

## Photochromic Pyranopyridines and Pyranoquinolines

HAMED A. AL-SEHAIBANI

Riyadh College of Technology

P.O. Box # 42826, Riyadh-115 51, Saudi-Arabia

The synthesis of [3,2-c], [3,2-b]-2,2-dimethyl-2H-pyranopyridines, 2,2-dimethyl-2H-quinolin-[1,2-b]-pyran and (1',3',3'-trimethyl-2-norborane)-2,2'-spiro-2H-pyrano-[1,2-b]-quinoline via Claisen arrangement of propargylether, photochromism and photochemical behaviour are described.

### INTRODUCTION

There has been a great deal of interest in organic photochromic compounds because of their commercial potential; especially spiroopyrans which have been documented in a comprehensive review by Brown and Durr<sup>1,2</sup> Becker *et al*.<sup>3</sup> established that findersine (1) undergoes a colourless to a very pale yellow colour change on exposure to ultraviolet light as expected from a mechanism involving the rupture of a C—O bond. Further understanding of detailed mechanism of photo colouring has been investigated by Russian workers.<sup>4</sup>

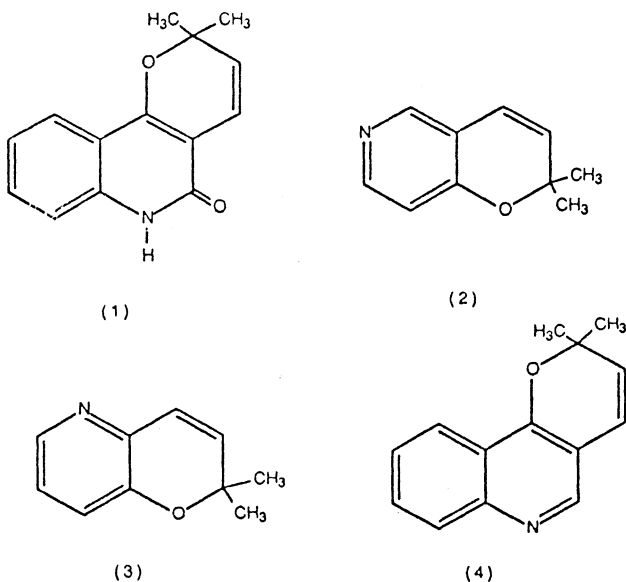


Fig. 1

This communication presents some preliminary results on the synthesis and the photochemical behaviour of the following pyrano-[1,2-*b*]-quinolines and pyrano pyridines.

Reisch and co-workers<sup>5,6</sup> recently reported the preparation of flindersine (1) by the reaction of 4-hydroxyquinolin-2-one with 3-chloro-3-methyl-but-2-ol (which can easily be prepared from 2-methyl-3-butyn-2-ol)<sup>7</sup>. They showed that flindersine (1) in methylcyanide underwent a photochemical 1,7-hydrogen shift.

## EXPERIMENTAL

Melting points were determined on a Reichert hot stage microscope with a thermometer which has been calibrated against a known standard. NMR spectra were recorded for solution in  $\text{CDCl}_3$  on a Perkin-Elmer R32 NMR spectrophotometer (90 MHz); chemical shifts were reported as  $\delta$  values, in ppm downfield from the internal standard tetramethylsilane.

Ultraviolet and visible absorption spectra were measured for solutions in toluene with a PU8700 uv/vis spectrophotometer.

3-Chloro-3-methyl-but-1-yne and 2-methyl-3-butyne-2-ol (1 mol) was added dropwise over 30 minutes to a well stirred mixture of anhydrous calcium chloride (56 g), copper (I) chloride (40 g), copper brozone (0.5 g), and concentrated hydrochloric acid (430 mL). The temperature was maintained between 0–5°C. After 1 h the upper layer was separated and washed with cold concentrated hydrochloric acid (3 × 100 mL) and water (3 × 100 mL) and dried over potassium carbonate. 3-Chloro-3-methyl-but-1-yne was obtained as a colourless liquid in 65% yield. NMR: 2.40 (1H, s, methylene), 1.52 (6H, s, methyls).

