IE II 3

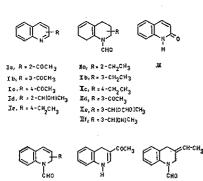
THE TRIETHYLAMMONIUM FORMATE REDUCTION OF 2-, 3- and 4-ACETYLQUINOLINES

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Suchbátarova 5, 166 28 Prague 6 -- Dejvice

Suchbätarova 5, 166 28 Prague 6 -- Dejvice The reductions of ketones 1a -- c with triethylommonium for-mate afforded 1-formyl-C-ethyl-1,2,3,4-tetrahydroquinolines (Ila--c). In addition to these products of reduction of the acetyl group and the pyridine part of the molecule some other pro-ducts 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 14-addition, i.e. V, in addition to Ild-f, IV, VI and finally IIb, already mentioned. Reduction of 3-acetyl-1,4-dihydroquinoline (V) and 3-acetyl-1,4-tetrahydroquinoline (Id) car-ried out separately produced the same products as the reduc-tion of 3-acetylquinoline (Ib). Thus we assume the reduction of 1b proceeds through the 1,4-dihydroquinoline (Ie) and 4-ethyl-1-formyl-1,2,3-dihydroquinoline (IVb) in addition to Ilc.



IVe, R=3-CH,CH, Wb, Re4-CH_CH_

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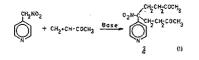
MICHAEL TYPE ADDITIONS WITH 2-NITROMETHYLPYRIDINE AND 4-NITROMETHYLPYRIDINE

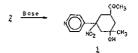
vi

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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 cnly product 1-methyl-2-acetyl-4-nitro-4-(4--pyridyl)-1-cyclohexánol (1). Apparently, the cyclic nitro alcohol was formed during the reaction from the original Michael diadduct 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)-buta-noate (4), even when an excess of methyl acrylate was em-ployed (eq 2).

$$\left(\bigcup_{N} C_{H_2NO_2} + C_{H_2^{\pm}CHCO_2CH_3} \xrightarrow{A \subseteq O^{\pm}NO_2^{\pm}}_{THF} \bigcup_{g} C_{H_2}^{(2)} C_{O_2CH_3}^{(2)} \right)$$

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

$$4_{0}^{+} + \frac{1.KOH}{Br_{2}^{-2.HOAC}} \qquad \bigcirc 1_{c}^{Br} + \frac{1.KOH}{c^{-(CH_{2})_{2}-CO_{2}H}} \qquad (3)$$

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

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The readily available 2-amino-3-cyanothiophenes were ollowed to react with ethyl aminocrotonate to give 80—95 per cent yield of the corresponding 2-[N-{3'-ethoxycarbonyl-2'-propeny]]--amino-3-cyanothiophenes. The latter compounds were cyclized in the presence of sodium ethoxide to give ethyl 4-aminothieno lysis of the esters obtained afforded the corresponding amino-[2,3-b]pyridine-5-carboxylates, in high yields. The base hydro-arids. acids.

