an intense peak at *m/z* = 272 corresponding to the molecular ion.

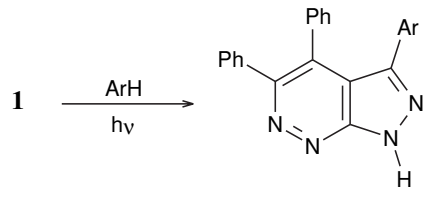
Photolysis of **1** in diethyl ether gave compound **5** as the only isolatable product, formed by electrophilic singlet carbene attack on the ether oxygen to form an oxonium ylide followed by rearrangement to give the product.

These results prompted us to exploit the photoreactivity of the 3-diazo compound **1** in synthetic projects. To this aim, we have investigated irradiation of **1** in the presence of various reagents, such as acetonitrile, dimethylformamide and dimethyl sulfoxide on one hand, and suitable aromatics (benzene, anisole, toluene, chloro(bromo)benzene, nitrobenzene, thiophene and pyridine), on the other. As expected irradiation of **1** in acetonitrile gave the acetylamino compound **7** (70%), reasonably through the intermediate **6** (Scheme 1). The structure of compound **7** was confirmed from analytical and spectral data. Its MS showed an intense peak at *m/z*: 329 corresponding to the molecular ion. Also it was found to be identical (m.p., mixed m.p. and superimposable IR) with an authentic sample synthesised unambiguously by acetylation of the 3-amino-4,5-diphenyl-1*H*-pyrazolo[3,4-*c*]pyridazine with acetic anhydride.[9] Analogous results were obtained when the diazo compound **1** was irradiated in dimethyl sulfoxide, dimethyl formamide and in morpholine, where **8–10** were produced, respectively. The structures of photoproducts **8–10** were elucidated on the basis of spectral data and analytical results. The most salient features of the IR, ^1H NMR and mass spectra are given in the experimental section.

Irradiation of **1** in benzene and in benzene derivatives showed different reaction patterns. Selective electrophilic attack of the carbene **1a** on the π-system of the aromatic rings occurred to give the spironorcaradiene **I** which can collapse to the dipolar σ-complex **II**, by heterolytic cleavage of the cyclopropane moiety and not to the ring expansion compounds **III**. The formation of the ring substitution product **IV** was observed in all the series. Fast conversion of **I** to the dipolar intermediate **II** is driven by the electronic effects of the substituents rather than by steric effects. Thus, electron-donating groups, give rise to *ortho* and *para* substitution and electron-withdrawing group yield the *meta* substitution product.

Irradiation in benzene afforded the corresponding 3-phenyl derivative **11**. Irradiation in substituted benzenes such as anisole, toluene, chloro and bromobenzene, gave a mixture of *ortho* and *para* substituted products **12a–h**. Photoreaction in nitrobenzene also proceeded smoothly leading to the meta substitution product **12i** (Scheme 2).

In the photolysis of compound **1** in pyridine, the behaviour is analogous to that observed for the benzene series leading,



11, Ar = C_6H_5

12a, Ar = *o*-$MeOC_6H_4$ **b,** Ar = *p*-$MeOC_6H_4$

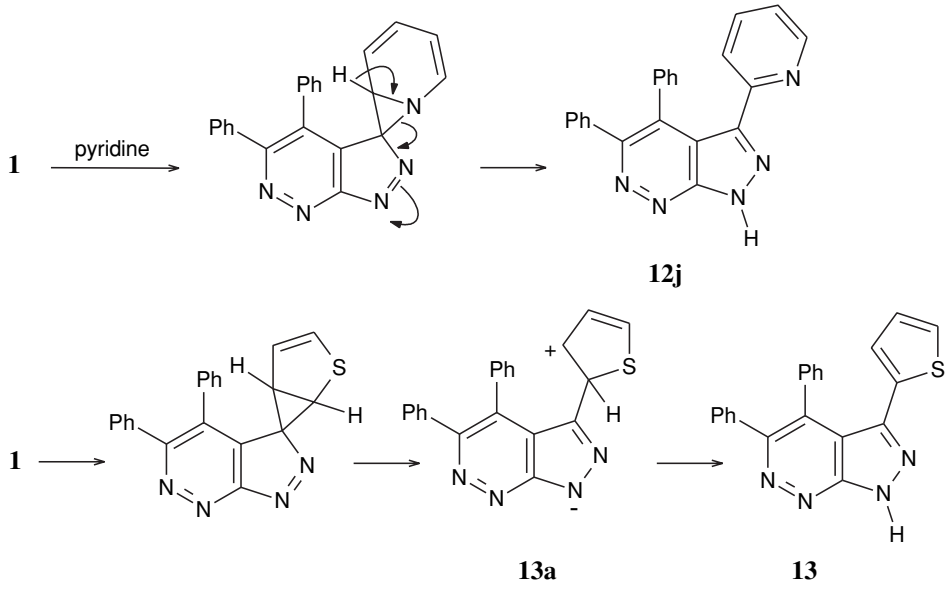
c, Ar = *o*-MeC_6H_4 **d,** Ar = *p*-MeC_6H_4

