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DIELS-ALDER REACTION OF α-SUBSTITUTED 5-VINYLISOXAZOLES

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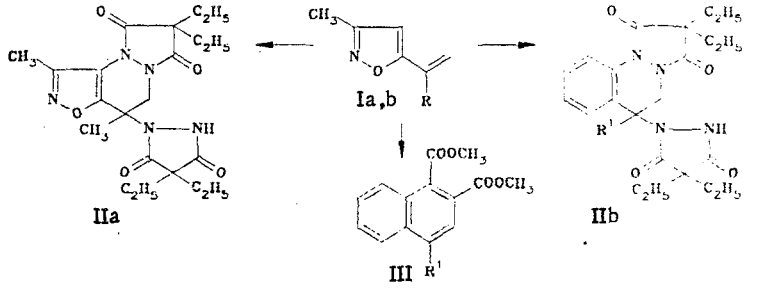
3-Methyl-5-vinylisoxazole forms a [4 + 2]-cycloaddition adduct of composition 1:1 with maleic acid under forcing conditions [1]. By contrast, the α-substituted 5-vinylisoxazoles Ia, b form adducts of 1:2 composition (structures IIa, b) when treated with 4,4-diethylpyrazolin-3,5-dione under mild conditions (dioxane, 20°C, 3 h). For the α-methyl substituted vinylisoxazole Ia cycloaddition involves the diene system which includes the $C_{(4)}$—$C_{(5)}$ isoxazole bond (as also in [1]). For the competing diene system in the case of the α-phenyl substituted vinylisoxazole Ib the cycloaddition involved the more reactive styryl diene system giving adduct IIb. Treatment of Ib with dimethylacetylenedicarboxylate leads to reaction at the same diene (m-xylene, refluxing for 5 h) to give adduct III.



I a R=CH_3; b R=C_6H_5; IIb, III R^1= 3-methylisoxazol-5-yl

Adduct IIa. Yield 45%, mp 151-152°C. PMR spectrum ($CDCl_3$): 0.70-0.98 and 1.56-1.90 (m, 12H and 8H, CH_3CH_2), 1.93 (s, 3H, 4-CH_3), 2.70 (s, 3H, 1-CH_3), 3.63 (d, 1H, 5-H, J_{gem} = 14 Hz), 5.52 ppm (d, 1H, 5-H, J_{gem} = 14 Hz). Mass spectrum, m/z: 431 (M^+).

Adduct IIb. Yield 37%, mp 169-170°C. PMR spectrum (DMSO-d_6): 0.76-0.98 and 1.60-1.94 (m, 12H and 8H, CH_3CH_2), 2.17 (s, 3H, 3-CH_3 isoxazole), 4.61 (d, 1H, 5-H, J_{gem} = 12.5 Hz), 4.91 (d, 1H, 5-H, J_{gem} = 12.5 Hz), 6.00 (s, 1H, 4-H isoxazole), 7.10-7.52 (m, 3H, 7,8,9-H), 8.58 ppm (d, 1H, 10-H). Mass spectrum, m/z: 493 (M^+).

Adduct III. Yield 13%, mp 170-171°C. PMR spectrum (DMSO-d_6): 2.39 (s, 3H, 3-CH_3, isoxazole), 3.94 (s, 3H, $COOCH_3$), 4.02 (s, 3H, $COOCH_3$), 7.05 (s, 1H, 4-H isoxazole), 7.75-8.10 (m, 3H, 5,6,7-H), 8.27 (s, 1H, 3-H), 8.40 ppm (d, 1H, 8-H). Mass spectrum, m/z: 325 (M^+).

Compounds IIa, b and III were characterized by elemental analytical data and by IR and UV spectra.

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