LITERATURE CITED

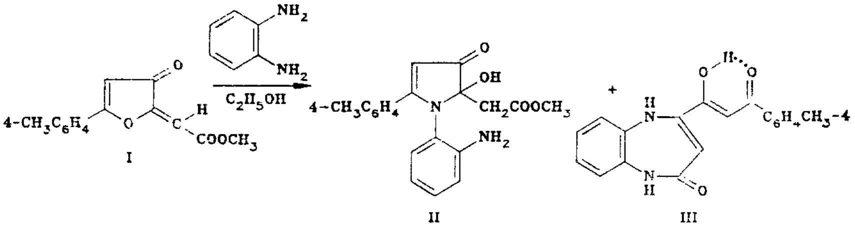
1. V. I. Khvostenko, Mass Spectrometry of Negative Ions in Organic Chemistry [in Russian], Nauka, Moscow (1981).
2. B. I. Khvostenko, V. A. Mazunov, V. S. Fal'ko, et al., Khim. Fizika, No. 9, 905 (1982).
3. A. Kupermann, W. M. Fliker, and O. A. Mosher, Chem. Rev., 79, 78 (1979).

UNUSUAL RECYCLIZATION OF 2-METHOXYCARBONYLMETHYLENE-5-p-TOLYL-2,3-DIHYDROFURAN-3-ONE UPON TREATMENT WITH o-PHENYLENEDIAMINE

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

UDC 547.722/725+547.745/746

It has previously been shown that the reaction of 2-alkoxycarbonylmethylene-5-aryl-2,3-dihydrofuran-3-ones with o-phenylenediamine in benzene leads to the formation of addition products at the 2-exo-ethylene bond, therefore, to derivatives of 1,2,3,4-tetrahydro-2-quinoxalone [1]. In an unexpected result, for the reaction of 2-methoxycarbonylmethylene-5-p-tolyl-2,3-dihydrofuran-3-one (I) with o-phenylenediamine in benzene solution, we isolated 1-o-aminophenyl-2-hydroxy-2-methoxycarbonylmethyl-5-p-tolyl-2,3-dihydropyrrol-3-one (II) in 48% yield, along with a small amount of 4-p-toluoylacetyl-2,5-dihydro-1H-benzo-1,5-diazepin-2-one (III).



The formation of compounds II and III is probably the result of nucleophilic attack by the diamine at the electrophilic site of the $C_{(2)}$ atom in furanone I, and subsequent recyclization, which can occur via two pathways.

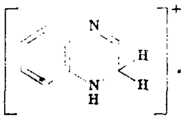
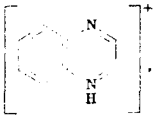
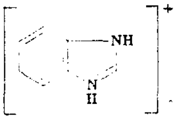
To a solution of 2.44 g (0.01 mole) 2-methoxycarbonylmethylene-5-p-tolyl-2,3-dihydrofuran-3-one [2] in 100 ml ethanol was added a solution of 1.08 g (0.01 mole) o-phenylenediamine in 50 ml ethanol, and the mixture was refluxed for 20 min. The solvent was evaporated and the residue crystallized from ethanol (compound II) and acetone (compound III).

Compound II. Orange substance, yield 1.7 g (48%), mp 162-163°C (dec). IR spectrum: (in KBr): 3457 (NH_{2as}), 3385 (NH_{2s}), 3240-3180 (OH), 1738 (CO ester), 1660 cm^{-1} ($C_{(3)}$ = O). PMR spectrum (DMSO-D_6): 2.23 (3H, s, CH_3); 2.72 (2H, d.d, CH_2, J_{gem} = 17.0 Hz); 3.42 (3H, s, OCH_3); 5.37-5.50 (3H, broadened singlet, NH_2, OH); 5.56 (1H, s, 4-H); 6.45-7.38 ppm (8H, m, $2C_6H_4$). The spectral data are consistent with published data [3].

Compound III. Brick red substance, yield 0.1 g (3%), mp 247-248°C (dec). IR spectrum (in KBr): 3180-3150 (NH), 1693 (CO amide), 1608-1587 cm^{-1} (CO chelate, C=C). PMR spectrum (DMSO-D_6): 2.34 (3H, s, CH_3); 6.08 (1H, s, 3-H); 6.52 (1H, s, CH chelate); 7.12-7.47 (8H, m, $2C_6H_4$); 11.91 ppm (1H, broadened singlet, NH amide). The spectral data are consistent with the results of [4, 5]. Mass spectrum, m/z (% of maximum peak): 320 (34.0) M^+, 160 (34.2) $[p\text{-}CH_3C_6H_4COCH{=}C{=}O]^+$ 132 (28.5)

Perm' Pharmaceutical Institute, Perm'. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 277-278, February, 1990. Original article submitted May 4, 1989.

