NEW SYNTHESIS OF CYCLOPROPYLPYRIDINES

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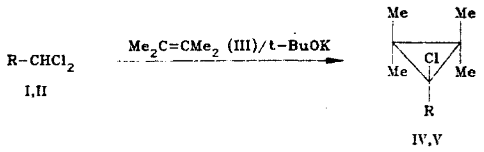
Methods for the preparation of 2- and 4-cyclopropylpyridines are known and include the reaction of the corresponding vinylpyridines with ethyl diazoacetate and dimethylsulfonium and dimethylsulfoxonium methylids or cyclization of the side chain of some 2- and 4-substituted pyridines (see [1, 2] and the literature cited in them). A number of 4-cyclopropylpyridine derivatives have also been synthesized from 4-chloromethylpyridine and alkenes in the presence of sodium hydride [3]. 3-Cyclopropylpyridines are unknown.

We have established that 2- and 3-cyclopropylpyridines are formed in the reaction of 2- (I) and 3-dichloromethylpyridine (II) with alkenes in the presence of potassium tert-butoxide. Thus the reaction of I with 2,3-dimethyl-2-butene (III) in benzene at room temperature in the presence of tert-BuOK leads to 2-(2,2,3,3-tetramethyl-1-chlorocyclopropyl)pyridine (IV) [34% yield, mp 50°C; PMR spectrum (90 MHz, $CDCl_3$), δ: 1.06 (s, 6H, $2CH_3$), 1.38 (s, 6H, $2CH_3$), 7.04-7.78 (m, 3H, β and γ protons of the pyridine ring), and 8.53-8.69 ppm (m, 1H, α proton of the pyridine ring); mass spectrum (70 eV), m/z (relative intensity, %): 196/194 ($M^+ - Me$, 32/100), 181/179 ($M^+ - 2Me$, 6/18), 174 ($M^+ - Cl$, 25), 172 (11), 159 (17), 158 (47), 144 (10)].

Under similar conditions II reacts with alkene III to give 3-(2,2,3,3-tetramethyl-1-chlorocyclopropyl)pyridine (V) [72% yield, mp 52-53°C; PMR spectrum (90 MHz), $CDCl_3$, δ: 1.02 (s, 6H, $2CH_3$), 1.37 (s, 6H, $2CH_3$), 7.09-7.71 (m, 2H, β and γ protons of the pyridine ring), 8.38-8.60 ppm (m, 2H, α protons of the pyridine ring); mass spectrum (70 eV), m/z (relative intensity, %): 211/209 (M^+, 10/30), 196/194 ($M^+ - Me$, 28/85), 181/179 ($M^+ - 2Me$, 26/75), 175 ($M^+ - Cl$, 100), 159 (80), 158 (77), 144 (31)].



I, IV R=**2-pyridyl** ; II, V R=**3-pyridyl**

Compounds IV and V are formally adducts of 2- and 3-pyridylchlorocarbenes with alkene III. However, experiments showed that the introduction of an equimolar amount of 18-crown-6 (the "crown-ether test" [4, 5]) into the reaction mixtures completely suppresses the formation of cyclopropylpyridines IV and V. The reaction of dichloromethylpyridines with alkene III in the presence of tert-BuOK evidently proceeds via a carbenoid mechanism through intermediate pyridylchlorocarbenoids.

LITERATURE CITED

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