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SHORT COMMUNICATIONS

Chemistry of Iminofurans. New Example of Unusual Aza-Wittig Reaction at Lactone Carbonyl Group

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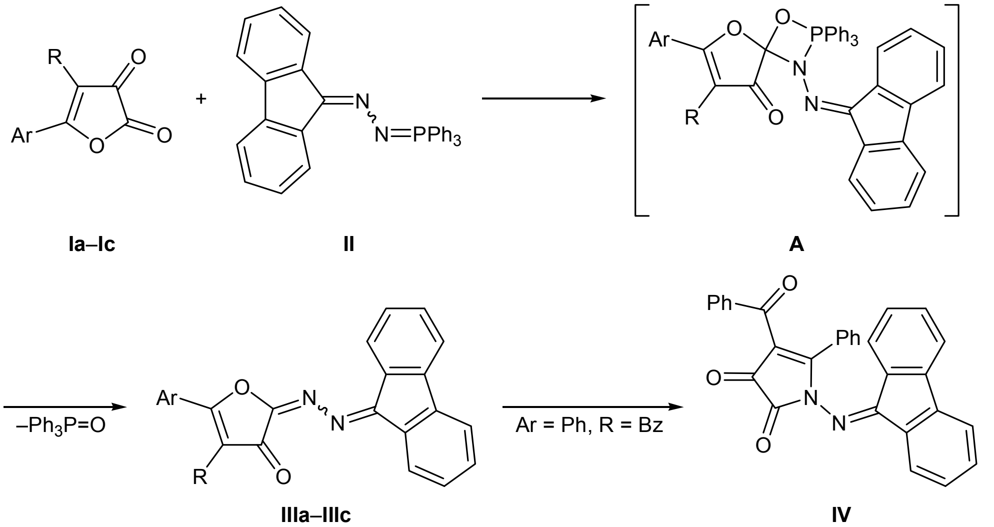
Aza-Wittig reaction provides a convenient method for building up a new carbon–nitrogen double bond [1, 2]. Three examples of the aza-Wittig reaction involving lactone carbonyl group were reported, where the substrates were substituted 3-methylidene-5-phenyloxazol-2-ones [3] and 5-aryl-2,3-dihydrofuran-2,3-diones [4, 5]. In the present work we used as substrate 5-aryl-2,3-dihydrofuran-2,3-diones **Ia**–**Ic** having a bulky substituent in position *4* of the furan ring.

The reactions of 4-benzoyl-5-phenyl-2,3-dihydrofuran-2,3-dione (**Ia**) and 5-aryl-4-(3-arylquinoxalin-2-yl)-2,3-dihydrofuran-2,3-diones **Ib** and **Ic** with 9*H*-fluoren-9-one (triphenyl-λ^5-phosphanylidene)hydrazone (**II**) gave 4-benzoyl-5-phenyl-2,3-dihydrofuran-2,3-dione 2-(9*H*-fluoren-9-ylidene)hydrazone (**IIIa**) and 5-aryl-4-(3-arylquinoxalin-2-yl)-2,3-dihydrofuran-2,3-dione 2-(9*H*-fluoren-9-ylidene)hydrazones **IIIb** and **IIIc**.

Presumably, initial nucleophilic attack by phosphazine **II** at the lactone carbonyl group in the furan ring gave zwitterionic intermediate which underwent rearrangement into spiro-fused oxazaphosphetidine **A**. Elimination of triphenylphosphine oxide from structure **A** afforded compound **III**. The classical Wittig reaction of compound **Ia** with methyl phosphanylideneacetate was also reported to give product of addition at the lactone carbonyl group despite the presence of other carbonyl groups in the substrate molecule [6].

Prolonged storage of a solution of **IIIa** in toluene resulted in the formation of 4-benzoyl-1-(9*H*-fluoren-9-ylideneamino)-5-phenyl-2,3-dihydro-1*H*-pyrrole-2,3-dione (**IV**) whose spectral parameters were consistent with published data for structurally related compounds synthesized previously by other methods [7].

