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STUDIES ON NOVEL HETEROCYCLIC SYSTEM: REACTION OF 2-CHLOROQUINOLINE WITH 2-MERCAPTOANILINE

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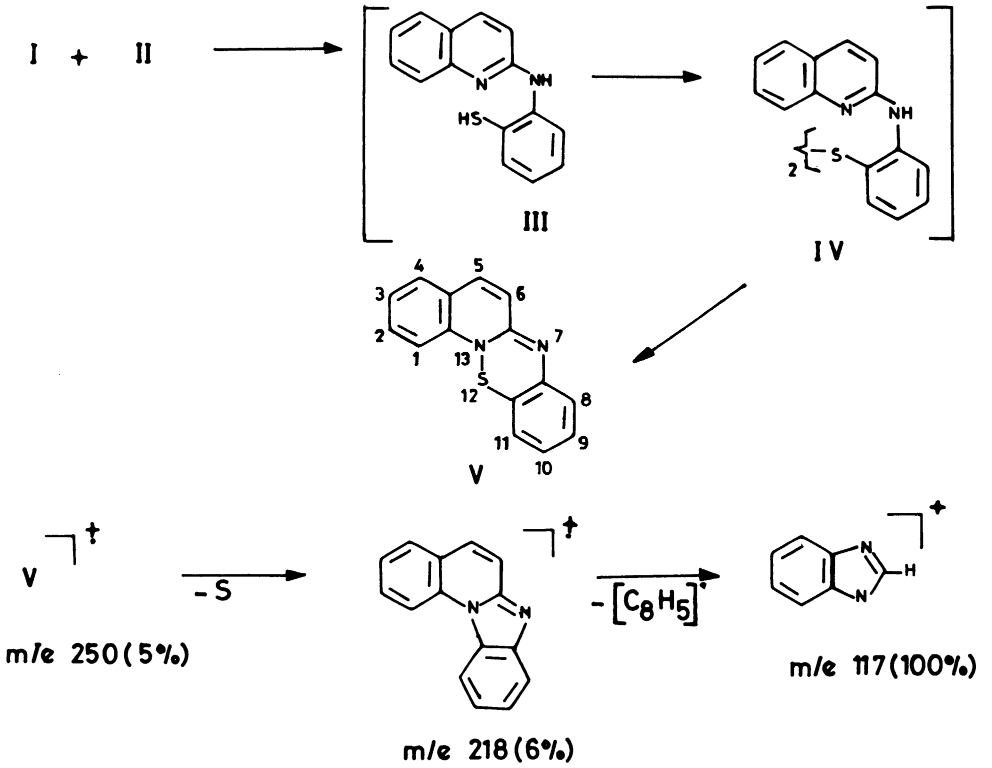
Reaction of 2-chloroquinoline (I) with 2-mercaptoaniline (II) has been investigated. The product has been characterised as the yet unreported 12-thia-7,13-diazabenz[a]anthracene (V) system on the basis of spectral and analytical data. Probable mechanism for the formation of V has been discussed.

In this communication we wish to report the synthesis of the novel heterocyclic ring system 12-thia-7,13-diazabenz[a]anthracene (V). This ring system is of particular interest in view of pronounced antihypertensive activity exhibited by 2H-1,2,4-benzothiadiazine derivative. Heating a mixture of 2-chloroquinoline (I) and 2-mercaptoaniline (II) at 160°C in DMSO for 90 minutes and purification of the reaction product by column chromatography (silica gel, benzene: chloroform = 50:50) afforded V in 15% yield as a green solid melting at 84°C.

Structural assignment for V comes from its elemental analysis[1] and spectral data. The mass spectrum shows M^+ at m/e 250. IR:2940, 1610, 1575, 1515, 1490, 1305 cm^{-1}; the pmr spectrum ($CDCl_3$, δ) exhibited a multiplet between 6.80 and 8.00 (9H) and a broad doublet at 8.90 (J=7Hz, 1H). The down field signal can be assigned to C-1 proton and this marked deschielding may be ascribed to the presence of N-S bond in the peri-position. Additional support for the structure comes from the mass fragmentation pattern which is depicted in the scheme.

Mechanistically, formation of the compound V may be considered to proceed via the disulfide (IV). It is reasonable to assume that the initial thiol (III) formed from I and II can undergo oxidation to IV[2] under the reaction conditions. Nucleophilic attack of the ring nitrogen on the disulfide linkage with the concomitant fission of the S-S bond leads to V. Similar reports in the literature[3,4] supports this assumption. Alternately, the bis-o-aminophenyl disulfide (IIa), which is readily formed from II under the reaction conditions, can condense with I to give the same disulfide IV, that can cyclize to V. But reaction of IIa and I under identical conditions did not give either IV or V in isolable yields.

Scheme



Notes and references

1. Presence of sulfur in the compound V has been inferred by the positive reactions of lead tetraacetate and sodium nitroprusside. Analysis calculated for $C_{15}H_{10}N_2S$: N, 11.20. Found: N, 11.12.

2. The assumed intermediate compounds III and IV could not be isolated from the reaction mixture. However, reaction of I and II in ethanol gave the disulfide IV, whose structure has been established from its elemental analysis and spectral data.

3. S.Miyano, N.Abe, K.Sumato, and K.Teramato, J.Chem.Soc., Perkin Trans.I, 1146 (1976).

4. F.M.Moracci, M.Cardellini, F.Liberatore Beratore, P.Marchini, G.Liso, and G.Ugo., Int. J. Sulphur Chem., 8, 341 (1973).

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