

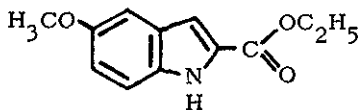
MECHANISM OF C-C BOND FORMATION DURING FISCHER INDOLIZATION
AND PSEUDOCONTACT SHIFT
OF ETHYL INDOLE-2-CARBOXYLATE DERIVATIVES

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In order to confirm the mechanism of the new C-C bond formation during Fischer indolization, we attempted the intramolecular competitive cyclization of ethyl pyruvate N_1 -substituted phenyl- N_1 -phenylhydrazones. Cyclization of these hydrazones proceeded mainly to the electron-rich aromatic nucleus. This shows the hitherto-postulated mechanism to be true. The same hydrazones were subjected to the cyclization under sigmatropic conditions. In this case less substituent effect was observed. In this connection we applied the McConnell-Robertson's pseudo-contact equation to the interpretation of the $\text{Eu}(\text{DPM})_3$ -induced proton chemical shifts in ethyl 5-methoxyindole-2-carboxylate. An excellent agreement was obtained between the observed and the calculated shift ($R = 0.042$) by assuming the most favorable conformer (1). The same treatments were done on ethyl 4-, 6- and 7-methoxyindole-2-carboxylates with satisfactory results.



(1)