4-Benzoyl-2-[*N'*-(9*H*-fluoren-9-ylidene)hydrazono]-5-phenyl-2,3-dihydrofuran-3-one (IIIa). A so-



Ar = Ph, R = Bz (**a**), 3-phenylquinoxalin-2-yl (**b**); Ar = 4-MeC_6H_4, R = 3-(4-methylphenyl)quinoxalin-2-yl (**c**).

lution of 2.78 g (10 mmol) of compound **Ia** [8] and 4.54 g (10 mmol) of phosphorane **II** in 30 ml of anhydrous toluene was kept for 24 h at room temperature, and the precipitate was filtered off and recrystallized from toluene. Yield 4.04 g (89%), yellow crystals, mp 170–171°C (from toluene). IR spectrum, ν, cm^{-1}: 1693 (C^3=O), 1646 (PhCO), 1601, 1589, 1565 (C=C, C=N). ^{1}H NMR spectrum: δ 7.27–8.38 ppm, m (18H, H_{arom}). Found, %: C 79.24; H 4.00; N 6.17. $C_{30}H_{18}N_2O_3$. Calculated, %: C 79.28; H 3.99; N 6.16.

5-Phenyl-4-(3-phenylquinoxalin-2-yl)-2-[*N*′-(9*H*-fluoren-9-ylidene)hydrazono]-2,3-dihydrofuran-3-one (IIIb). A solution of 0.76 g (2 mmol) of furandione **Ib** [9] and 0.9 g (2 mmol) of phosphorane **II** in 30 ml of anhydrous benzene was kept for 24 h at room temperature. The mixture was evaporated, and the residue was recrystallized from acetonitrile. Yield 0.80 g (72%), orange crystals, mp 216–218°C (from acetonitrile). IR spectrum, ν, cm^{-1}: 1704 (C^3=O), 1622 (C=N). ^{1}H NMR spectrum, δ, ppm: 7.27–8.25 m (22H, H_{arom}). Found, %: C 80.14; H 4.03; N 10.08. $C_{37}H_{22}N_4O_2$. Calculated, %: C 80.13; H 4.00; N 10.10.

5-(4-Methylphenyl)-4-[3-(4-methylphenyl)quinoxalin-2-yl]-2-[*N*′-(9*H*-fluoren-9-ylidene)hydrazono]-2,3-dihydrofuran-3-one (IIIc) was synthesized in a similar way from compounds **Ic** and **II**. Yield 0.88 g (75%), orange crystals, mp 208–210°C (from acetonitrile). IR spectrum, ν, cm^{-1}: 1692 (C^3=O), 1600 (C=N). ^{1}H NMR spectrum, δ, ppm: 2.34 s (3H, Me), 2.35 s (3H, Me), 7.09–8.26 m (20H, H_{arom}). Found, %: C 80.41; H 4.51; N 9.60. $C_{39}H_{26}N_4O_2$. Calculated, %: C 80.39; H 4.50; N 9.62.

4-Benzoyl-1-(9*H*-fluoren-9-ylideneamino)-5-phenyl-2,3-dihydro-1*H*-pyrrole-2,3-dione (IV). A solution of 2.27 g (5 mmol) of compound **IIIa** in 20 ml of toluene was kept for 10 days at room temperature. It was then cooled to –20°C, and the precipitate was filtered off. Yield 1.8 g (79%), dark red crystals, decomposition point 176–177°C (from toluene). IR spectrum, ν, cm^{-1}: 1766 (C^2=O), 1706 (C^3=O), 1654 (PhCO), 1596, 1579 (C=C, C=N). ^{1}H NMR spectrum: δ 7.2–8.2 ppm, m (18H, H_{arom}). Found, %: C 79.30; H 3.96; N 6.20. $C_{30}H_{18}N_2O_3$. Calculated, %: C 79.28; H 3.99; N 6.16.

The IR spectra were recorded on an FSM-1201 spectrometer from samples dispersed in mineral oil. The ^{1}H NMR spectra were measured on a Varian Mercury Plus-300 instrument at 300 MHz using DMSO-d_6 as solvent and HMDS as internal reference. The purity of the isolated compounds was checked, and the progress of reactions was monitored, by TLC on Silufol UV-254 plates using diethyl ether–benzene–acetone (10:9:1) as eluent.

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