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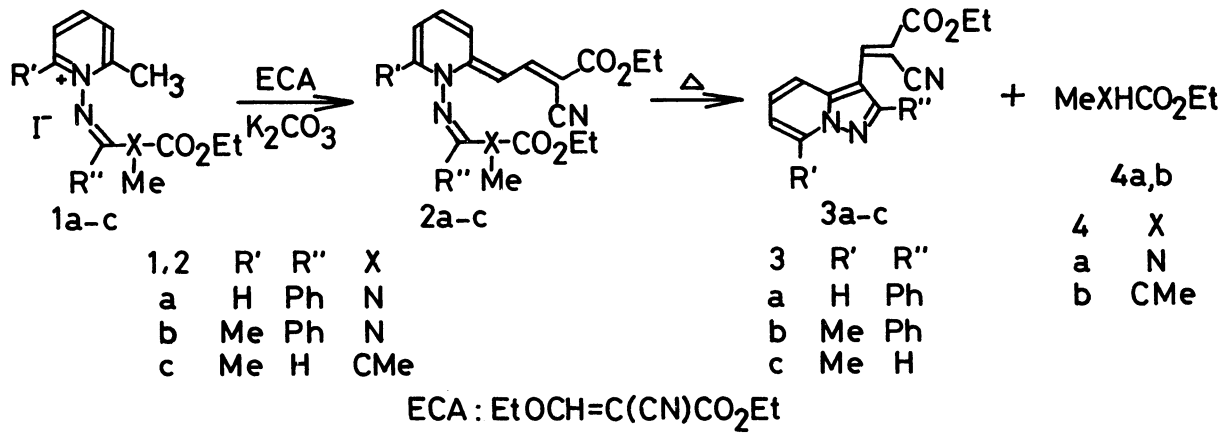
SYNTHESIS USING ALLYLIDENEDIHYDROPYRIDINES I. CONVENIENT SYNTHESIS OF 3-ETHENYLPYRAZOLO[1,5-a]PYRIDINES

Akikazu KAKEHI, Suketaka ITO, Kenji UCHIYAMA, and Kenji KONDO
Department of Industrial Chemistry, Faculty of Engineering,
Shinshu University, Wakasato, Nagano 380

2-Allylidene-1,2-dihydropyridines possessing an electrophilic center in the 1-substituent were prepared by the reactions of pyridinium salts with ethyl ethoxymethylenecyanoacetate in the presence of alkali, and their thermolyses gave 3-ethenylpyrazolo[1,5-a]pyridines in nearly quantitative yields.

Recently, we have reported the convenient syntheses of 1-alkyl-2-allylidene-1,2-dihydropyridines and the wide applicability of this reaction.[1,2] In these molecules, the ionic structure in which a negative charge delocalizes on the 2-allylidene group is also possible, and their nucleophilic reaction due to this structure would be expected. In this communication we wish to report the preparation of some allylidenedihydropyridines and their intramolecular nucleophilic reactions leading to 3-ethenylpyrazolopyridines.

