

SHORT  
COMMUNICATIONSChemistry of Iminofurans. Wittig Reaction  
of 5-Aryl-3-methylidenehydrazono-2,3-dihydrofuran-2-ones

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It was shown previously that 5-aryl-2,3-dihydrofuran-2,3-diones react with acylmethylidene(triphenyl)phosphoranes to give 5-aryl-2-acylmethylidene-2,3-dihydrofuran-3-ones [1, 2]. Here, among two possible directions of the Wittig reaction (i.e., at the ketone or lactone carbonyl group), its unusual version involving the lactone carbonyl group occurs due to specific electron density distribution in the heteroring [3]. According to the data of [4–6], introduction of a halogen atom (chlorine or bromine) or aroyl or methyl substituent into the 4-position of the furan ring does not change the reaction direction.

We tried to modify the substrate structure to a stronger extent. For this purpose, we synthesized 5-aryl-3-(benzylidenehydrazono)-2,3-dihydrofuran-2-ones **Ia** and **Ib** [7] and examined their reaction with an equimolar amount of methyl (triphenyl- $\lambda^5$ -phosphanylidene)acetate in an inert solvent. The results showed that, as in the above examples, the Wittig reaction of compounds **Ia** and **Ib** involves the lactone carbonyl group to give methyl 2-{5-aryl-3-[2-(diphenylmethylidene)hydrazono]furan-2-ylidene}acetates **IIa** and **IIb**. Moreover, compounds **Ic** and **Id** having a benzoyl group in the hydrazone fragment reacted with methyl (triphenyl- $\lambda^5$ -phosphanylidene)acetate to form substituted furans **IIc** and **IId**. Compounds **IIa**–

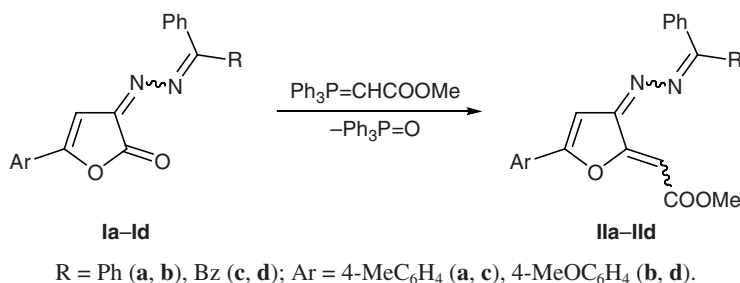
**IId** are red crystalline substances that are soluble in acetonitrile, chloroform, aromatic hydrocarbons, DMSO, and DMF, poorly soluble in alcohols and carbon tetrachloride, and insoluble in saturated hydrocarbons, diethyl ether, and water.

Although compounds **II** were formed as the only products apart from triphenylphosphine oxide (according to the TLC data), their yields were fairly poor (16–44%) because of difficulties in the separation of triphenylphosphine oxide by fractional crystallization.

There are no published data on transformations of iminofuranones in reactions with phosphoranes [8], and the described reaction is a new example of quite rare Wittig reaction involving lactone carbonyl group.

**Methyl [5-aryl-3-(2-benzylidenehydrazono)-2,3-dihydrofuran-2-ylidene]acetates IIa–IId (general procedure).** A mixture of 0.01 mol of 5-aryl-3-(2-benzylidenehydrazono)-2,3-dihydrofuran-2-one **Ia–Id** and 0.01 mol of methyl (triphenyl- $\lambda^5$ -phosphanylidene)acetate in 10 ml of anhydrous toluene was heated for 3 h under reflux. The precipitate was filtered off, and recrystallized from acetonitrile.

**Methyl {3-[2-(diphenylmethylidene)hydrazono]-5-(4-methylphenyl)-2,3-dihydrofuran-2-ylidene}-acetate (IIa).** Yield 1.8 g (44%), red crystals, mp 129–



130°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1716 (COOMe); 1668, 1612, 1585 (C=N, C=C).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 2.35 s (3H,  $\text{CH}_3$ ), 3.73 s (3H,  $\text{OCH}_3$ ), 5.9 s (1H, CH), 6.74 s (1H, CH), 7.5 m (14H,  $\text{H}_{\text{arom}}$ ). Found, %: C 76.84; H 5.14; N 6.51.  $\text{C}_{27}\text{H}_{22}\text{N}_3\text{O}_3$ . Calculated, %: C 76.76; H 5.25; N 6.63.

