

A Novel Preparation of Benzo[*c*]quinolizinium Compounds

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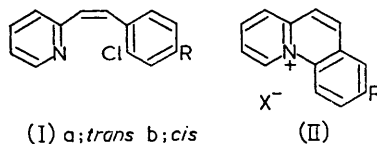
THE only preparation of the benzo[*c*]quinolizinium system (II) is that of Glover and Jones¹ who obtained the unsubstituted picrate and perchlorate salts from 2-cyanoquinoline and 1-bromo-3-ethoxypropane by a three-step synthesis. We report a simple procedure, using readily available starting materials, which can be extended to the preparation of substituted compounds of this series.

2-Chloro-5-nitrobenzaldehyde when refluxed with 2-picoline in acetic anhydride condensed to give *trans*-2'-chloro-4'-nitro-2-stilbazole² (Ia; R = NO₂) in good yield. *trans*-2-Stilbazole undergoes isomerisation when irradiated in benzene solution,³ and this technique was extended to the nitro-stilbazole (Ia; R = NO₂). During 48 hours' irradiation a salt-like compound, m.p. 306–307°, was precipitated in 70% yield. The characteristic ultraviolet spectrum¹ (λ_{\max} 255, 288, 343, 357, 374 m μ ; $\log_{10}\epsilon$ 4.54, 4.10, 3.66, 4.02, 4.06) and elemental analysis suggested that the new product was 8-nitrobenzo[*c*]quinolizinium chloride (II; R = NO₂, X = Cl).

trans-2'-Chloro-2-stilbazole (Ia; R = H), prepared in good yield from 2-picoline and *o*-chlorobenzaldehyde,² when irradiated gave a high yield of the *cis*-isomer (Ib; R = H), b.p. 130°/0.8 mm. (λ_{\max} 285; $\log_{10}\epsilon$ 4.03). Heating the *cis*-isomer (Ib; R = H) at 170° for 1 hr. precipitated pure

benzo[*c*]quinolizinium chloride (II; R = H, X = Cl) in 50% yield based on the *trans*-isomer initially used. The only by-product was the *trans*-stilbazole. It was subsequently found that isomerisation and quaternisation could be accomplished in one stage by heating the *trans*-stilbazole (Ia; R = H) in the presence of small amounts of iodine for 6 hr. at 240°. The product however, was much less pure than that from the photochemical reaction. Benzo[*c*]quinolizinium perchlorate (II; R = H, X = ClO₄) prepared by these reactions had the same ultraviolet spectrum and melting point as was reported previously.¹

The method has been extended to the synthesis of several other compounds in the series including benzologues. As expected, higher yields are obtained when there are electron-withdrawing groups in the benzene ring or electron-donating groups in the pyridine ring of the stilbazole.



(Received, June 9th, 1965.)

¹ E. E. Glover and G. Jones, *J. Chem. Soc.*, 1958, 3021.

² The great majority of stilbazoles prepared in this manner are obtained in the *trans*-form. *cis*- and *trans*-isomers are readily distinguished by their ultraviolet absorption spectra. See, for example, L. Horwitz, *J. Org. Chem.*, 1956, 21, 1039.

³ J. L. R. Williams, S. K. Webster, and J. A. Van Allan, *J. Org. Chem.*, 1961, 26, 4893.