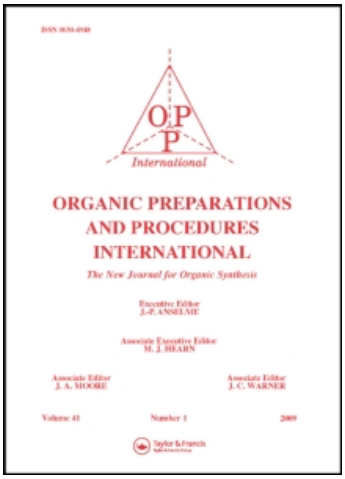

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SYNTHESIS OF 3-ACETOXY-1-METHYL AND 1-ETHYLINDOLES

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2. For example, chromatography on silica gel using a mixture of hexane and benzene (1:1) as eluent, gave diphenyldisulfide and 2,4,6-tri-(t-butyl)phenol in 63% and 69% yields respectively.

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SYNTHESIS OF 3-ACETOXY-1-METHYL AND 1-ETHYLINDOLES

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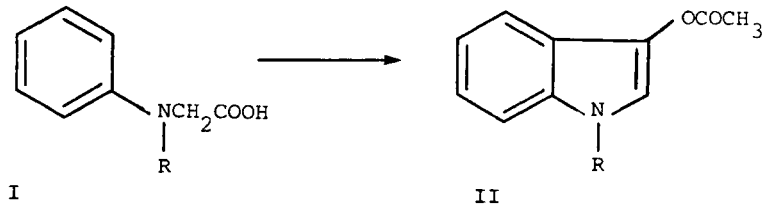
Indol-3(2H)-ones (indoxyls) (II) may be synthesized by the cyclization of the appropriate phenylglycines (I) or the appropriate 2-carboxyphenylglycine. Cyclizing agents for the former include sodium or potassium hydroxide[1] at 260° or sodamide with cyanide moderators;[2] however, the indoxyl once formed has a great tendency to oxidize to indigo unless air is rigorously excluded from the reaction and work-up procedures and yields tend to be low. Although cyclization of 2-carboxyphenylglycines proceeds smoothly using acetic anhydride and sodium acetate at reflux temperatures,[3,4] the corresponding N-substituted 2-carboxyphenylglycines are not readily available and



I II

a) R = CH_3 b) R = CH_3CH_2

require extra synthetic stages for their preparation. The titled compounds were required for further studies and we have developed the present procedure for their easy production.

EXPERIMENTAL SECTION

Mps are uncorrected. IR and PMR spectra (TMS as internal standard) were recorded using Perkin-Elmer Model 157G and R32 spectrometers.

General Procedure.- The appropriate N-substituted-N-phenylglycine (I) as its hydrochloride[5] (0.033 mol), anhydrous sodium acetate (5.5 g, 0.067 mol), acetic anhydride (10 ml, 0.10 mol) and dimethylformamide (30 ml) was boiled under reflux for 3 hrs and then evaporated to dryness. The residue was treated with water (40 ml) and extracted with dichloromethane (2 x 40 ml). The extract was washed with sodium bicarbonate solution (2 x 10 ml) and water (2 x 10 ml). Evaporation of the dried extract yielded the appropriate crude product. Recrystallization from aqueous ethanol yielded IIa; IIb was purified by vacuum distillation. IIa, 89% yield, mp. 56.5°, lit.[4] mp. 56.5°; IR(KBr): 1740 (CO), 1615 (C=C) cm^{-1}; PMR (DMSO-d_6): δ 2.32 (s, 3H, $OCOCH_3$), 3.72 (s, 3H, $N-CH_3$), 7.38 (s, 1H, CH), 6.99-7.50 (m, 4H, arom. H). IIb, 63% yield, pale green semi-solid, bp. 120°/3mm Hg; IR(KBr): 1735 (CO), 1610 (C=C) cm^{-1}; PMR (DMSO-d_6): δ 1.13 (t, 3H, J = 7.5 Hz, $CH_2\underline{CH}_3$), 2.33 (s, 3H, $OCOCH_3$), 4.08 (q, 2H, J = 7.5 Hz, $\underline{CH}_2CH_3$), 7.34 (s, 1H, CH), 6.97-7.50 (m, 4H, arom. H).

Anal. Calcd for $C_{12}H_{13}NO_2$: C, 70.91; H, 6.45; N, 6.89

Found: C, 70.86; H, 6.41; N, 6.82.

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PREPARATION OF 3-BROMO-4-NITROPYRIDINE 1-OXIDE

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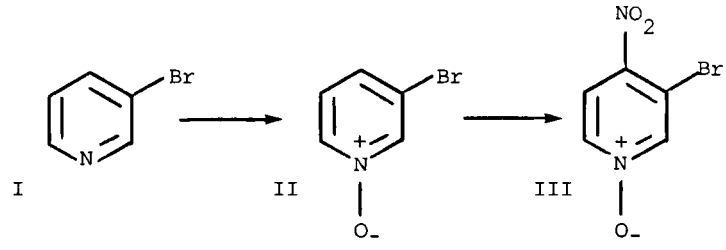
The preparation of 3-bromo-4-nitropyridine 1-oxide (III) from 3-bromopyridine (I) has been described by several workers.



In the initial synthesis,[1] the intermediate 3-bromopyridine 1-