SYNTHESES OF ISOXAZOLE AND PYRROLE DERIVATIVES VIA O-ACYLATION OF ALIPHATIC NITRO COMPOUNDS

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O-Acylation of aliphatic nitro compounds such as phenylnitromethane and nitroethane, with acetyl chloride in the presence of 2 or 3 fold excess of several 1,3-ketoesters or 1,3-diketones afforded the corresponding 4-acylisoxazoles(1) in good yields respectively.

However, when dibenzoylmethane was used as a 1,3-diketone, 2,4-dibenzoyl-3,5-diphenylpyrrole(2a) (mp. 234-235°), a novel type product, was obtained as a main product in 32 % yield instead of above-cyclization product probably via 2H-azirine derivative(3). In order to clarify the mechanism of the formation of 2, p-substituted phenylnitromethane derivatives, nitroparaffins (such as nitroethane and 1-nitropropane), and ethyl nitroacetate were reacted with acetyl chloride and dibenzoylmethane in a similar manner, and then next results could be obtained : 1) p-tolylnitromethane and p-chlorophenylnitromethane gave the corresponding pyrrole derivatives(2b and 2c) in 49 and 48 % yields, respectively; 2) p-nitrophenylnitromethane gave 3-(p-nitrophenyl)-5-phenylisoxazole(4a) (59%); 3) nitroparaffins and ethyl nitroacetate gave the corresponding 4-acylisoxazoles(1) in 30-50 % yields; 4) the reaction of phenylnitromethane, acetyl chloride and an equivalent of dibenzoylmethane at 80°C afforded 3,5-diphenylisoxazole(4b) and 2,5-diphenyloxazole(5a) in 12 and 14 % yields, respectively.

The reaction mechanism is discussed.