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A NOVEL PHOTOCHEMICAL CYCLISATION OF 4-CHLORO-3-(N-ARYLIMINOMETHYL) (2H)BENZOPYRANS AND BENZOTHIOPYRANS

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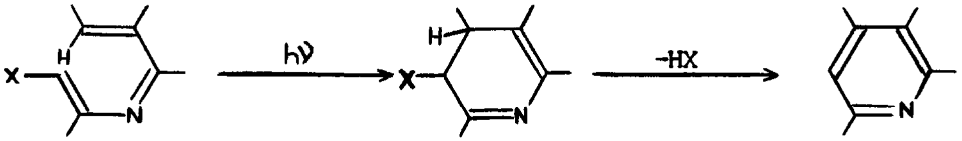
Abstract: Photolysis of 4-chloro-3-(N-Aryliminomethyl) (2H)benzopyrans and benzothiopyrans, 1a - g, yielded the respective quinolines 3a - g.

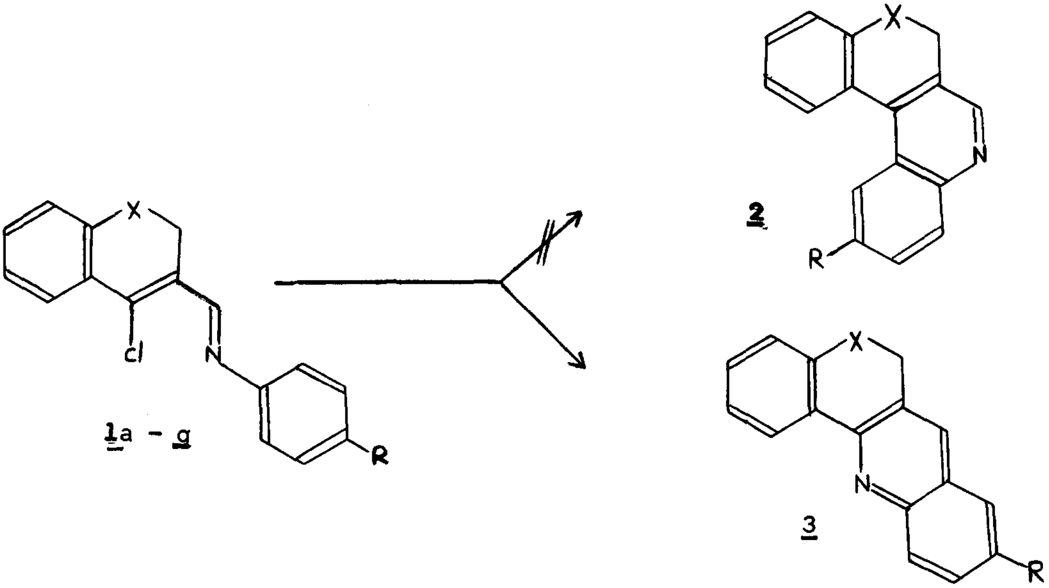
There has been considerable interest in the study of the photochemical cyclisation of imines derived from aromatic aldehydes or ketones, and aryl amines. In contrast to the smooth oxidative photocyclisation undergone by the stilbenes, the photochemistry of the aza analogues has been found to be more complex[1a-j]. While the non-oxidative photocyclisations (elimination of HX) have been well investigated and synthetically exploited in the field of stilbene and enamide photolysis[2a-c], reports on analogous studies involving the ω-haloazahexatrienes (Scheme I) are lacking.

Scheme I



In this communication, we wish to report a novel transformation encountered in an attempted photocyclisation of the N-arylimines (1) derived from 4-chloro-3-formyl(2H)benzopyrans and benzothiopyrans. Reaction of 4-chloro-3-formyl(2H)benzopyrans and benzothiopyrans with arylamines in dichloromethane at 0° C, in the presence of p-toluene sulfonic acid as catalyst, afforded the respective Schiff's bases 1 (Scheme II) in good yields[3] . NOE studies on 1 indicate the configuration to be anti. Irradiation of a methanolic solution of the chloroimines 1[4](10^{-3}M) in an Argon atmosphere in a Rayonet reactor or in an immersion reactor with a 125W lamp[+], for 13-20 hours at room temperature or around 20°C, followed by chromatographic purification yielded the corresponding condensed Quinolines 3 albeit in low yields, identical in all respects with those obtained by an unambiguous route[5a,b,c]. There was no reaction in the dark even after two days. Upon exposure to laboratory light conditions, the yellow methanolic solution of the chloroimine 1c gradually turned to dark red. Tlc analysis of the red solution showed the presence of mostly starting compound, with a little of the cyclised product 3c. Prolonged exposure however, resulted in the complete conversion to the cyclised product 3c.

