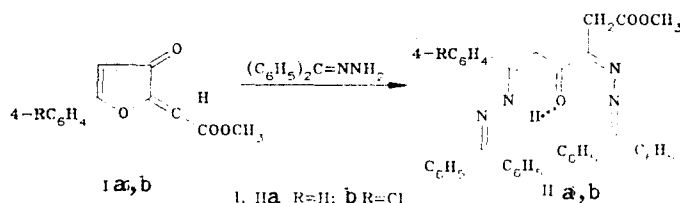


REACTION OF 5-ARYL-2-METHOXYCARBONYLMETHYLENE-2,3-DIHYDROFURAN-3-ONES WITH BENZOPHENONE HYDRAZONE

V. O. Koz'minykh, E. N. Koz'minykh,
and Yu. S. Andreichikov

UDC 547.388.3.07+547.724

It is known that 5-aryl-2-methoxycarbonylmethylene-2,3-dihydrofuran-3-ones I react with aromatic amines or hydrazine to give cyclic products of nucleophilic addition, viz., derivatives of 2-hydroxy-2,3-dihydropyrrol-3-one [1] or 1,2,3,4-tetrahydropyridazino[4,3-c]pyridazin-3-one [2]. As a result of the reaction of Ia, b with benzophenone hydrazone in ethanol we unexpectedly obtained methyl 6-aryl-6-diphenylmethylenehydrazino-3,4-dioxo-5-hexenoate 3-diphenylmethylenehydrazones IIa, b in 56-61% yields.



The presence of an ion peak with a mass number of 325 in the mass spectrum of IIa and the absence of splitting of the signal of the CH₂ group in the PMR spectrum provide evidence that the compound cannot have the isomeric 2-hydroxy-1-diphenylmethyleneamino-2-methoxycarbonylmethyl-5-phenyl-2,3-dihydropyrrol-3-one 3-diphenylmethylenehydrazone structure.

Compounds II are evidently formed as a result of nucleophilic addition of the hydrazone due to attack at the electrophilic center at the C₍₅₎ atom of furanones I with the subsequent reaction of a second molecule of the hydrazone with the β-keto ester fragment of the intermediate methyl 6-aryl-6-diphenylmethylenehydrazino-3,4-dioxo-5-hexenoates.

A 3.92-g (0.02 mole) sample of benzophenone hydrazone was added to a solution of 0.01 mole of 5-aryl-2-methoxycarbonylmethylene-2,3-dihydrofuran-3-ones Ia, b [3] in 200 ml of ethanol, and the mixture was refluxed for 15-20 min. The precipitate was removed by filtration and crystallized from acetonitrile or chloroform-hexane (1:1).

Compound IIa. This compound was obtained in 61% yield and had mp 156-157°C (decomp.). IR spectrum (KBr): 1726 (C=O, w, ester); 1605, 1555-1583 cm⁻¹ (C₍₄₎=O, C₍₅₎=C₍₆₎, C=N). PMR spectrum (d₆-DMSO): 3.42 (3H, s, OCH₃), 3.53 (2H, s, CH₂), 5.78 (1H, s, CH), 7.17-7.72 (25H, m, 5C₆H₅), 12.81 ppm (1H, br.s, NH). UV spectrum (ethanol), λ_{max} (log ε): 280 (4.31), 432 nm (4.83). Mass spectrum, m/z (I, % relative to the maximum peak): 604 (2) M⁺, 410 (5) [M - (C₆H₅)₂CN₂]⁺, 325 (6) [(C₆H₅)₂C=NNH-C(C₆H₅)=CH-C≡O]⁺, 283 (11) [(C₆H₅)₂C=N-N≡C-C₆H₅]⁺, 196 (16) [(C₆H₅)₂C=NNH₂]⁺, 180 (100) [(C₆H₅)₂C=N]⁺, 104 (38) [C₆H₅C≡NH]⁺, 103 (13) [C₆H₅-C≡N]⁺, 77 (43) [C₆H₅]⁺.

Compound IIb. This compound was obtained in 56% yield and had mp 161-162°C (decomp.). IR spectrum (KBr): 1735 (C=O, w, ester); 1570-1585, 1535-1550 cm⁻¹ (C₍₄₎=O, C₍₅₎=C₍₆₎, C=N). PMR spectrum (d₆-DMSO): 3.43 (3H, s, OCH₃), 3.53 (2H, s, CH₂), 5.75 (1H, s, CH), 7.15-7.67 (24H, m, 4C₆H₅, C₆H₄), 12.78 ppm (1H, br.s, NH).

LITERATURE CITED

1. Yu. S. Andreichikov and V. O. Koz'minykh, *Zh. Org. Khim.*, **25**, 618 (1989).
2. Yu. S. Andreichikov, E. N. Koz'minykh, L. O. Kon'shina, and V. O. Koz'minykh, *Khim. Geterotsikl. Soedin.*, No. 10, 1428 (1985).
3. Yu. S. Andreichikov, V. O. Koz'minykh, and E. N. Manelova, *Zh. Org. Khim.*, **21**, 402 (1985).