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FISCHER INDOLIZATION OF PHENYLHYDRAZONES HAVING A VARIOUS SUBSTITUENT AT THE *ORTHO* POSITION

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Fischer indolization of ethyl pyruvate phenylhydrazone derivatives having a various substituent at the *ortho* position was examined. These reactions afforded some unpredictable products together with a normal product. The description is limited on the abnormal product in this abstract.

i) Ethyl pyruvate 2-methylthiophenylhydrazone afforded ethyl 3-methylthioindole-2-carboxylate on treatment with HCl·EtOH or $ZnCl_2$·AcOH. The structure of it was confirmed by comparison with an authentic sample which was synthesized by treatment of methylthiopyruvic acid phenylhydrazone with HCl in EtOH.

ii) Fischer indolization of ethyl pyruvate 2-chloro-N^1-methylphenylhydrazone with HCl·EtOH proceeded according to the *ortho*-C_6 process of abnormal Fischer indolization to give ethyl 6-chloro-N^1-methylindole-2-carboxylate.

iii) Product analysis of Fischer indolization of ethyl pyruvate 2-methylphenylhydrazone using liquid chromatography disclosed formation of ethyl 4- or 5-methylindole-2-carboxylate.

iv) Fischer indolization of ethyl pyruvate 2-biphenylylhydrazone produced two ethyl phenylindole-2-carboxylate in *ca*.20 % and 60 % yields. The minor product was indicated as ethyl 4-phenylindole-2-carboxylate by an alternative synthesis.

v) Fischer indolization of ethyl pyruvate 2-trifluoromethylphenylhydrazone with $ZnCl_2$·AcOH gave only the expected ethyl 7-trifluoromethylindole-2-carboxylate.

These results show that Fischer indolization of the phenylhydrazone having an electron donative group at the *ortho* position produces a mixture of an expected and an unpredictable indole. The latter may be formed by cyclization at the *ortho* position occupied by a substituent.