e, Ar = *o*-ClC_6H_4 **f,** Ar = *p*-ClC_6H_4

g, Ar = *o*-BrC_6H_4 **h,** Ar = *p*-BrC_6H_4

i, Ar = *m*-$NO_2C_6H_4$

Scheme 2



Scheme 3

by the same mechanism, to the corresponding ring substitution product 3-(2-pyridyl) derivative **12j** (Scheme 2).

Furthermore, irradiation of **1** in thiophene may involve formation of a spirocyclo-propane, followed by heterolytic rupture of the cyclopropane ring, through the intermediate **13a**, to give 3-(2-thienyl) derivative **13** (Scheme 3).

Next we examined the photoreactivity towards active methylene compounds. Thus, 3-diazo derivative **1** irradiated in acetylacetone and in ethyl acetoacetate gave good yields of the cyclic triazine compounds **14** and **15**, respectively. The identity of these products was confirmed by analytical and spectroscopic evidence, as well as on the basis of our previous work.[7] These results could be explained by assuming that the photoreaction of active methylene compounds with the diazo compound **1** is faster than carbene formation and gives the corresponding coupling products which can directly cyclise to pyridazinopyrazolotriazine derivatives. With diethyl malonate, the open-chain compound **16** derived by a Japp-Klingemann decarboxylation reaction was obtained. Structural elucidation of compound **16** was accomplished from analytical and spectroscopic data, which showed a single quartet at δ 4.3 ppm, a triplet at δ 1.34 ppm and a singlet at δ 8.1 ppm in the ^{1}H NMR spectrum that was assigned to the =CHCOOEt group. Its MS showed an intense peak at *m/z* 386 corresponding to the molecular ion.

The photoreaction of 3-diazo derivative **1** with a variety of reagents, therefore, proceeds smoothly to yield 3-substituted, 1,3-disubstituted pyrazolo-pyridazine and/or pyridazino-pyrazolo-triazine derivatives, depending on the nature of the reagent. Although a few syntheses of these derivatives have been reported,[7] the photoreaction described here should prove to be an efficient and novel method for their synthesis.

Experimental

Melting points were determined on a Büchi 510 apparatus and are reported uncorrected. IR spectra were recorded on potassium bromide disks using a Perkin-Elmer 383 spectrophotometer. ^{1}H and C^{13} NMR spectra were obtained on a Bruker Ac 200 F instrument. Mass spectra were obtained at 70 eV by using a AEI MS 30 mass spectrometer. All reactions were monitored by thin layer chromatography, carried out on 0.2 mm silica gel 60 F-254 (Merck) plates using UV, light (254 and 366 nm). The photoreactions were carried out in a Pyrex immersion apparatus equipped with a 300 w high-pressure mercury lamp at room temperature. Commercially available reagents and solvents were usually reagent grade and distilled or recrystallised prior to use.

