SYNTHESIS OF 3-ARYL-5-METHYL-3-(ISOXAZOLYL)-3-OXOPROPIONATE OXIMES

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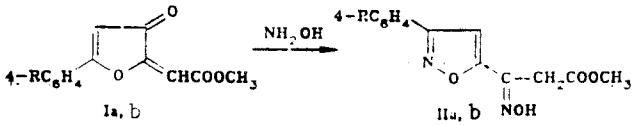
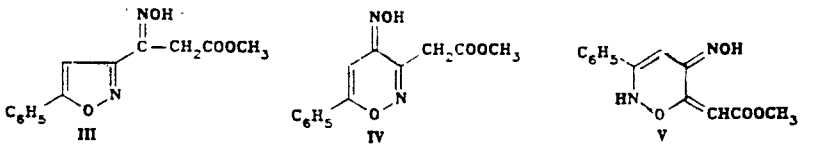
UDC 547.786'724.07

We have found that methyl (5-aryl-2,3-dihydro-3-oxo-2-furylidene)acetates (Ia, b) react with hydroxylamine in methanol to give the methyl 3-(3-aryl-5-isoxazolyl)-3-oxopropionate oximes (IIa, b).



I, II a R=H; b R=Cl

The presence in the mass spectrum of (IIa) of a peak with m/z 103 ($C_6H_5CN^+$) enables the presence of the alternative structures for the oximes (III and IV) to be excluded. In addition, the spectrum shows a peak with m/z 144 (the 3-phenylisoxazolyl ion), but no peak for an ion with m/z 100 ($CH_3OCO–CH=CH=O^+$), which is evidence against the oxime structure (V).



The reaction appears to proceed via the intermediate nucleophilic addition product methyl 6-hydroxyamino-3,4-dioxo-6-phenyl-5-hexenoate, formed by attack of the hydroxylamine amino-group on the electrophilic center at $C_{(5)}$ of the furanones (I), followed by heterocyclization and formation of the oxime.

To a solution of 0.01 mole of (Ia) or (Ib) [1, 2] in 150 ml of methanol was added 5 ml of a 13% aqueous solution of hydroxylamine, obtained by mixing solutions of equimolar amounts of hydroxylamine hydrochloride and sodium hydroxide, and the mixture boiled for 15-20 min. The solvent was removed, and the residue washed with water and crystallized from chloroform to give (IIa, b).

Compound (IIa). Yield 46%, mp 145-146°C (decomp.). IR spectrum (KBr): 3210-3180 (OH), 3080-3060 (CH), 1743 ($COOCH_3$), 1610-1580 cm^{-1} (C=C, C=N). PMR spectrum (DMSO-D_6): 3.59 (3H, s, OCH_3); 3.77 (2H, s, CH_2); 7.39 (1H, s, 4-H); 7.55-7.90 (5H, m, C_6H_5); 12.34 ppm (1H, br.s, OH). Mass spectrum, m/z (I_{rel},.%): 260 (16) $[M]^+$, 228 (12) $[M - CH_3O–H]^+$, 170 (10) (3-phenyl-5-cyanoisoxazolyl ion), 144 (80) (3-phenylisoxazolyl ion), 119 (44) $[C_6H_5CNO]^+$, 116 (21) $[CH_3OCOCH_2CHNO]^+$, 103 (33) $[C_6H_5CN]^{+\cdot}$.

Compound (IIb). Yield 54%, mp 167-168°C (decomp.).

LITERATURE CITED

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Perm Institute of Pharmacy, Perm 614600. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1141-1142, August, 1990. Original article submitted November 20, 1989.

0009-3122/90/2608-0957$12.50