**Methyl {3-[2-(diphenylmethylidene)hydrazono]-5-(4-methoxyphenyl)-2,3-dihydrofuran-2-ylidene}acetate (IIb).** Yield 1.5 g (34%), red crystals, mp 120–121°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1716 (COOMe); 1670, 1614, 1585 (C=N, C=C).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 3.65 s (3H,  $\text{OCH}_3$ ), 3.8 s (3H,  $\text{OCH}_3$ ), 5.6 s (1H, CH), 7.06 s (1H, CH), 7.5 m (14H,  $\text{H}_{\text{arom}}$ ). Found, %: C 73.98; H 5.16; N 6.45.  $\text{C}_{27}\text{H}_{22}\text{N}_3\text{O}_4$ . Calculated, %: C 73.96; H 5.06; N 6.39.

**Methyl {5-(4-methylphenyl)-3-[2-(2-oxo-1,2-diphenylethylidene)hydrazono]-2,3-dihydrofuran-2-ylidene}acetate (IIc).** Yield 1.0 g (22%), red crystals, mp 160–161°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1731 (COOMe); 1678 (C=O); 1614, 1587 (C=N, C=C).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 2.36 s (3H,  $\text{CH}_3$ ), 3.69 s (3H,  $\text{OCH}_3$ ), 5.76 s (1H, CH), 6.85 s (1H, CH), 7.5 m (14H,  $\text{H}_{\text{arom}}$ ). Found, %: C 74.47; H 5.12; N 6.41.  $\text{C}_{28}\text{H}_{22}\text{N}_3\text{O}_4$ . Calculated, %: C 74.31; H 4.99; N 6.30.

**Methyl {5-(4-methoxyphenyl)-3-[2-(2-oxo-1,2-diphenylethylidene)hydrazono]-2,3-dihydrofuran-2-ylidene}acetate (IId).** Yield 0.9 g (16%), red crystals, mp 162–163°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1726 (COOMe); 1678 (C=O); 1608, 1852 (C=N, C=C). Found, %:

C 73.11; H 4.98; N 6.01.  $\text{C}_{28}\text{H}_{22}\text{N}_3\text{O}_5$ . Calculated, %: C 73.00; H 4.90; N 6.19.

The IR spectra were recorded on an FSM-1201 spectrometer from samples dispersed in mineral oil. The  $^1\text{H}$  NMR spectra were measured on a Varian Mercury Plus-300 instrument (300.05 MHz) from solutions in  $\text{CDCl}_3$  using hexamethyldisiloxane as internal reference. The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates using diethyl ether–benzene–acetone (10:9:1) as eluent. The melting points were determined on a PTP-2 melting point apparatus.

## REFERENCES

1. Rubtsov, A.E. and Zalesov, V.V., *Russ. J. Org. Chem.*, 2007, vol. 43, p. 735.
2. Andreichikov, Yu.S. and Koz'minykh, V.O., *Zh. Org. Khim.*, 1985, vol. 21, p. 402.
3. Zalesov, V.V., Kataev, S.S., Pimenova, E.V., and Nekrasov, D.D., *Russ. J. Org. Chem.*, 1998, vol. 34, p. 98.
4. Koz'minykh, V.O., Koz'minykh, E.N., and Andreichikov, Yu.S., *Khim. Geterotsikl. Soedin.*, 1989, p. 1034.
5. Koz'minykh, V.O., Igidov, N.M., Koz'minykh, E.N., and Aliev, Z.G., *Pharmazie*, 1993, vol. 45, p. 99.
6. Ungoren, S.H., Sacmaci, M., Akcamur, Y., Arici, C., and Ulku, D., *J. Heterocycl. Chem.*, 2004, vol. 41, p. 151.
7. Rubtsov, A.E. and Zalesov, V.V., *Russ. J. Org. Chem.*, 2003, vol. 39, p. 869.
8. Rubtsov, A.E. and Zalesov, V.V., *Khim. Geterotsikl. Soedin.*, 2004, p. 163.