2-Ethyl-(1',3',3'-trimethyl norborane) chloride in a nearly quantitative yield as a crude oil which was used in the next step without further purification. NMR: 2.8 (1H, s, methylene), 1.3–0.15 (14H norborane).

*2,2-Dimethyl-2H-pyrano-[3,2-*c*]-pyridine (2)*: 3-Chloro-2-but-1-yne (4.9 g, 0.48 mmol) was added to a mixture of 4-hydroxypyridine (4.69 g, 0.48 mmol), benzyltrimethyl ammonium chloride (1 g), 1 M sodium hydroxide (30 mL) and toluene (50 mL). The reaction mixture was stirred at 55°C for 88 h; work-up gave a crude of propargyl ether which was heated under reflux in *ortho*-dichlorobenzene for 1 h. The solvent was removed in vacuum and the residue was distilled to give 2,2-dimethyl-2H-pyrano-[3,2-*c*]-pyridine (2) (2.1 g) as a pale yellow oil having b.p. 63.5°C; NMR: 8.28 (1H, d, J6 Hz); 8.17 (1H, s); 6.67 (1H, d, J6 Hz); 6.37 (1H, d, J10 Hz, 4-H); 5.67 (1H, d, J10 Hz, 3-H); 1.47 (6H, s, methyls).

*2,2-Dimethyl-2H-pyrano [3,2-*b*] pyridine (3)*: By a similar procedure, 3-hydroxypyridine (5 g, 0.42 mmol) gave the [3,2-*b*] isomer (3) (1.5 g) as a pale yellow oil having b.p. 95.5°C; NMR 7.95 (1 H, m); 6.90 (2H, m); 6.4 (1H, d, J10 Hz, 4-H); 5.73 (1H, d, J10 Hz, 3-H); 1, 45 (6H, s, methyls).

*2,2-Dimethyl-2H-pyrano-[1,2-*b*]-quinoline (4)*: 3-Chloro-3-but-1-yne (5.19 g, 0.5 mmol) was added to a mixture of 4-hydroxy quinoline (5.19 g, 0.5 mmol),

benzyltrimethylammonium chloride (0.5 g), 1 M sodium hydroxide (40 mL) and toluene (100 mL).

The reaction mixture was stirred at 55°C for 4 days workup gave a crude mixture of 2,2-dimethyl-2H-pyrano-[1,2-b] quinoline (4) and 4-quinolyl-3-methyl-3-butyryl ether as indicated by NMR. The mixture was boiled in *ortho*-dichlorobenzene for 2 h. After removing the solvent by distillation, a brown oil was left and chromatographed on silicagel using (20–80%) ethyl acetate and petroleum ether as eluant. 2,2-Dimethyl-2H-pyrano-[1,2-b]-quinoline (4) was obtained as colourless photochromic oil (0.1 g). NMR 7.50 (1H, s, J8 Hz, 8-H); (1H, t, J8 Hz 8-H); 6.45 (1H, d, J9 Hz, 3-H); 1.55 (6H, s, methyls).

(1',3',3'-Trimethyl-2-norborane)-2-2'-spiro-2H-pyrano-[1,2-b]-quinoline (8): 2-Ethyl-2-chloro-(1',3',3'-trimethyl norborane) (8 g, 0.4 mmol) was added to a mixture of 4-hydroxyquinoline (6 g, 0.43 mmol), 1 M sodium hydroxide (40 mL), toluene (100 mL) and benzyltriethylammonium chloride (0.75 g). The mixture was stirred at 55° C for 4 days. The organic layer was washed with 10% HCl and extracted with ether. The aqueous layer was washed with 10% NaOH, extracted with ether, dried and filtered.

The solvent was removed from the filtrate leaving yellow photochromic oil in low yield which could not be induced to be crystallized (0.1 g). NMR: 8.45 (1H, s, 5-H); 8.1 (1H, d, J8 Hz, 10-H); 7.95 (1H, d, J8 Hz, 7-H); 7.60 (1H, t, J8 Hz, 9-H); 7.45 (1H, t, J8 Hz, 8-H); 6.6 (1H, d, J9 Hz, 4-H); 5.75 (1H, d, J9 Hz, 3-H); 2.5–0.95 (14H, m, norborane).