The reactions of the pyridinium salts 1a and 1b, readily obtainable from 1-imidoyliminopyridinium ylides[3] and methyl iodide, with ethyl ethoxymethylenecyanoacetate(ECA) in chloroform in the presence of potassium carbonate gave the corresponding 2-allylidene-1,2-dihydropyridines 2a, reddish crystals, 84%, mp 130-132 °C, ν^{KBr} 1731(CO) and 2220 cm^{-1}(CN), $\delta(CDCl_3)$ 1.02(3H, t, J=7.5 Hz, $OCH_2\underline{CH_3}$), 1.30(3H, t, J=7.5 Hz, $OCH_2\underline{CH_3}$), 2.98 (3H, s, NCH_3), 4.14(2H, q, J=7.5 Hz, $O\underline{CH_2}CH_3$), 4.29(2H, q, J=7.5 Hz, $O\underline{CH_2}CH_3$), 5.77(1H, d, J=13.0 Hz, 2-(=$\underline{CH}$-CH=)), 6.50(1H, br t, J=7.5 and 7.5 Hz, C_5-H), 7.2-8.1(8H, m, C_3-, C_4-, C_6- and phenyl-H), and 8.37(1H, d, J=13.0 Hz, 2-(=CH-$\underline{CH}$=)), and 2b, reddish crystals, 77%, mp 110-112 °C, ν^{KBr} 1726(CO) and 2220 cm^{-1}(CN), $\delta(CDCl_3)$, inter alia, 2.42(3H, s, C_6-CH_3), 3.02(3H, s, NCH_3), 5.63(1H, d, J=13.0 Hz, 2-(=$\underline{CH}$-CH=), 6.52(1H, dd, J=7.5 and 1.0 Hz, C_5-H), 7.1-8.1(7H, m, C_3-, C_4- and phenyl-H), and 8.30(1H, d, J=13.0 Hz, 2-(=CH-$\underline{CH}$=)), respectively.[4] Since there are both a nucleophilic center on the 2-allylidene group and an electrophilic center of the amidine carbon atom in these molecules, the possibility of intramolecular cyclizations between them was examined. When



allylidenedihydropyridines 2a and 2b were refluxed in xylene for 3 hours, rapid disappearance of reddish color due to the dihydropyridines was observed and the chromatographic treatments of the reaction mixtures gave compounds 3a, yellow needles, 96%, mp 190-192 °C, ν^{KBr} 1716(CO) and 2240 cm^{-1}(CN), $\delta(CDCl_3)$ 1.37(3H, t, J=7.5 Hz, $OCH_2\underline{CH_3}$), 4.46(2H, q, J=7.5 Hz, $O\underline{CH_2}CH_3$), 7.26(1H, br t, J=7.5 and 6.5 Hz, C_6-H), 7.5-7.8(6H, m, C_5- and phenyl-H), 8.42(1H, dd, J=9.0 and 1.0 Hz, C_4-H), 8.57(1H, s, 3-(vinyl-H)), and 8.86(1H, dd, J=6.5 and 1.0 Hz, C_7-H), and 3b, yellow needles, 96%, mp 159-162 °C, ν^{KBr} 1713(CO) and 2240 cm^{-1}(CN), $\delta(CDCl_3)$, inter alia, 2.91(3H, s, C_7-CH_3), 7.08(1H, br d, J=7.5 Hz, C_6-H), 7.5-7.9(6H, m, C_5- and phenyl-H), 8.33(1H, dd, J=9.0 and 1.0 Hz, C_4-H), and 8.60 (1H, s, 3-(vinyl-H)). Furthermore, the presence of N-methylurethan 4a in the reaction mixtures was confirmed by glc.

On the other hand, the similar reaction of pyridinium salt 1c, which was prepared from the reaction of 1-vinyliminopyridinium ylide[5] and methyl iodide, with ECA did not give the corresponding allylidenedihydropyridine 2c, but directly gave compound 3c, pale yellow needles, 47%, mp 150-153 °C, ν^{KBr} 1711(CO) and 2235 cm^{-1}(CN), $\delta(CDCl_3)$, inter alia, 2.89(3H, s, C_7-CH_3), 7.00(1H, br d, J=7.5 Hz, C_6-H), 7.56(1H, q, J=9.0 and 7.5 Hz, C_5-H), 7.85(1H, dd, J=9.0 and 1.5 Hz, C_4-H), 8.49(1H, s, 3-(vinyl-H)), and 9.26(1H, s, C_2-H), and ethyl iso-butyrate 4b was also detected by glc. These results are given above. The structures of these compounds 3a, 3b and 3c were assigned to be 3-ethenylpyrazolo-[1,5-a]pyridine derivatives by their physical and spectral analyses and by the mechanistic consideration of these reactions. Further investigations are in progress.

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