THE PHOTOREARRANGEMENT OF SOME 4-ARYLAZOPYRAZOLIN-5-ONE DERIVATIVES.

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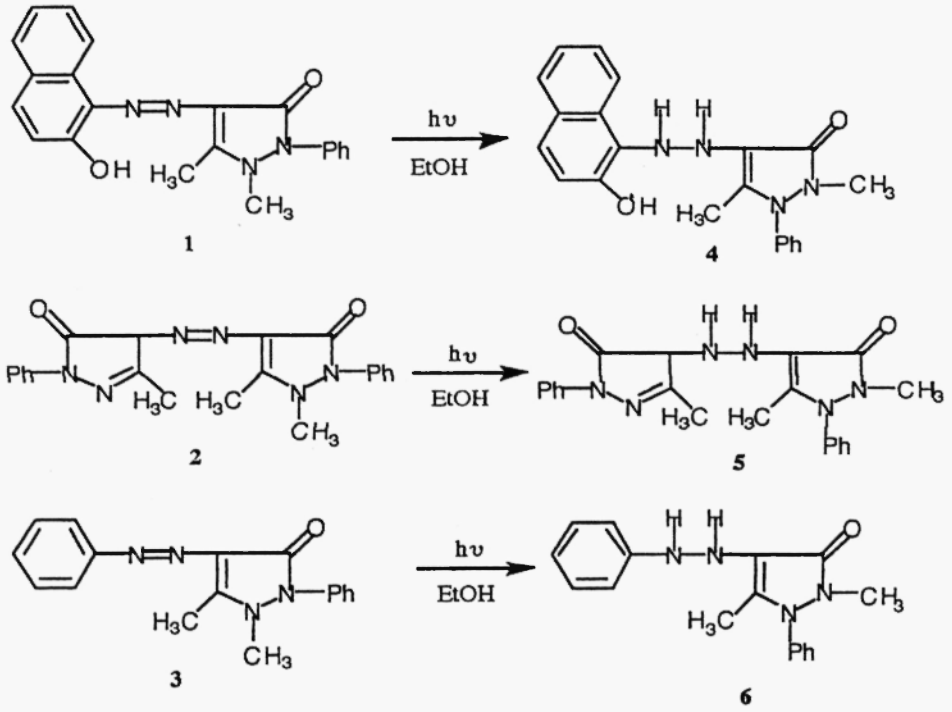
Abstract:- The photochemical reactions of some azo derivatives of substituted pyrazolin-5-one were examined. Irradiation of 4-arylazopyrazolin-5-one **1-3** gave the corresponding hydrazo derivatives **4-6** via reduction of the azo group and rearrangement of the pyrazolinone ring. The photo α-cleavage of (-CO-N-Ph) in the pyrazolinone ring is suggested leading to the formation of a diradical component followed by cyclization to give the final rearrangement products.

Introduction: Diazopyrazole derivatives are known as versatile reagents that have been extensively utilized in synthetic heterocyclic chemistry[1-4]. A variety of pyrazolinone derivatives are known to exhibit analgesic and antiflammatory effect[5,6]. Continuation to our previous work aiming towards the synthesis of new substituted pyrazoles with expected pharmacological activity[7-10], it is of interest to study the photochemistry of the corresponding azo derivatives. Thus, when 2,3-dimethyl-1-phenyl-4-(2-hydroxynaphthyl-azo)-pyrazolin-5-one 1 readily accessible from the reaction of diazotized 4-amino-2,3-dimethyl-1-phenyl-pyrazolin-5-one with β-naphthol[11] was irradiated for 20 hours in ethanol under nitrogen using a high pressure mercury lamp equipped in a pyrex vessel. A product in which the reduction of the azo group to hydrazo group accompanied by rearrangement in the pyrazolinone ring was obtained to give 1,3-dimethyl-2-phenyl-4-(2-hydroxynaphthyl-hydrazo)-pyrazolin-5-one 4 (Scheme 1). The structure of 4 was confirmed by a study of its MS and ^{1}H-NMR spectrum. The MS spectrum revealed the correct molecular ion peak (c.f. experimental section). Comparison between the ^{1}H-NMR of 4 and its starting material 1 revealed essentially the downfield shift of the N-methyl pryazoline protons at δ=4.10 which is attributed to its attachment to the carbonyl group of the ring. The naphthyl proton H-8 appeared very downfield in the reactant 1 at δ=7.65 ppm due to the fact that this proton suffers from anisotropic effect of the -N=N- group in 1 which disappeared in the product 4 (c.f. experimental section). The proton of the -NH group in the



