

Photolysis of Some Diaryl Benzothiazolopyrazolines

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ABSTRACT

The irradiation of a series of benzothiazolopyrazoline derivatives by UV Light in acidic medium using benzophenone as photo sensitizer resulted into rearranged pyrazolines. The effect of various substituents on the rate of photolysis and yield of the photoproducts were also studied.

Keywords: Irradiation, benzothiazolopyrazolines, photosensitizer, photolysis, photoproducts.

INTRODUCTION

The photochemistry of organic compounds has been a vast field of research. Photochemistry of all classes of compounds has been studied, but very few reports are there in the literature of photochemical reactions of pyrazolines.¹⁻¹² Pyrazolines are important N-containing heterocyclic compound which possesses wide spectrum of biological activities¹³⁻¹⁵ Benzothiazolopyrazolines also have various biological and pharmacological activities.¹⁶⁻²²

Therefore in the present paper we report the photolysis of some benzothiazolopyrazolines in acidic medium using benzophenone as a photosensitizer. The effect of various substituents on rate of photolysis and yield of the photoproducts also studied.

RESULTS AND DISCUSSION

All the photoproducts have been characterized with the help of spectral data as follows- The IR (KBr) of the product **4a** shows absorptions at 2966 cm⁻¹ & 2922 cm⁻¹ (CH Str.) 1668 cm⁻¹ (C=N str.), 1601 cm⁻¹ (C=C str.)etc. ¹H NMR (CDCl₃) of the product shows

following signals: δ 7.05-7.82 (aromatic protons), δ 5.6 (CH proton of pyrazoline ring) and δ 4.2 (CH₂ protons of pyrazoline ring). ¹³C NMR (CDCl₃) of the product shows important signals at δ 113-118, 152 (carbon atoms of pyrazoline ring) δ 120 to 150 (carbon atoms of aromatic rings), and δ 162 (S-C=N, thiazole ring). LCMS spectrum of the photoproduct shows molecular ion peak at m/z 355 corresponding to the molecular weight of the product. Other important peaks were observed at m/z 357(M+2), 278 (355-C₆H₅) etc.

Effects of various substituents

On the basis of the results obtained, broadly speaking, it appears that the presence of an electron donating OCH₃ group particularly on ring B makes the reaction little faster giving higher yield in lesser time and the presence of electron withdrawing Cl on ring B makes the reaction slower giving lesser yields. This may be due to the fact that an electron donating group on ring B would stabilize the radical **II** produced by the opening of pyrazoline ring whereas an electron withdrawing group would destabilize it. However, the difference in the results of pyrazolines containing these groups is not much which may be because the Cl is not very strongly electron withdrawing due to the presence of lone pair of electrons. It is also observed that in pyrazoline **4b** the yield obtained is the minimum and the time required is the maximum. This may be due to that an ortho-OH group would increase the steric repulsion in the product in a particular conformation thereby defacilitating its formation. The results of **4e** are also almost same; the slight difference is due to the presence of OCH₃ group which shows an activating effect.

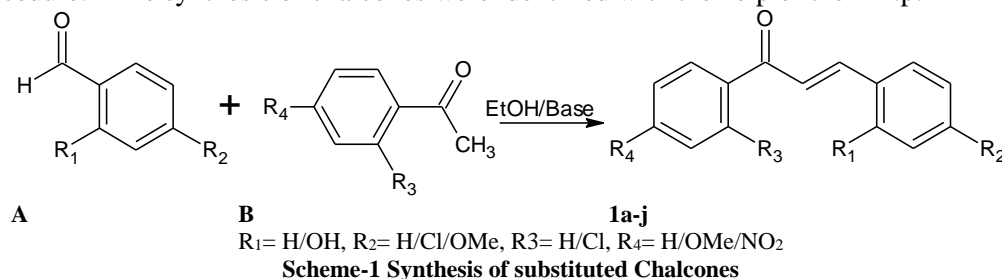
EXPERIMENTAL

Material and methods

The pyrazoline derivatives have been synthesized using substituted chalcones and 2-hydrazinobenzothiazole (*Across Chem*) as follows using the standard procedure reported earlier.¹³ The benzothiazolopyrazolines when irradiated by UV light undergoes rearrangement to give the photoproducts from V301-V310. The structures of the products have been characterized by IR, ¹H NMR, ¹³C NMR and mass spectral analysis.

Synthesis of substituted chalcones

Substituted chalcones were prepared by the base catalysed Claisen Schmidt condensation of substituted aryl aldehydes and substituted acetophenones using reported procedure.²³ The synthesis of chalcones were identified with the help of their m.p.