0009-3122/90/2602-0241$12.50


, 131(24.0)

, 119(100.0)

.

91 (32.9) $[p\text{-}CH_3M_6H_4]^+$, in agreement with the data in [6].

LITERATURE CITED

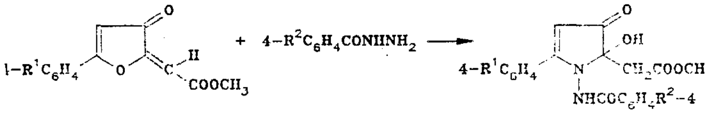
1. Yu. S. Andreichikov, V. O. Kozminych, N. M. Igidov, and E. N. Kozminych, Vth Int. Symp. on Furan Chemistry, Riga (1988), p. 127.
2. Yu. S. Andreichikov, V. O. Koz'miykh, and E. N. Manelova, Zh. Org. Khim., 21, 402 (1985).
3. Yu. S. Andreichikov and V. O. Koz'minykh, Zh. Org. Khim., 25, 618 (1989).
4. R. M. Acheson and W. R. Tully, J. Chem. Soc., No. 8, 1117 (1970).
5. A. N. Kost, Z. F. Solomko, V. A. Budylin, and T. S. Semenova, Khim. Geterotsikl. Soedin., No. 5, 696 (1972).
6. A. N. Kost, P. A. Sharbatyan, P. B. Terent'ev, Z. F. Solomko, V. S. Tkachenko, and L. G. Gergel', Zh. Org. Khim., 8, 2113 (1972).

SYNTHESIS OF 5-ARYL-1-(AROYLAMINO)-2-HYDROXY-2-(METHOXYCARBONYLMETHYL)-2,3-DIHYDROPYRROL-3-ONES

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

UDC 547.724'725+547.745'746+547.775

Previously it was determined that 5-aryl-2-(methoxycarbonylmethylene)-2,3-dihydrofuran-3-ones (I) react with a 70% aqueous solution of hydrazine in ethanol with the formation of 7-aryl-1,2,3,4-tetrahydropyridazino[4,3-c]pyridazin-3-ones [1]. In carrying out the reaction of compounds Ia and Ib with aroylhydrazines under similar conditions, we unexpectedly obtained 5-aryl-1-(aroylamino)-2-hydroxy-2-(methoxycarbonylmethyl)-2,3-dihydropyrrol-3-ones (IIa and IIb).



Ia, IIa $R^1=H$, Ib, IIb $R^1=CH_3$; IIa $R^2=CH_3$, IIb $R^2=CH_3O$

Apparently, pyrrolones II are formed as a result of nucleophilic addition due to attack of the amino group of aroylhydrazine at the electrophilic center at the $C_{(5)}$ atom of the heterocycle with subsequent recyclization of the intermediate enehydrazine. The amide group NH does not participate in recyclization because of significantly decreased nucleophilicity.

To a solution of 0.01 mole of compounds Ia and Ib [2] in 150 ml of 96% ethanol is added 0.01 mole of aroylhydrazine, and the whole is boiled for 10-15 min. The solvent is evaporated, the residue is washed with acetonitrile and crystallized from ethanol or a chloroform–hexane mixture (1:1), and compounds IIa and IIb are obtained.

Compound IIa. The yield was 78%, with mp 118-119°C (with decomposition). IR spectrum (KBr): 3430-3420 (NH), 1740 (CO ester), 1712 (CO ring), 1625 (CO amide), 1610-1590 cm^{-1} (C=C). PMR spectrum ($CDCl_3$): 3.65 (3H, singlet, OCH_3); 3.70 (2H, double doublet, CH_2, $J_{gem} = 21.0$ Hz); 5.37 (2H, broadened singlet, 4-H, OH); 7.23-7.78 (10H, multiplet, $2C_6H_5$); 8.01 ppm (1H, broadened singlet, NH). Mass spectrum, m/z (relative intensity, %): 366 (1) $[M]^+$, 348 (5) $[M - H_2O]^+$, 334 (11) $[M - CH_3CH]^+$, 290 (9) $[M - COOCH_3 - OH]^+$, 266 (19) [M −

Perm Pharmaceutical Institute, Perm 614600. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 278-279, February, 1990. Original article submitted May 12, 1989.