1 4 2 5 3 6

Scheme 1

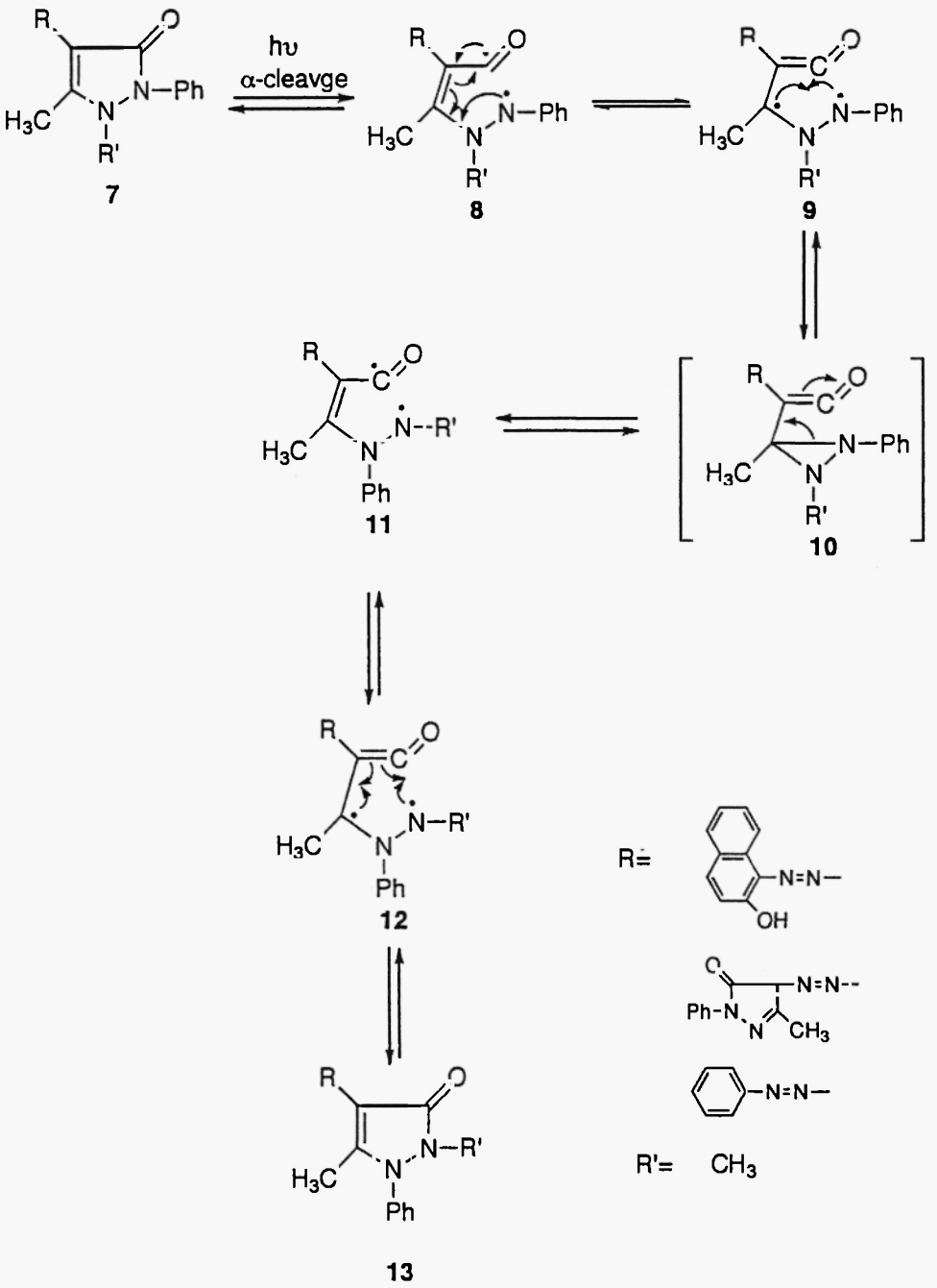
product 4 appeared at δ=9.80 proving the reduction phenomena. The photoreduction of the azo group to hydrazo group was also previously observed[12]. It has also been reported that the photoreduction of the azo group to hydrazo in azobenzene using isopropanol as solvent increased in the presence of little oxygen[13]; therefore, the previous reaction in the presence of air where the same product was obtained was repeated. Similarly when 2,3-dimethyl-1-phenyl-4-(3'-methyl-1'-phenylpyrazolin-5-one-4'-yl-azo)pyrazolin-5-one 2 and 2,3-dimethyl-1-phenyl-4-(phenylazo)-pyrazolin-5-one 3 were irradiated under the same previous conditions gave the corresponding products 5 and 6 respectively (Scheme 1). The ^{1}H-NMR of both products showed the appearance of the N-methyl pyrazolinone protons at δ=4.17 and 4.14 ppm respectively. Also the proton of the -NH group in both products appeared at δ=9.70 and 10.10 ppm respectively (c.f. experimental section). The previous results proved that both products 5 and 6 were also formed via reduction of the azo group and rearrangement of pyrazolinone ring as occured in the case of 4.