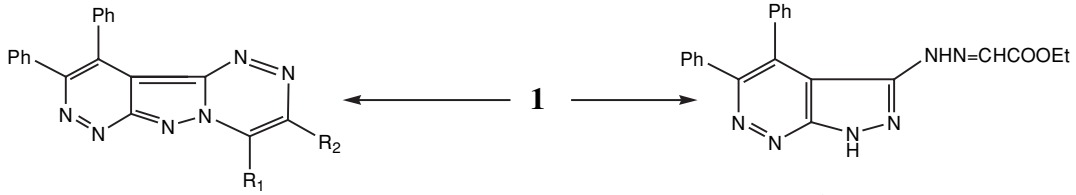
3-Diazo-4,5-diphenylpyrazolo[3,4-*c*]pyridazine **1**, m.p. 162°C (dec), was prepared from the corresponding 3-amino derivative, as reported previously.[8]

General procedure for photochemical reactions

A sample of compound **1** in the appropriate 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 in methanol: Irradiation of compound **1** (1.0 g, 3.3 mmol) in methanol (400 ml) for 2 h gave 3-methoxy-4,5-diphenyl-1*H*-pyrazolo[3,4-*c*]pyridazine **2**, 0.44 g (48.3%), m.p. 246–247°C (from methanol). IR (cm^{-1}): 3408 (NH), 3062 (C-H, aromatic), 1625 (C=N), ^{1}H NMR (DMSO-d_6): δ 3.98 (s, 3H, OMe), 7.01–7.51 (m, 10H, 2Ph); 12.12 (s, 1H, NH); MS *m/z*: 302 (M^+, 91.5%), 301 (M^+-1, 100%), 243 (M^+-59, 9.2%). Anal. Calcd for $C_{18}H_{14}N_4O$: C,71.5; H, 4.7; N, 18.5. Found : C, 71.4; H, 4.6; N, 18.3.

Irradiation in ethanol: Irradiation of compound **1** (0.4 g, 1.3 mmol) in absolute ethanol (250 ml) for 2 h gave 3-ethoxy-4,5-diphenyl-1*H*-pyrazolo[3,4-*c*]pyridazine **3**, 0.25 g (58.9%), m.p. 267–268°C (from ethanol). IR (cm^{-1}): 3166 (NH), 3062 (C-H, aromatic), 2977, 2926 (C-H, aliphatic), 1626 (C=N), 1567, 1430, 1384, 1148, ^{1}H NMR ($CDCl_3$): δ 1.34 (t, 3H, CH_3), 4.23 (q, 2H, CH_2), 7.06–7.31 (m, 10H, 2Ph), 9.8 (s, 1H, NH); MS *m/z*: 316 (M^+, 57.3%), 315 (M^+-1, 55.3%), 287 (M^+–Et, 100%) and 271 (M^+–OEt, 30.6%). Anal. Calcd



14, R_1 = Me, R_2 = COMe
15, R_1 = Me, R_2 = COOEt

for $C_{19}H_{16}N_4O$: C, 72.1; H, 5.1; N, 17.7. Found: C, 72.0; H, 5.1; N, 17.5.

Irradiation in 1-propanol, 2-propanol and in aq. acetone: Irradiation of compound **1** (0.5 g, 1.7 mmol) in each of 1-propanol (500 ml) for 8 h, 2-propanol (250 ml) for 3 h and in 99% aqueous acetone (250 ml) for 23 h gave 4,5-diphenyl-1*H*-pyrazolo[3,4-*c*]pyridazine **4** in yields of 81%, 70% and 65.7%, respectively, m.p. 223–224°C (from ethanol). IR (cm^{-1}): 3283 (NH), 3183 (C-H, aromatic), 1629 (C=N), 1562 (C=C). ^1H NMR (DMSO-d_6): δ 8.21 (s, 1H, C^3-H), 7.32–7.50 (m, 10H, 2Ph), 9.8 (s, 1H, NH); ^{13}C NMR (DMSO-d_6): δ 117.86 (C-3a), 124.2 (C-3), 124.5 (C-5), 152.6 (C-4), 154.9 (C-7a), 126.2, 126.6, 130.2, 131.0, 132.4, 134.1, 134.9, 137.5, (C_6H_5); MS *m/z*: 272 (M^+, 42%), 271 (M^+-1, 100%), 242 (M^+-30, 10%). Anal. Calcd for $C_{17}H_{12}N_4$: C, 75.05; H, 4.4; N, 20.4. Found: C, 75.3; H, 4.5; N, 20.3. An authentic sample of **4** was obtained by dediazonation of **1** with hypophosphorous acid.[7]

