

Furan derivatives. LXXII.

Synthesis and some properties of 1-(5-nitro-2-furyl)- -2-(5-aryl-2-furyl)ethylenes

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1-(5-Nitro-2-furyl)-2-[5-(4-X-phenyl-2-furyl)]ethylenes where X = H, CH₃, Cl, Br, COOC₂H₅, and NO₂ were synthesized from 5-(4-X-phenyl)-2-furaldehydes and 5-nitrofurfurylphosphate. The olefin-forming reagent, hitherto unknown 5-nitrofurfurylphosphate was prepared from 5-nitrofurfuryl bromide and triethyl phosphite using the conditions of Arbuzov reaction.

Wittig reaction has recently been applied also in the preparation of 5-nitrofuran derivatives of ethylene [1–5]. The quoted syntheses were accomplished starting either from 5-nitrofurfuryl halides which were converted into 5-nitrofurfurylidene-phosphoranes and subsequent condensation of the latter with carbonyl compounds [1–4], or the intermediate phosphoranes were prepared from other furfuryl halides and these were condensed with 5-nitro-2-furaldehyde [5]. The reported yields were most of the time low and sometimes not given at all.

The present work describes the synthesis of the basic olefin-forming reagent, namely 5-nitrofurfurylphosphate (*I*), and its use in the synthesis of hitherto unknown 1-(5-nitro-2-furyl)-2-(5-aryl-2-furyl)ethylenes under the conditions of Wittig reaction as modified by Horner. This modification is known to give better yields, is simpler as to the isolation of the produced olefins and has not yet been applied in the synthesis of 5-nitrofuran derivatives of ethylene.

Experimental

The starting 5-(4-X-phenyl)-2-furaldehydes were prepared as described: X = H [6], CH₃ [7], Cl [8], Br [9], COOC₂H₅ [10], and NO₂ [11].

Infrared absorption spectra were measured with a UR-20 (Zeiss, Jena) spectrophotometer in reagent grade chloroform which was rid of alcohol by passing it (twice) through a column of indicating silica gel. The calibration was made against a polystyrene foil. The concentration of the solutions was 0.02 M and the sodium chloride-cell thickness was 1.02 mm.

Electronic spectra were obtained using a Specord UV-VIS (Zeiss, Jena) instrument. The measurements were performed in ethanol using 10-mm cells at the concentration of $3-5 \times 10^{-5}$ M and with the accuracy of ± 1 nm. Spectral data of the synthesized compounds are in Table 2.

5-Nitrofurfurylphosphate (I)

5-Nitrofurfuryl bromide (10.3 g; 0.05 mole), triethyl phosphite (8.4 g; 0.05 mole), and dry toluene (10 ml) were put into a three-necked flask equipped with a thermometer, gas-inlet tube, and a condenser connected to a collecting flask immersed in an efficient cooling bath. With the exclusion of moisture a gentle stream of nitrogen was passed through the reaction mixture while its temperature was kept at 60–70°C for one hour. The temperature of the content of the flask was then raised to 80–100°C and after an additional 1 hour the reaction mixture was kept at 100–110°C for 20–30 min. The formed ethyl bromide continuously distilled off while the colour of the reaction mixture changed from pale-orange to dark-brown. Some unchanged starting materials together with the solvent were extracted with petroleum ether and the product (10–12 g, 76–92%) was obtained as a dark viscous oil.

For $C_9H_{14}NO_6P$ (263.2) calculated: 41.07% C, 5.35% H, 5.32% N; found: 41.16% C, 5.23% H, 5.54% N.

1-(5-Nitro-2-furyl)-2-[5-(4-X-phenyl-2-furyl)]ethylenes (II–VII)

A suspension of sodium methoxide (1.08 g; 0.02 mole) in dimethylformamide (10 ml) was added gradually and with cooling to a solution of I (5.26 g; 0.02 mole) in dimethyl-

Table 1

Characteristic data for the synthesized compounds

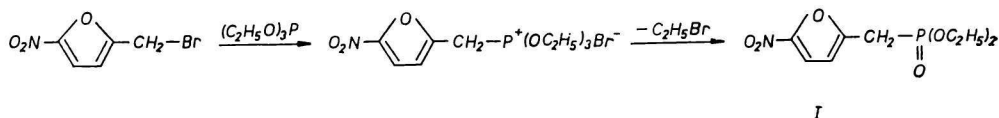
No.	X	Formula	M	Calculated/found			Yield [%]	M.p. [°C]
				% C	% H	% N		
II	H	$C_{16}H_{11}NO_4$	281.2	68.34 68.37	3.94 3.80	4.98 4.89	17	136–140
III	CH ₃	$C_{17}H_{13}NO_4$	295.3	69.15 69.24	4.43 4.50	4.74 4.78	8.5	173–175
IV	Cl	$C_{16}H_{10}NO_4Cl$	315.7	60.90 60.83	3.19 3.09	4.43 4.49	8	219–220
V	Br	$C_{16}H_{10}NO_4Br$	360.2	53.21 53.37	2.79 2.68	3.88 3.78	14	210–215
VI	COOC ₂ H ₅	$C_{19}H_{15}NO_6$	353.3	64.59 64.80	4.27 4.27	3.96 3.92	17	202–205
VII	NO ₂	$C_{16}H_{10}N_2O_6$	326.3	58.90 59.20	3.08 3.11	8.58 8.31	18.5	272–274

formamide (10 ml) contained in a three-necked flask. After a few minutes the corresponding 5-(4-X-phenyl)-2-furaldehyde (0.015 mole) in dimethylformamide (10 ml) was added and the reaction mixture was stirred at 25–30°C for one hour. The mixture was poured onto crushed ice, the formed precipitate was filtered, sucked dry, and crystallized from dioxan, ethanol or acetic acid to give reddish products. The characteristic of the obtained substances is given in Table 1.