The rearrangement of the pyrazolinone ring presumably proceeds as outlined in Scheme 2. The photo α-cleavage of the (-CO-N-Ph) group in 7 takes place to give diradical 8 and/or 9 which gives the ketone 10. The latter then undergoes ring opening to give 11 or 12 which then cyclized to the rearranged product 13. Certainly the phenyl group stabilizes the nitrogen radical due to the delocalization and allows for a more easy homolysis of -CO-N-Ph than -CO-N-CH_3 or -CO-N-H and this could be the main driving force for this rearrangement (Scheme 2).

Experimental

All melting points were uncorrected. The IR spectra were obtained on a Pu 9712 IR spectrophotometer. The ^{1}H-NMR spectra were recorded on Jeol 270 MHz and ^{13}C-NMR is measured on Jeol 68.5 MHz. The chemical shifts were expressed as δ ppm. the mass spectra were run at 75 ev on Kratos MS equipment. Analytical data were obtained from the Microanalytical Unit at the National Research Center. N_2 gas were purified using literature method[14].

2,3-Dimethyl-1-phenyl-4-(2-hydroxynaphthylazo)pyrazolin-5-one (1). Red crystals, m.p. 238°C. IR.ν : 3550-3350 (OH), 3070 (CH aromatic), 2920, 2890 ($2CH_3$), 1670 (C=O) and 1630 (C=C). ^{1}H-NMR δ : 3.28 (s, 3H, CH_3), 3.43 (s, 3H, CH_3), 7.21-7.90 (m, 10H, C_6H_5 and naphthyl H-3, H-4, H-6, H-7, H-9), 8.6 (d, 1H, naphthyl H-8) and 14.2 (s, 1H, OH). Analysis for $C_{21}H_{18}N_4O_2$=358. Calcd : C 70.30, H 5.00, N 15.60. Found : C 70.10, H 5.00, N 15.40. M^+(m/e)=358.



Scheme 2

Irradiation of 1:- A solution of (0.358 g, 1 mmol) of **1** in 200 ml absolute dried ethanol was irradiated using a high mercury lamp/pyrex vessel, λ>313 nm for 20 h. The reaction progress was followed by TLC. The colour of the reaction solution changed from red to pale yellow. The solvent was evaporated under air. The oil formed was triturated with methanol and left overnight in refragerator. The product formed was collected by filteration and the crystalization was carried out using chloroform-n-hexane mixture (8 : 1) to produce **4**.

