ACID RECYCLIZATION OF 1,4-DIHYDROPYRIDINES

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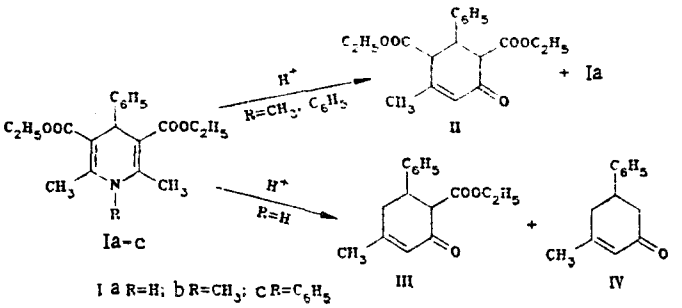
We have found that the 1,4-dihydropyridine ring opens in acid media with subsequent recyclization to give cyclohexenones. Acid hydrolysis of the enaminocarbonyl compounds leads to an acyclic 1,5-diketone which undergoes intramolecular crotonic condensation to give the cyclohexenone.



I a R=H; b R=CH_3; c R=C_6H_5

N-Methyl or N-phenyl-2,6-dimethyl-4-phenyl-3,5-dicarbethoxy-1,4-dihydropyridines (Ib, c; 1 mmole) were refluxed for 2 h in aqueous alcohol with HCl (8 mmole). Fractional crystallization and preparative TLC (silica gel plates, eluent chloroform:hexane:acetone 9:7:1) gave 3-methyl-4,6-dicarbethoxy-5-phenylcyclohex-2-enone II [1] and the product of desalkylation (or desarylation) of Ib or Ic, i.e., 2,6-dimethyl-4-phenyl-3,5-dicarbethoxy-1,4-dihydropyridine (Ia). The yields of II and Ia from Ib were 53 and 12% and Ic were 27 and 8% respectively.

The products from ring opening of the N-unsubstituted 1,4-dihydropyridine Ia were 3-methyl-6-carbethoxy-5-phenylcyclohex-2-enone (III) [2] and 3-methyl-5-phenylcyclohex-2-enone (IV) [3] and were also separated using preparative TLC with hexane:acetone (3:1) as eluent. In this case more forcing conditions were needed, i.e., the amount of acid was increased to 55 mmole per 1 mmole of Ia and refluxing was continued for 14 h. According to liquid chromatographic data the yields of III and IV were 30 and 55%. A difference in the cyclohexenones formed from the N-unsubstituted and substituted 1,4-dihydropyridines was evidently attributable to the increase in acidity of the reaction medium.

The identities of the products were confirmed by comparison with known samples.

LITERATURE CITED

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