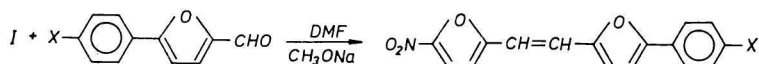
Results and discussion

The olefin-forming reagent *I* was synthesized from 5-nitrofurfuryl bromide [12] and triethyl phosphite [13] which were first condensed in toluene to give the phosphonium salt, followed by elimination of ethyl bromide at 60°C. To bring the reaction to the completion the temperature of the reaction mixture was raised near the end of the reaction to 100–110°C. The end of the reaction was indicated by termination of the evolution of ethyl bromide.

The olefin-forming reagent *I* was obtained as a dark-brown viscous liquid which could not be purified by vacuum distillation. It was rid of the unaltered starting materials by the extraction of the latter with petroleum ether in which compound *I* is insoluble. Thus obtained *I* gave satisfactory elemental analysis. To prepare the ethylene derivatives the phosphate *I* was generated as usually *in situ*, directly in the reaction mixture.



Attempts to prepare substance *I* without the use of an external solvent and an inert atmosphere of nitrogen were unsuccessful. The addition of even a small amount of triethyl phosphite to 5-nitrofurfuryl bromide was followed by a vigorous exothermic reaction, the mixture turned dark and resinuous products were formed from which no pure components could be isolated.



The condensation of the phosphate *I* with 5-(4-X-phenyl)-2-furaldehydes was carried out in dimethylformamide using sodium methoxide as the base. It can be seen from the data in Table 1 that the yields obtained were low. Attempts to improve the yields by reversing the order of the addition of the reaction components, altering their molar ratios, or by changing the time and the temperature of the reaction were met with little success. In all cases a considerable amount of the starting aldehyde was recovered. The low yields may be caused either by the instability of the phosphate *I* or of the produced 5-nitrofuran derivatives in the presence of strongly basic sodium methoxide.

Of the characteristic absorption bands in the i.r. spectra (Table 2) that band is important which is in the region of 1630–1628 cm⁻¹ corresponding to the aliphatic C=C vibrations which consistently appeared at this value as a medium or strong band. The absorption bands corresponding to $\nu_{\text{as}}(\text{NO}_2)$ appear in the region of 1524–1503 cm⁻¹ as medium bands and they are markedly affected by the nature of the substituents. As can be seen in Fig. 1 there is a good linear correlation between σ_p Hammett constants and the wavenumber at which this band appears ($r = 0.935$).

Table 2
Spectral data for the synthesized compounds

No.	λ_{\max} [nm] log ϵ				$\nu_{\text{aliph}}(\text{C}=\text{C})$	$\nu_{\text{as}}(\text{NO}_2)$	$\nu_{\text{s}}(\text{NO}_2)$	$\nu(\text{C}-\text{O}-\text{C})$	$\nu_{\text{def}}(\text{C}-\text{H})$	$\nu_{\text{def}}(\text{C}-\text{H})$
<i>II</i>	204	240	328	447	1630	1512	1355	1025	973	885
	4.22	4.31	4.18	4.48						
<i>III</i>	204	246	340	437	1630	1503	1355	1023	973	888
	4.19	4.22	4.12	4.72						
<i>IV</i>	203	247	332	446	1630	1510	1355	1022	973	885
	4.22	4.29	4.16	4.59						
<i>V</i>	205	244	331	440	1630	1511	1355	1022	974	882
	4.28	4.18	4.41	4.22				1013		
<i>VI</i>	204	253	340	442	1628	1520	1355	1024	973	883
	4.21	4.28	4.17	4.55						
<i>VII</i>	205	233	348	448	1631	1524	1358	1026	973	880
	4.33	4.23	4.29	4.29			1340			

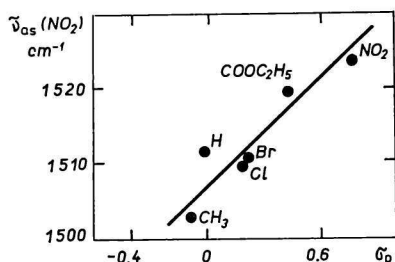


Fig. 1. The dependence of σ_p Hammett constants of the substituents upon $\nu_{as}(\text{NO}_2)$.

The bands corresponding to $\nu_s(\text{NO}_2)$, except for the dinitro derivative VII in which case this band is split into two bands at 1358 and 1340 cm^{-1} , appear consistently at 1355 cm^{-1} as a very strong band. The absorption bands at 1026–1022 cm^{-1} and mainly the narrow weak band at 880–888 cm^{-1} [14] are characteristic of the furan arrangement. The absorption bands of weak to medium intensity at 973 cm^{-1} prove the *trans* configuration of the synthesized substances. In the u.v. spectra of the compounds under investigation four absorption bands at 203–205, 233–253, 328–348, and 440–448 nm are present. Compounds where X = NO_2 , COOC_2H_5 , and Br show, in addition, an inflexion at 220–230 nm. The bands at 203–253 nm can be assigned to $\pi \rightarrow \pi^*$ electron transitions localized in the benzene ring and those at 328–348 nm most probably correspond to the electron transitions of the 5-nitrofur or arylfuran part of the molecule. The most intense of all the absorption bands is the K band in the visible region (at 440–448 nm) which indicates that the system concerned is a planar conjugated one. This arrangement is possible only when the substituents on the ethylene carbon atoms are *trans*-oriented. The intensity of the K band and its hypsochromic shift [10, 15, 16] results from twisting off the plane of the substituents.

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