

LE II 3

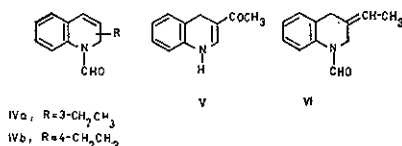
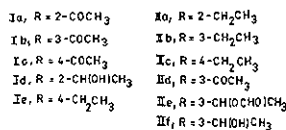
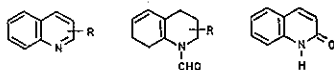
THE TRIETHYLAMMONIUM FORMATE REDUCTION OF 2-, 3- and 4-ACETYLQUINOLINES

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The reductions of ketones Ia — c with triethylammonium formate afforded 1-formyl-1,2,3,4-tetrahydroquinolines (IIa-c). In addition to these products of reduction of the acetyl group and the pyridine part of the molecule some other products were also isolated. 2-Acetylquinoline (Ia) yields also 2(1H)-quinolone (III) and 1-(2-quinolyl)ethanol (Id). Analogous reduction of 3-acetylquinoline (Ib) gives rise to the product of 1,4-addition, i.e. V, in addition to IId-f, IV, VI and finally IIb, already mentioned. Reduction of 3-acetyl-1,4-dihydroquinoline (V) and 3-acetyl-1-formyl-1,2,3,4-tetrahydroquinoline (IId) carried out separately produced the same products as the reduction of 3-acetylquinoline (Ib). Thus we assume the reduction of Ib proceeds through the 1,4-dihydroproduct V. The reduction of 4-acetylquinoline (Ic) gives rise to 4-ethylquinoline (Ie) and 4-ethyl-1-formyl-1,2-dihydroquinoline (IVb) in addition to IIc.



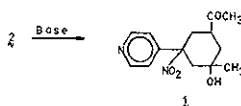
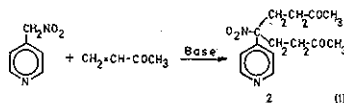
LE II 4

MICHAEL TYPE ADDITIONS WITH 2-NITROMETHYLPYRIDINE AND 4-NITROMETHYLPYRIDINE

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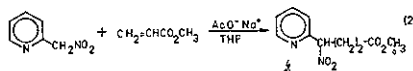
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Michael type additions of 4-nitromethylpyridine with one or four equivalents of methyl vinyl ketone in the presence of base afforded as the only product 1-methyl-2-acetyl-4-nitro-4-(4-pyridyl)-1-cyclohexanol (1). Apparently, the cyclic nitro alcohol was formed during the reaction from the original Michael adduct 2 by an intramolecular aldol condensation (eq 1).

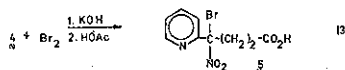


2-Nitromethylpyridine reacted similarly with methyl vinyl ketone to give the cyclic alcohol, 1-methyl-2-acetyl-4-nitro-4-(2-pyridyl)-1-cyclohexanol (3). The structures of compounds 1 and 3 were indicated by their spectral data and by their conversions to monosemicarbazones.

The reaction of 2-nitromethylpyridine with methyl acrylate gave exclusively the monoadduct, methyl 4-nitro-4-(2-pyridyl)-butanoate (4), even when an excess of methyl acrylate was employed (eq 2).



On bromination in basic medium compound 4 was converted to 4-bromo-4-(2-pyridyl)-butanoic acid (5) (eq 3).



LE II 5

A CONVENIENT METHOD FOR THE PREPARATION OF THIENO[2,3-b]PYRIDINES

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The readily available 2-amino-3-cyanothiophenes were allowed to react with ethyl aminocrotonate to give 80–95 per cent yield of the corresponding 2-[N-(3'-ethoxycarbonyl-2'-propenyl)]-2-amino-3-cyanothiophenes. The latter compounds were cyclized in the presence of sodium ethoxide to give ethyl 4-aminothieno[2,3-b]pyridine-5-carboxylates, in high yields. The base hydrolysis of the esters obtained afforded the corresponding amino-4-thieno[2,3-b]pyridine-5-carboxylic acids.