1,3-Dimethyl-2-phenyl-4-(2-hydroxynaphthylhydrazo)pyrazolin-5-one (4): Yellow crystals, m.p. 158°C, yield (0.250 g, 70%). IR.ν : 3440-3500 (OH), 3360 (NH), 3070 (CH aromatic), 2910, 2880 ($2CH_3$), 1670 (C=O) and 1630 (C=C). ^{1}H-NMR δ : 2.95 (s, 3H, CH_3), 4.10 (s, 3H, N-CH_3), 6.64-7.40 (m, 11H, C_6H_5, naphthyl H-3, H-4, H-6, H-7, H-9 and OH proton), 7.65 (d, 1H, naphthyl H-8) and 9.56 (s, 2H, 2NH). Analysis for $C_{21}H_{20}N_4O_2$=360. Calcd : C 70.00, H 5.55, N 15.55. Found : C 70.01, H 5.50, N 15.55. M$^+$(m/e)=360.

2,3-Dimethyl-1-phenyl-4-(3'-methyl-1'-phenylpyrazolin-5-one-4'-yl-azo)-pyrazolin-5-one (2): Orange crystals, m.p. 195°C. IR.ν : 3064 (CH aromatic), 2979, 2966-2882 ($2CH_3$), 1749, 1672 (C=O). ^{1}H-NMR : 11.22, 11.18, 35.99 ppm ($3CH_3$), 118.39, 124.14, 128.89, 129.38 (CH, o, m of the 2 aryl group), 124.84, 127.23 (CH p of the aryl group), 157.92, 159.00 (2C=O), 114.29, 128.61, 134.31, 138.37, 143.33, 143.88 other C's.

Irradiation of 2: Using the previous conditions, a solution of (1 mmol) of **2** in 200 ml absolute dry ethanol was irradiated for 8h. The solvent was evaporated under air. The oil formed was triturated with chloroform-cyclohexane. The solid crystals formed was collected by filteration and crystallized from chloroform-cyclohexane (6 : 4).

1,3-Dimethyl-2-phenyl-4-(3'-methyl-1'-phenylpyrazolin-5-one-y'-yl-hydrazo)-pyrazolin-5-one (5): Yellow crystals, m.p. 147°C, yield (0.25g, 65%). IR.ν : 3550-3400 (2NH), 3060 (CH aromatic), 2975, 2965 and 2900 ($3CH_3$), 1750, 1690 (2C=O) and 1595 (C=N). ^{1}H-NMR δ : 2.07 (CH_3), 2.75 (CH_3), 4.17 (N- CH_3), 6.50-8.05 (m, 11H, ArH's and pyrazolone CH) and 9.7(s, 2H, 2NH). ^{13}C-NMR: 10.00, 12.50, 35.80 ($3CH_3$), 119.70, 120.70 (0, CH aromatic), 128.66, 129.10 (m, CH aromatic), 124.10, 125.35 (p, CH aromatic). Analysis for $C_{21}H_{22}N_6O_2$=390. Calcd : C 64.61, H 5.64, N 21.53. Found : C 64.60, H 5.62, N 21.50. M$^+$(m/e)=390.

2,3-Dimethyl-1-phenyl-4-(phenylazo)pyrazolin-5-one (3): Compound **3** was prepared as literature method[15].

Irradiation of 3: A solution of (1 mmol) of **3** in 200 ml ethanol was irradiated under the same conditions for 12 h. The solvent was evaporated under air. The oil formed was triturated with chloroform-n-hexane. The solid formed was collected by filteration and crystallized from chloroform-n-hexane.

1,3-Dimethyl-2-phenyl-4-(phenylhydrazo)pyrazolin-5-one (6): Yellow crystals, m.p. 103°C, yield (1.91 g, 65%). IR.ν : 3550-3400 (2NH), 3045 (CH aromatic), 2945, 2925 ($2CH_3$), 1685 (C=O), 1640 (C=C). ^{1}H-NMR δ : 1.24 (s, 3H, CH_3), 2.86 (s, 3H, CH_3), 7.04-7.73 (m, 10H, ArH's) 10.10 (s, 2H, 2NH). Analysis for $C_{17}H_{18}N_4O$=294. Calcd: C 69.39, H 6.12, N 19.04. Found : C 69.30, H 6.10, N 19.08. M^+(m/e)=294.

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