Irradiation in diethyl ether: Irradiation of compound **1** (0.5 g, 1.7 mmol) in diethyl ether (250 ml) for 4 h gave 3-ethoxy-1-ethyl-4,5-diphenylpyrazolo[3,4-*c*]pyridazine **5**, 0.3 g (51.9%), m.p. 263–264°C (from ethanol). IR (cm^{-1}): 3266 (NH), 3095 (C–H, aromatic), 2812 (C–H, aliphatic), 1662 (C=N); MS *m/z:* 344 (M^+, 25%), 315 (M^+–Et, 65%), 299 (M^+–OEt, 100%), 270 [M^+–(Et + OEt), 30%]. Anal. Calcd for $C_{21}H_{20}N_4O$: C, 73.2; H, 5.85; N, 16.3. Found **:** C, 73.0; H, 5.6; N, 16.0.

Irradiation in acetonitrile: After irradiation of compound **1**, 0.5 g (1.7 mmol) in acetonitrile (250 ml) for 19 h, the reaction solution was poured into water (100 ml). The solid was filtered off and recrystallised from methanol to obtain 0.5 g (54.5%) of 3-acetamido-4,5-diphenyl-1*H*-pyrazolo[3,4-*c*]pyridazine **7**, m.p. 145–146°C. IR (cm^{-1}): 3386 (NH), 3060 (C–H, aromatic), 2927 (C–H, aliphatic), 1660 (C=O), 1640 (C=N) and 1444, 1386, 1319, 1285 (for aromatic system). MS *m/z* : 329 (M^+, 13.3%), 313 (M^+–CH_4, 4.31%), 286 (M^+–C(=O)Me, 50.61%), 271 (M^+–NH–C(=O)Me, 38.49%). Anal. Calcd for $C_{19}H_{15}N_5O$: C, 69.3; H, 4.6; N; 21.3. Found: C, 69.0; H, 4.3; N, 21.0.

Irradiation in dimethylsulfoxide: After irradiation of compound **1** (0.5 g, 1.7 mmol) in dimethyl sulfoxide (250 ml) for 20 h, the reaction solution was poured into ice water (100 ml). The solid was filtered off and recrystallised from ethanol to obtain 0.25 g (44.6%) of 3-methylthiomethyl-4,5-diphenyl-1*H*-pyrazolo[3,4-*c*]pyridazine **8** m.p. 156–157°C. IR (cm^{-1}): 3155 (NH), 3059 (C–H, aromatic), 2922 (C–H, aliphatic), 1633 (C=N); MS *m/z:* 348 (M^+, 35%), 287 (M^+–S(=O)Me, 25%), 271 (M^+–CH_2S(=O)Me, 100%). Anal. Calcd for $C_{19}H_{16}N_4OS$: C, 65.5; H, 4.6; N, 16.1. Found: C, 65.2; H, 4.8; N, 16.1.

Irradiation in dimethylformamide: After irradiation of compound **1** (0.5 g, 1.7 mmol) in dimethylformamide (250 ml) for 10 h, the reaction solution was poured into ice water (100 ml). The solid was filtered off and recrystallised from ethanol to give 0.3 g (52.1%) of 3-*N*,*N*-dimethylaminocarbonyl-4,5-diphenyl-1*H*-pyrazolo[3,4-*c*] pyridazine **9**, m.p. 217–218°C. IR (cm^{-1}): 3152 (NH), 3060 (C–H, aromatic), 2954, 2921 (C–H, aliphatic), 1674 (C=O), 1640 (C=N) and 1441, 1305; ^1H NMR (DMSO-d_6): δ 3.2 (s, 6H, 2Me), 7.69–7.9 (m, 10H, 2Ph), 12.06 (s, 1H, NH); MS *m/z*: 343 (M^+, 43%), 271 (M^+–C(=O)NMe_2, 100%). Anal. Calcd for $C_{20}H_{17}N_5O$ **:** C, 69.95; H, 5.0; N, 20.4. Found **:** C, 69.7; H, 4.8; N, 20.1.