Scheme II

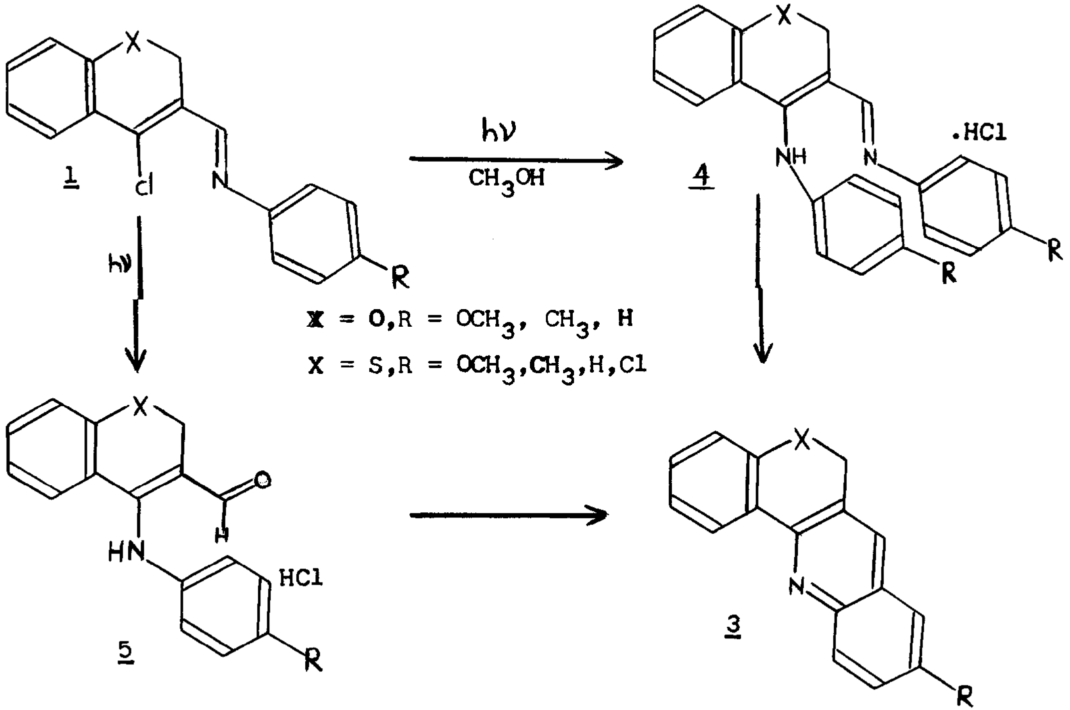


TABLE

Chloroimine 1	M.P^{o}C	Yield %	Cyclised product 2	M.P^{o}C	Yield %	Reaction time
1a X = O, R = OCH_3	118–119	70	2a	140	20	12 h
1b X = O, R = CH_3	127–129	68	2b	120	20	14 h
1c X = O, R = H	75	62	2c	118–119	15	12 h
1d X = S, R = OCH_3	93–94	78	2d	174	12	18 h
1e X = S, R = CH_3	90–92	75	2e	148	18	15 h
1f X = S, R = H	84–85	78	2f	100	14	13 h
1g X = S, R = Cl	90–92	70	2g	186	15	15 h

Though the non-oxidative photochemical cyclisations are carried out in the presence of bases like NaOH, K_2CO_3 etc., the photoreaction of 1 is found to be inhibited by acid scavengers. Thus, 1 remained unchanged on irradiation for more than 50 hours in the presence of potassium carbonate or sodium methoxide. Further, the transformation of 1 to 3 has been found to be specific for alcoholic solvents. No reaction was observed on irradiation of 1 in hexane or benzene for more than 50 hrs. Careful monitoring of this reaction by tlc in each case revealed the formation of enaminoimine 4. In a preliminary study, irradiation of a methanol solution of the enaminoimine 4c, prepared according to literature methods[6], also afforded the same product 3c while in the dark, no reaction was observed. The photochemical transformation of 1 to 3^{8a} clearly involves a number of steps and may proceed either through the intermediacy of the enaminoimine 4 arising by a disproportionation of 1^{7}, or through the 4-anilino-3-formyl derivative 5^{8b} as in Scheme III.

Scheme III



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3. Very few methods are known for the synthesis of such β-halovinylaldimines, eg., H. Harnish and A. Brack, Liebigs Ann.Chem., 740, 164 (1970); R. Niedlein and H. Heid, Synthesis, 65 (1977).

4. The (2H) benzopyrans and benzothiopyrans are known to be photolabile and undergo electrocyclic ring opening upon irradiation and lead to products arising either by nucleophilic attack on the heterotriene intermediate or by criss-cross addition. eg.,
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   - b. A. Padwa, A. Au, and W. Owens, J.C.S.Chem.Comm., 675 (1974).
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   On the basis of these literature reports, one could envisage additional interesting modes of electrocyclic reactions with the Schiff's bases 1.

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   - b. A.K. Kiang, and F.G. Mann, J.Chem.Soc. 1909 (1951).
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6. The cyclisation of the enaminoimines could give rise to 3 or 2. This aspect has been investigated in detail in the case of the thermal cyclisation of the enaminoimines 4^{6a}. In all these cases, only 3a-g were formed.
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7. A case of an acid catalysed formation of an enaminoimine, presumably from the disproportionation of a β-chlorivinyl(N-aryl) imine has been reported by A.M. Betrabet and S. Seshadri, Ind.J.Chem., 8, 502 (1970).

8. a. This selectivity has been explained on steric and conformational considerations by Gagan et al for the cyclisation of the enaminoimines from β-chlorocrotonaldehyde and 4-chlorobut-3-en-2-one, J.M.F. Gagan and D. Lloyd, J.Chem.Soc.C, 2488 (1970).
   - b. The 4-anilino-3-formyl-(2H)benzopyrans and benzothiopyrans are not reported in literature. So far, our attempts to prepare these compounds from the 4-chloro-3-formylchromene and thiochromene have been unsuccessful.

+The immersion reactor used was supplied by Applied Photophysics Ltd., London.

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