

REACTIONS OF ACYL-AMINOQUINONE TOSYLHYDRAZONES
 A NEW SYNTHESIS OF PYRROLO[1,2-a]INDOLOQUINONE AND RELATED COMPOUND

Mitsuo Akiba, Yoshiyuki Kosugi, and Toyozo Takada
 Tokyo College of Pharmacy
 3-20-1, Kitashinjuku, Shinjuku-ku, Tokyo 160

The report concerns novel syntheses of pyrrolo[1,2-a]indoloquinones, indazoloquinones and related compounds, which seem to possess the same biological activities as those of mitomycin and rifamycin derivatives. Tosylhydrazone prepared from 2-acetyl-5-methylhydroquinone was oxidized potassium nitrosodisulfonate affording 2-acetyl-5-methyl-1,4-benzoquinone tosylhydrazone (1). On treatment with amines (pyrrolidine (a), piperidine (b), morpholine (c) and diethylamine (d)), (1) furnished 2-acetyl-3-amino-5-methyl-1,4-benzoquinone tosylhydrazones (2a-d).

Heating (2a-d) at those melting points without a solvent, 2,3-dihydro-6,9-dimethyl-5,8-dioxo-1H-pyrrolo[1,2-a]indole and the analogous products (3) were obtained. Ditolyl disulfide, ditolyl thiol-sulfonate and 4,7-dihydroxy-3,6-dimethyl-1-tosyl-1H-indazole (4) were obtained as minor products in all these cases along with (3).

Similarly, thermolysis of 2-acetyl-3,6-diamino-5-methyl-1,4-benzoquinone tosylhydrazones (5a-c) prepared by the reaction of (2a-c) with the large excess of the corresponding amines gave 5-hydroxyindoloquinones (6) and 5-aminoindazoloquinones (7). The acid-catalyzed reaction of (2) and (5) afforded 3,6-dimethyl-4,7-dioxo-1-tosyl-1H-indazole (8) and (7) in a quantitative yield.