Irradiation in morpholine: After irradiation of compound **1** (0.2 g, 0.68 mmol) in morpholine (25 ml) for 20 h, the reaction mixture was poured into ice water (100 ml). The solid product was filtered off and recrystallised from methanol to give 0.1 g (39.7%) of 3-morpholino-4,5-diphenyl-1*H*-pyrazolo[3,4-*c*]pyridazine **10**, m.p. 140–141°C. IR (cm^{-1}): 3350 (NH), 3096 (C–H, aromatic), 2977, 2812 (C–H, aliphatic) 1660 (C=N); ^1H NMR ($CDCl_3$): δ 2.91 (t, 4H, *J* = 4.5, $2CH_2$), 3.64 (t, 4H, *J* = 4.5, $2CH_2$), 7.36–7.40 (m, 10H, 2Ph), 12.06 (s, 1H, NH), Anal. Calcd for $C_{21}H_{19}N_5O$: C, 70.6; H, 5.4; N, 19.6. Found **:** C, 70.3; H, 5.1; N, 19.4.

Irradiation in benzene: Irradiation of compound **1** (0.5 g, 1.7 mmol) in benzene (250 ml) for 4 h, gave 3,4,5-triphenyl-1*H*-pyrazolo[3,4-*c*]pyridazine **11** 0.35 g (59.7%), m.p. 282–283°C (from benzene). IR (cm^{-1}): 3498 (NH), 1547 (C=N) and 1473; ^1H NMR (DMSO-d_6): δ 7.25–7.40 (m, 15H, 3Ph), 12.5 (s, 1H, NH); MS *m/z***:** 348 (M^+, 63.5%), 347 (M^+- 1, 100%), 319(M^+–N_2H, 55%), 271(M^+–Ph, 36%). Anal. Calcd for $C_{23}H_{16}N_4$**:** C, 79.3; H, 4.6; N,16.1. Found: C,79.1; H,4.4; N,15.9.

Irradiation in substituted benzene. General procedure: After irradiation of compound **1** (0.5 g, 1.7 mmol) in anisole, toluene, chloro and/or bromobenzene (250 ml) for 6–30 h, the resulting mixture was concentrated to its half volume, the solid obtained was collected by filtration to give **12a,c,e,g**. The filtrate was evaporated under reduced pressure and the residue was triturated with ether to give **12b,d,f,h**.

3-(o-Anisyl)-4,5-diphenyl-1H-pyrazolo[3,4-c]pyridazine **12a**: Reaction time 6 h, 0.2 g (33%), m.p. 274–275°C (from ethanol). IR (cm^{-1}): 3420 (NH), 3110, 3150 (C–H, aromatic), 2931, 2855 (C–H, aliphatic), 1660 (C=N), 1445, 1348, (757, 701 for *ortho* position); ^1H NMR (DMSO-d_6): δ 3.7 (s, 3H, OMe), 7.29–7.40 (m, 14H, aromatic protons) and 12.0 (s, 1H, NH); MS *m/z*: 378 (M^+, 32.2%), 377 (M^+-1, 32.9%), 363 (M^+–Me, 8%), 347(M^+–OMe, 10%), 271(M^+–C_6H_4OMe, 100%). Anal. Calcd for $C_{24}H_{18}N_4O$: C, 76.2; H, 4.8; N, 14.8. Found: C, 75.9; H, 4.6; N, 14.6.

3-(p-Anisyl)-4,5-diphenyl-1H-pyrazolo[3,4-c]pyridazine **12b**: 0.3 g (47%), m.p. 245–246°C (from ethanol). IR (cm^{-1}): 3390 (NH), 3055 (C–H, aromatic), 2950, 2859 (C–H, aliphatic), 1600 (C=N), 1441, 1380, (920, 873, 845 for *para* position); ^1H NMR (DMSO-d_6): δ 3.74 (s, 3H, OMe), 7.01–7.34 (m, 10H, 2Ph), the AA'XX' system appeared as a pair of doublets: 7.56 (d, 2H, *J* = 7, aromatic), 7.84 (d, 2H, *J* = 7, aromatic) (the AA'XX' system appeared as a pair of doublets.) and 12.1 (s, 1H, NH); MS *m/z*: 378 (M^+, 32.2%), 377 (M^+-1, 32.9%), 363 (M^+–Me, 10%), 271 (M^+–C_6H_4OMe, 30%). Anal. Calcd for $C_{24}H_{18}N_4O$ **:** C, 76.2; H, 4.8; N, 14.8. Found: C, 75.9; H, 4.6; N, 14.9.