Synthesis of substituted pyrazolines

The chalcones (**1a-j**) and 2-hydrazinobenzothiazole (*Across Chem*) (**2**) were taken in equimolar amounts in a round bottomed flask containing ethanol and the mixture was refluxed for 3-4 hrs with constant stirring. The reaction mixture was then allowed to cool. The solid product **3a-j** obtained was filtered, washed with water and dried. The product was recrystallised by 95% ethanol.²⁴

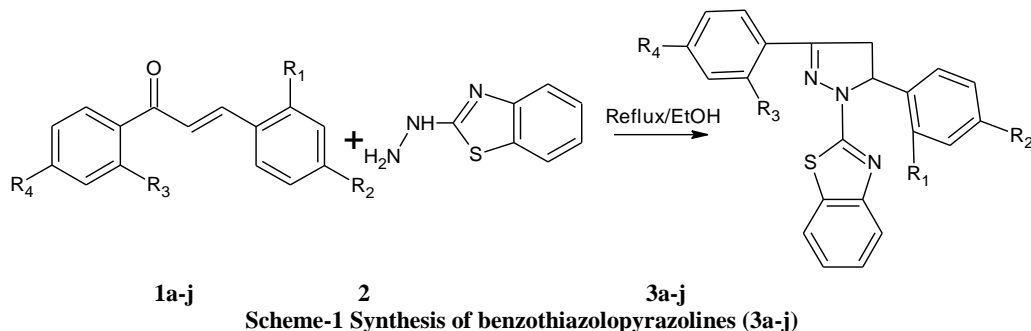


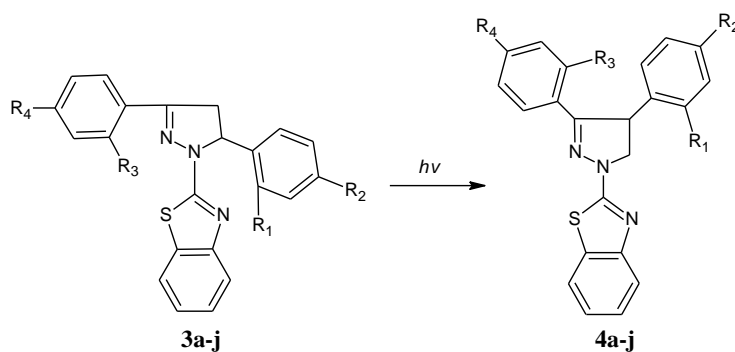
Table1: Physical data of synthesized pyrazolines

Product	R ₁	R ₂	R ₃	R ₄	m.p. (°C) ²⁴
3,5-diphenyl-1-benzothia-zolopyrazoline [3a]	H	H	H	H	173
3-phenyl, 5-(2'-hydroxyphenyl)-1-benzothiazolopyrazoline [3b]	OH	H	H	H	225
3-phenyl, 5-(4'-chlorophenyl)-1-benzothiazolopyrazoline [3c]	H	Cl	H	H	145
3-(4-methoxyphenyl)-5-phenyl-1-benzothiazolopyrazoline [3d]	H	H	H	OCH ₃	148
3-(4-methoxyphenyl)-5-(2'-hydroxyphe-nyl)-1-benzothia-zolopyrazoline [3e]	OH	H	H	OCH ₃	250-252
3-(4-methoxyphenyl)-5-(4'-chlorophe-nyl)-1-benzothia-zolopyrazoline [3f]	H	Cl	H	OCH ₃	125
3-(4-methoxyphenyl)-5-(4'-methoxy-phenyl)-1-benzothia-zolopyrazoline [3g]	H	OCH ₃	H	OCH ₃	120-122
3-(4-nitrophenyl)-5-(4'-chlorophenyl)-1-benzothia-zolopyrazoline [3h]	H	Cl	H	NO ₂	143
3-(4-nitrophenyl)-5-(4'-methoxyphenyl)-1-benzothia-zolopyrazoline [3i]	H	OCH ₃	H	NO ₂	189
3-(4-chlorophenyl)-5-(4'-chlorophenyl)-1-benzothia-zolopyrazoline [3j]	H	Cl	H	Cl	154-155

Photolysis of Benzothiazolopyrazolines

1.5 gms of benzothiazolopyrazoline (V201-210) was taken in 250 mL beaker and dissolved in 2:1 CHCl₃:EtOH and 0.01 gm benzophenone was added as a photosensitizer. The

solution was made acidic by adding 1-2 drops of conc. HCl. Then the solution was irradiated in an immersion well photo reactor with low pressure mercury vapor lamp placed inside the immersion well. The mixture was maintained at room temperature by constant water circulation. TLC of the reaction mixture was taken after every two hours. After 10hrs the TLC showed two spots corresponding to the reactant and the expected product. After 30-45hrs of irradiation, spot of the substrate became very faint, then the irradiation was stopped. The reaction mixture was concentrated on water bath under reduced pressure and was kept overnight at room temperature. The solid obtained was filtered, washed with water, dried and recrystallized from ethanol to give pure product (**4a-j**). The physical data of the products is given in table 2.



The reactions were carried out in neutral and alkaline medium also but no change in TLC was observed even after prolonged irradiation.