## RESULTS AND DISCUSSION

As expected from a mechanism involving a C—O bond in flindersine (1), the photochromism is not limited to 2-H benzo or naphthopyrans, but is a general property of molecules with a 2H pyran moiety. The reaction of 3-chloro-3-methylbut-1-yne and 4-hydroxypyridine in the presence of benzyltrimethyl ammonium chloride in toluene at 55°C gave the crude propargyl ether in *ortho*-dichlorobenzene which led to 2,2-dimethyl-2H-pyrano-[3,2-C]-pyridine (2).

The reaction involves a Claisen rearrangement followed by a 1,5-hydrogen shift, with an electrocyclic ring closure to complete the process. The ultraviolet/visible spectrum of (2) in toluene showed a narrow absorption band in the near ultraviolet region taling off at 330 nm. A sample, impregnated into filter paper, gave a poor yellow photochromic response when irradiated with light from a flashgun at a liquid nitrogen temperature. The colour form bleached rapidly on increasing the temperature to 0°C.

The reaction of 3-chloro-3-methyl-butyne and 3-hydroxy pyridine gave crude propargyl ether which on cyclization of *meta*-substituted aryl propargyl ether (6) did not give the expected mixture of the [3, 2-b], 3, and (2,3-c) isomers (Fig. 2). The NMR data indicated that almost exclusive formation of [2,3-c] pyridine 3 had occurred with less than 5% of the [2,3-c] isomer being present.

The ultraviolet/visible spectrum of 2,2-dimethyl-2H-pyrano-[3,2-b]-pyridine (3) is similar to that of 2,2-dimethyl-2H-pyrano-[3,2-c]-pyridine (2) tailing off at 330 nm and there are no effects on the change of nitrogen position. Impregnation of (3) into filter the paper and irradiation with light from a flash-gun at liquid

nitrogen gave a yellow colour which bleached rapidly on increasing the temperature to 0°C.

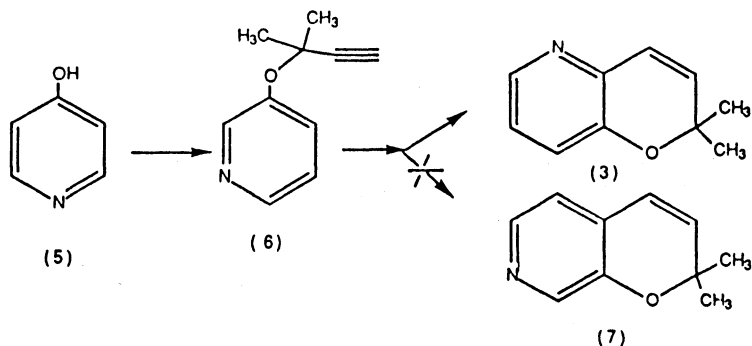


Fig. 2

The reaction of 3-chloro-3-methyl-but-1-yne and 4-hydroxy quinoline 11 in the presence of benzyltrimethyl ammonium chloride in toluene at 55°C gave 2,2-dimethyl-2H-pyrano-[1,2-b]-quinoline as well as 4-quinolyl-3-methyl-3-butynylether, which cyclized on boiling in *o*-dichlorobenzene to quinolino pyran. The ultraviolet/visible spectrum showed a sharp absorption band tailing off at 370 nm. Benzannulation at the 7, 8 position had resulted in a greater stabilization of the coloured form compared to the coloured form of the pyranopyridines (2) and (3).

Irradiation of the pyran impregnated into a filter paper with light from a flash-gun caused a pale yellow colour which faded rapidly at ambient temperature. The intensity of the coloured species was very weak compared with (1',3',3'-trimethyl-2-norborane)-2,2-spiro-2H-naphtho-[2,1]-pyran (9). The poor photochromic effect in toluene might be the result of fast thermal bleach or the low quantum efficiency in the spiro pyran.