3-(o-Tolyl)-4,5-diphenyl-1H-pyrazolo[3,4-c]pyridazine **12c:** Reaction time 10 h, 0.3 g (49.9%), m.p. 140–141°C (from diethyl ether). IR (cm^{-1}): 3400 (NH), 3001 (C–H, aromatic), 2820, 2801 (C–H, aliphatic), 1600 (C=N), 1340, 1218, (757, 701 for *ortho* position); ^1H NMR (DMSO-d_6): δ 1.27 (s, 3H, Me), 6.9–7.27 (m, 14H, aromatic protons) and 12.1 (s, 1H, NH); MS *m/z*: 362 (M^+, 56%), 361 (M^+-1, 69%), 347 (M^+–Me, 35%), 271 (M^+–C_6H_4Me, 49.2%). Anal. Calcd for $C_{24}H_{18}N_4$: C, 79.5; H, 5.0; N, 15.5. Found: C, 79.2; H, 4.7; N, 15.3.

3-(p-Tolyl)-4,5-diphenyl-1H-pyrazolo[3,4-c]pyridazine **12d**: 0.15 g (38.1%), m.p. 251–252°C (from toluene). IR (cm^{-1}): 3397 (NH), 3059 (C–H, aromatic), 2922, 2853 (C–H, aliphatic), 1600 (C=N), 1570, 1445, 1383, 1323, 1224, 1125, 1074, (923, 876, 698, for *para* position). ^1H NMR (DMSO-d_6): δ 1.41 (s, 3H, Me), 7.3–7.62 (m, 14H, aromatic protons) and 12.1 (s, 1H, NH); MS *m/z*: 362 (M^+, 50%), 361 (M^+-1, 65%), 347 (M^+–Me, 25%), 271 (M^+–C_6H_4Me, 100%). Anal. Calcd for $C_{24}H_{18}N_4$: C, 79.5; H, 5.0; N, 15.5. Found: C, 79.3; H, 4.8; N, 15.2.

3-(2-Chlorophenyl)-4,5-diphenyl-1H-pyrazolo[3,4-c]pyridazine **12e**: Reaction time**:** 30 h, 0.3 g (46.7%), m.p. > 300°C (from methanol). IR (cm^{-1}): 3420 (NH), 3090 (C–H, aromatic), 1626 (C=N), 1440, 1375, 1020 (745, 706 for *ortho* position). ^1H NMR (DMSO-d_6): δ 6.09–7.12 (m, 14H, aromatic protons) and 12.0 (s, 1H, NH). Anal. Calcd for $C_{23}H_{15}ClN_4$: C, 72.15; H, 3.95; N, 14.6. Found: C, 71.9; H, 4.0; N, 14.4.

3-(4-Chlorophenyl)-4,5-diphenyl-1H-pyrazolo[3,4-c]pyridazine **12f**: 0.21 g (42.1%), m.p. 180–181°C (from diethyl ether). IR (cm^{-1}): 3429 (NH), 3020 (C–H, aromatic), 1626 (C=N), 1443, 1382, 1319, 1029 (873, 833, for *para* position); ^1H NMR (DMSO-d_6): δ 7.12–7.4 (m, 14H, aromatic protons) and 12.0 (s, 1H, NH); MS *m/z*: 383 (M^+, 32%), 347 (M^+–HCl, 27.0%), 271 (M^+–C_6H_4Cl, 4.0%). Anal. Calcd for $C_{23}H_{15}ClN_4$: C, 72.15; H, 3.95; N, 14.6. Found: C, 71.9; H, 4.0; N, 14.4.

3-(2-Bromophenyl)-4,5-diphenyl-1H-pyrazolo[3,4-c]pyridazine **12g**: Reaction time 14 h, 0.15 g (20.93%) m.p. 227–228°C (from ethanol). IR (cm^{-1}): 3430 (NH), 3095 (C–H, aromatic), 1630 (C=N), 1444, 1313 (756 for *ortho* position), 689 (C–Br). ^1H NMR (DMSO-d_6): δ 7.52–7.92 (m, 14H, aromatic protons), 12.0 (s, 1H, NH). MS *m/z*: 427 (M^+, 100%), 347 (M^+–Br, 50%), 318 (M^+–Br, N_2H, 9.8%). Anal. Calcd for $C_{23}H_{15}BrN_4$: C, 64.1; H, 3.7; N, 18.9. Found: C, 63.8; H, 3.5; N, 18.8.