Table-2 Photoproducts of substituted benzothiazolopyrazolines (4a-j)

Product	Time (hrs)	Yield (gms)	m.p. (°C)	Elemental Analysis	
				Calculated	Observed
4a	38	1.01	64	C 74.34; H 4.82; N 11.82	C 74.25; H 4.56; N 11.68
4b	45	0.91	152	C 71.14; H 4.61; N 11.37	C 71.01; H 4.47; N 11.46
4c	40	0.99	96	C 67.77; H 4.14; Cl 9.09; N 10.78	C 67.61; H 4.21 Cl 9.15; N 10.86
4d	35	1.10	81	C 71.66; H 4.97; N10.9	C 71.53; H 4.89; N 10.81
4e	42	0.92	144	C 68.81; H 4.77; N 10.47	C 68.69; H 4.70; N 10.39
4f	37	0.99	115	C 65.78; H4.32; Cl 8.44; N 10.01	C 65.60; H4.23; Cl 8.31; N 9.95
4g	32	1.21	72	C 69.37; H 5.09; N 10.11	C 69.26; H 4.88; N 10.01
4h	36	1.00	132	C 60.76; H 3.48; N 12.88; Cl 8.15	C 60.65; H 3.40; N 12.78; Cl 8.22
4i	34	1.15	154	C 64.17; H 4.21; N 13.01	C 64.29; H 4.12; N 12.87
4j	38	0.99	102	C 62.27; H 3.56; Cl 16.71; N 9.90	C 62.10; H 3.43; Cl 16.56; N 9.81

PROPOSED MECHANISM

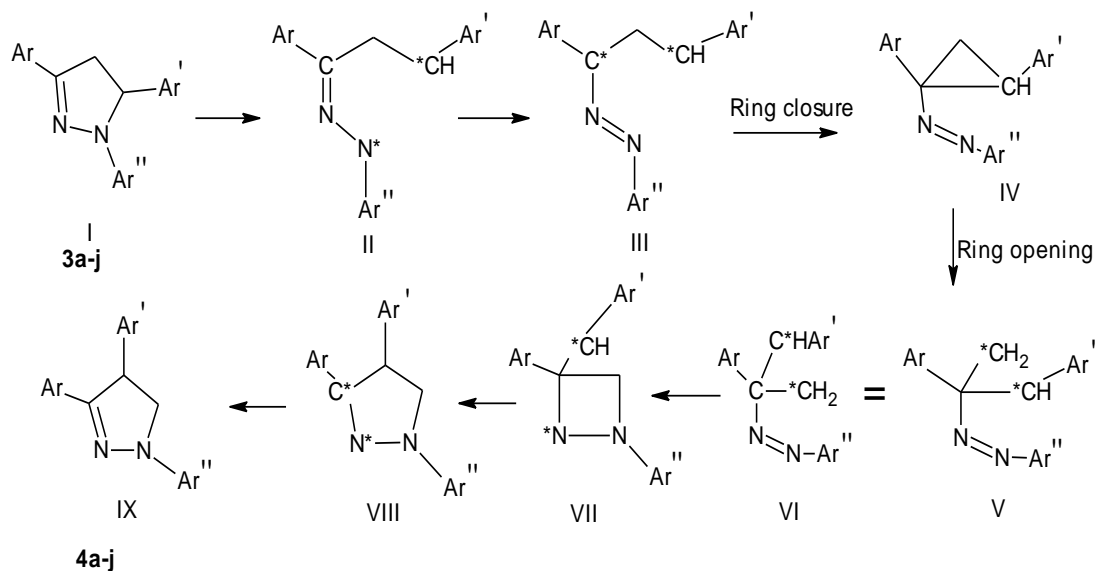


Fig.1: Proposed mechanism for the photolysis of benzothiazolopyrazolines

Upon irradiation carbon-nitrogen bond in 1-benzothiazolo-3,5-diaryl pyrazoline (**I**) undergoes cleavage giving biradical **II** which rearranges to another biradical **III**, followed by ring closure to form **IV**. Cyclopropane ring formed in **IV** being unstable opens up to give biradical **V** which forms a 4-membered diazetidine ring (**VII**) involving N=N through **VI** after rotation of tetrahedral carbon. Finally **VII** undergoes ring expansion to give the rearranged 1-benzothiazolo-3,4-diaryl pyrazoline **IX**.

CONCLUSION

In the present paper, various benzothiazolopyrazolines have been synthesized and their photochemical transformation was studied in acidic, neutral and alkaline medium. No change in the reaction is observed in alkaline and neutral medium even after prolonged irradiation. It is observed that in 3-phenyl, 5-(2'-hydroxyphenyl)-1-benzothiazolopyrazoline (**4b**) the yield obtained is minimum and the time required is maximum. It is also noted that electron withdrawing substituents like chlorine on ring make the reaction slower giving lesser yield.

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