The reaction of 2-ethynyl-2-(1',3',3'-trimethyl norborane)chloride and 4-hydroxy-quinoline in the presence of benzyltriethylammonium chloride in toluene at 55°C gave the pyrano quinoline (8) as yellow oil.

The ultraviolet/visible spectrum showed a sharp absorption band tailing off at 355 nm which revealed a hypsochromic effect of 30 nm compared with the corresponding (1',3',3'-trimethyl-2-norborane)-2,2-spiro-2H-naphtho-[2,1]-pyran<sup>9</sup>. Irradiation of the spiro-quinolinopyran at room temperature with light from a flash-gun caused a yellow colour which bleached rapidly at room temperature. The yellow solution showed two distinct fade rates, a fast initial (30 sec) and then a slow secondary fade (10 min); in toluene, the two fade rates are presumably due to cyclization of the *cis-o*-quinealeallide (9) and the *trans* (10) to *cis*-isomerization of the *trans-o*-quinealeallide and subsequent cyclization (9) (Figure 3). This is in accordance with the proposal by Chaud<sup>10</sup> for the complex fade rates characteristic of a number of coloured forms of nitro BIPS. The spiro-1,3,3-trimethyl-2-norborane group is believed to increase the sensitivity and stability of the coloured form.

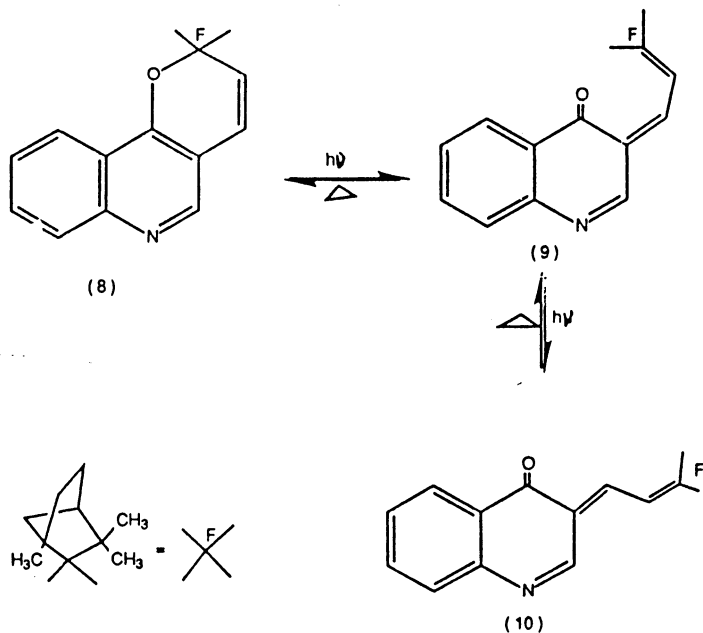


Fig. 3

### ACKNOWLEDGEMENT

The author wishes to thank the technicians at the College of Technology in Riyadh, Chemistry Department for their help.

### REFERENCES

1. G.H. Brown (Ed.) Photochromism, Vol. III, Techniques of Chemistry, Wiley Interscience (1971).
2. H. Durr and H. Bouan (Ed.) Photochromism Molecules and Systems, Elsevier (1990).
3. R.S. Becker and J. Kole, *J. Phys. Chem.* **72**, 997 (1968).
4. V.A. Murin, V.F. Mandhikov and A Barachevskii, *Opt. Spectrosc.*, **37**, 674(1974); Engl. Transl. **42**, 43 (1977).
5. J. Reisch, A. Bathe, B. Rosenthal and A.S. Selehiartimani, *J. Heterocyclic Chem.*, **24**, 869 (1987).
6. ———, *Artimani Archiv. Dev. Oharinazie*, **319**, 720 (1986).
7. G.F. Hennion and A.P. Boisselle, *J. Org. Chem.*, **26**, 725 (1961).
8. R.S. Becker and J. Michi, *J. Am. Chem. Soc.*, **88**, 5931 (1966).
9. H. Al Sehabani (unpublished work).
10. O. Chud, *Cahiers Physique (France)*, **52**, 39 (1954).
11. C.C. Price and R.M. Roberts, *J. Am. Chem. Soc.*, **68**, 1204 (1946).