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BROMINATION REACTIONS OF 2-PHENYLTETRAHYDROQUINOLONES

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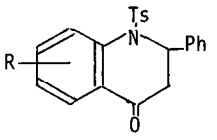
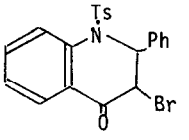
In 1945 Diesbach and Kramer reported[1] that treatment of N-tosyl-2-phenyl-1,2,3,4-tetrahydroquinol-4-one (Ia) with bromine in chloroform solution gave a monobromo derivative (Ib). These authors suggested that the bromine atom had entered ring A, possibly at position-6,



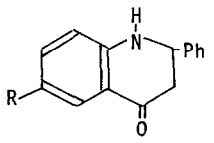
Ia, R = H; b, R = Br



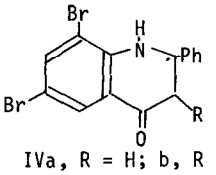
II

since the compound did not eliminate hydrogen bromide with pyridine. The reaction was repeated in the present work and the product was shown, by NMR spectroscopy (the C_2 and C_3 protons appeared as doublets, J = 2.67 Hz, at δ 6.4 and δ 4.9), to be the 3-bromo-derivative II.

Bromination of 2-phenyl-1,2,3,4-tetrahydroquinol-4-one (IIIa), which was prepared by



IIIa, R = H; b, R= Br



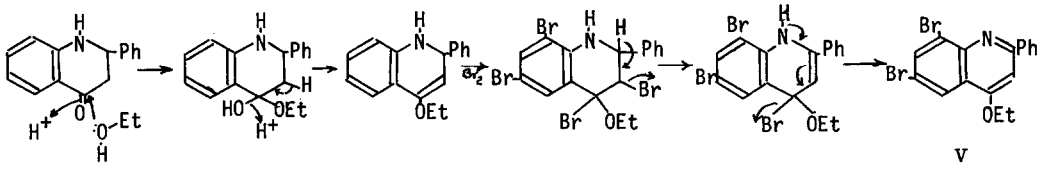
IVa, R = H; b, R = Br

the cyclisation of 2-aminochalcone,[2] with one molecular equivalent of bromine in chloroform at room temperature, gave the 6-bromo derivative IIIb in 30% yield. When four molecular equivalents of bromine were used in the reaction the main product was 2-phenyl-3,6,8-tribromoquinol-4-one {IVb; m.p. 239°; ν_{max} 1622 cm^{-1}; δ 8.5 (d, J 2.53, 5-H), 7.97 (d, J 2.53, 7-H); M^+ m/e 455}, along with smaller amounts of 6,8-dibromo-2-phenylquinol-4-one {IVa; m.p. 213°; ν_{max} 1620 cm^{-1}, δ 6.82 (s, 3-H), 8.51 (d, J 2.53, 5-H), 8.0 (d, J 2,53, 7-H); M^+, m/e 377},

and a crystalline compound, m.p. 167°.

The IR spectrum of the product, m.p. 167° did not have a carbonyl peak. Its NMR spectrum had signals corresponding to an aromatic ethoxy group; triplet, δ 1.56; quartet, δ 4.25; (J = 6 Hz), two meta-coupled aromatic protons (J = 2.3 Hz) and a sharp singlet δ 7.09. On the basis of this data structure V was assigned to the compound. Its UV and mass spectra also supported this structure.

This compound (V) presumably originated from the participation of ethanol (present as a stabilizer in the chloroform reaction medium) in the reaction. A suggested pathway for its formation is outlined in Scheme 1.



V

Scheme 1

When ethanol-free chloroform was used in the bromination reactions, the ethoxyquinoline derivative V was not formed and the yield of 2-phenyl-3,6,8-tribromoquinolone increased from 43% to 89%. TLC examination revealed the presence of some new by-products in this reaction.

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REFERENCES

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2. C. Mannich, M. Dannehl, Chem. Ber., 71, 1899 (1938).