3-(4-Bromophenyl)-4,5-diphenyl-1H-pyrazolo[3,4-c]pyridazine **12h**: 0.4 g (55.8%), m.p. 153–154°C (from methanol). IR (cm^{-1}): 3427 (NH), 3177, 3092, 3061 (C–H, aromatic), 1631 (C=N), 1560, 1127, 1071, 996 (957, 876, 830 for *para* position), 699 (C–Br). ^1H NMR ($CDCl_3$): δ 7.2–7.52 (m, 10H, 2Ph), 7.9–8.1 (m, 4H, bromophenyl), 12.5 (s, 1H, NH). Anal. Calcd for $C_{23}H_{15}BrN_4$: C, 64.1; H, 3.7; N, 18.9. Found: C, 63.8; H, 3.8; N, 18.7.

Irradiation in nitrobenzene: Irradiation of compound **1** (0.5 g, 1.7 mmol) in nitrobenzene (150 ml) for 6 h gave 3-(3-nitrophenyl)-4,5-diphenyl-1*H*-pyrazolo[3,4-*c*]pyridazine **12i**, 0.39 g (59.1%), m.p. >300°C (from methanol). IR (cm^{-1}): 3128 (NH), 3055 (C–H, aromatic), 1651 (C=N), 1514, 1345 (for NO_2); ^1H NMR (DMSO-d_6): δ 7.17–7.58 (m, 14H, aromatic protons), 15.07 (s, 1H, NH). MS *m/z*: 393 (M^+, 82%), 392 (M^+- 1, 100%), 377 (M^+–O, 14%), 347 (M^+–NO_2, 27%), 271 (M^+–$C_6H_4NO_2$, 41%). Anal. Calcd for $C_{23}H_{15}N_5O_2$: C, 70.2; H, 3.8; N, 17.8. Found: C, 69.9; H, 3.7; N, 17.5.

Irradiation in pyridine: After irradiation of compound **1** (0.5 g, 1.7 mmol) in pyridine (250 ml) for 6 h, the reaction solution was evaporated under reduced pressure and the oily residue was diluted with water (100 ml). The solid formed was filtered off and recrystallised from benzene to give 0.4 g (68.3%) of 3-(2-pyridyl)-4,5-diphenyl-1*H*-pyrazolo[3,4-*c*]pyridazine **12j**, m.p. 188–189°C. IR (cm^{-1}): 3419 (NH), 3090 (C–H, aromatic), 1677 (C=N), 1123, 852; ^{1}H NMR (DMSO-d_6): δ 7.24 (m, 10H, 2Ph), 7.66 (dd, 1H, *J* = 5.5, =C^5-H, pyridyl), 7.88 (dd, 1H, *J* = 7.5, =C^4-H, pyridyl), 8.00 (dd, 1H, *J* = 5.5, =C^3-H, pyridyl), 8.33 (dd, 1H, *J* = 5.5, =C^6-H, pyridyl), 12.0 (s, 1H, NH); MS *m/z:* 349 (M^+, 80%), 348 (M^+ -1, 100%), 321 (M^+–N_2, 5%), 271 (M^+–C_5H_4N, 14.4%). Anal. Calcd for $C_{22}H_{15}N_5$: C, 75.5; H, 4.3; N, 20.0. Found: C, 75.3; H, 4.1; N, 19.8.

Irradiation in thiophene: After irradiation of compound **1** (0.5 g, 1.7 mmol) in thiophene (250 ml) for 48 h, the reaction mixture was evaporated under reduced pressure and the solid residue was washed several times with diethyl ether and recrystallised from ethanol to give 3-(2-thienyl)-4,5-diphenyl-1*H*-pyrazolo[3,4-*c*]pyridazine **13**, 0.3 g (50.5%), m.p. 299–300°C. IR (cm^{-1}): 3425 (NH), 3075 (C–H, aromaric), 1645 (C=N), 1208, 1130. ^{1}H NMR (DMSO-d_6): δ 5.92 (dd, 1H, *J* = 5.5, =C^4-H, thienyl), 6.65 (dd, 1H, *J* = 5.5, =C^5-H, thienyl), 7.08 (dd, 1H, *J* = 4.5, =C^3-H, thienyl), 7.24–7.45 (m, 10H, 2Ph) and 12.10 (s, 1H, NH); MS *m/z*: 354 (M^+, 100%), 353 (M^+- 1, 90%), 321 (M^+–SH, 9.6%). Anal. Calcd for $C_{21}H_{14}N_4S$: C, 71.2; H, 4.0; N, 15.8. Found: C, 70.9; H, 3.7; N, 15.7.

Irradiation in acetylacetone: Irradiation of compound **1** (0.5 g, 1.7 mmol) in acetylacetone (150 ml) for 3 h, gave 3-acetyl-4-methyl-9,10-diphenylpyridazino[3`,4`:3,4]pyrazolo[5,1-*c*]-1,2,4-triazine **14**, 0.5 g (83%), m.p. 260–261°C (from methanol). IR (cm^{-1}): 3067 (C–H, aromatic), 2920, 2812 (C–H, aliphatic), 1730 (C=O, ketone), 1645 (C=N), 1213, 849. ^{1}H NMR (DMSO-d_6): δ 2.91 (s, 3H), 3.28 (s, 3H, CH_3), 7.24–7.47 (m, 10H, 2Ph). MS *m/z*: 380 (M^+, 81%), 337 (M^+–COMe, 64% ion A), 271 (ion A–N=NC=C–Me, 9%). Anal. Calcd for $C_{22}H_{16}N_6O$: C, 69.5; H, 4.2; N, 22.1. Found: C, 69.2; H, 4.0; N, 21.9.

Irradiation in ethyl acetoacetate: Irradiation of compound **1** (0.5 g, 1.7 mmol) in ethyl acetoacetate (150 ml) for 5 h, gave ethyl 4-methyl-9,10-diphenylpyridazino[3`,4`:3,4]-pyrazolo[5,1-*c*]-1,2,4-triazine-3-carboxylate **15**, 0.5 g (78.1%), m.p. 237–238°C (from ethanol). IR (cm^{-1}): 3059 (C–H, aromatic), 2929, 2850 (C–H, aliphatic), 1775 (C=O), 1665 (C=N), 1535, 1442, 1051. ^{1}H NMR (DMSO-d_6): δ 1.41 (t, 3H, CH_3), 4.54 (q, 2H, CH_2) for ethoxy group proton, 2.91 (s, 3H, CH_3), 7.02–7.46 (m, 10H, 2Ph). MS *m/z*: 410 (M^+, 87.3%), 337 (M^+–COOEt, 48.6% ion A), 271 (ion A–N=N-C=C–Me, 17.4%). Anal. Calcd for $C_{23}H_{18}N_6O_2$ **:** C, 67.3; H, 4.4; N, 20.5. Found: C, 67.1; H, 4.2; N, 20,2.

Irradiation in diethyl malonate: Irradiation of compound **1** (0.5 g, 1.7 mmol) in diethyl malonate (125 ml) for 5 h gave ethyl 3-(4,5-diphenyl-1*H*-pyrazolo[3,4-*c*]pyridazine-3-ylhydrazono)glyoxalate **16**, 0.2 g (33.6%), m.p. 199–200°C (from ethanol). IR (cm^{-1}): 3322 (NH), 3220, 3059 (C–H, aromatic), 2980, 2927, 2856 (C–H, aliphatic), 1733 (C=O), 1605 (C=N), 1565, 1443. ^{1}H NMR (DMSO-d_6): δ 1.34 (t, 3H, CH_3), 4.3 (q, 2H, CH_2), 7.29–7.46 (m, 10H, 2Ph), 8.1 (s, 1H, CH), 12.07 (s, 1H, NH). MS *m/z*: 386 (M^+, 20%), 313 (M^+–COOEt, 100% ion A), 286 (ion A–N=CH–COOEt, 15% ion B), 271 (ion B–NH, 5% ion C), 258 (ion C–N_2, 70%). Anal. Calcd for $C_{21}H_{18}N_6O_2$: C, 65.3; H, 4.7; N, 21.75. Found: C, 65.1; H, 4.5; N, 21.5.

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