SYNTHESIS OF 5-NITRO-2-VINYLFURAN BY WITTIG METHOD*

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The conversion of furfuryl alcohol to 5-nitro-2-vinylfuran (*VI*) is described. The new method of preparation is based on the Witting reaction carried out in aqueous formaldehyde.

Excepting one paper[1], there is no reference concerning the synthesis of 5-nitro-2-vinylfuran, a convenient monomer for preparation of biologically active polymers and a starting material for syntheses of biologically interesting 5-nitro-2-furan derivatives. The above-mentioned preparation[1] of 5-nitro-2-vinylfuran *via* decarboxylation of 3-(5-nitro-2-furyl)-2-propenoic acid in quinoline at 200–240°C under catalysis of Cu gave a little stable product in low yields (12·5%) only and is, therefore, inconvenient for preparation on a large scale. The nitration of 2-vinylfuran, as an alternative preparation of the title compound has hitherto not been successful, since in the presence of HNO_3 and acetic anhydride at low temperature the formation of resins and decomposition took place.

The successful synthesis of 5-nitro-2-furfuryl bromide[2] (*III*) from furfuryl alcohol offered an opportunity to use this compound for preparation of 5-nitro-2-vinylfuran (*VI*). The reaction of 5-nitro-2-furfurylidenetriphenyl phosphorane (*V*), which is a stabilized ylide[3], proceeds with aqueous formaldehyde very smoothly. Generation of the ylide *V in situ* from *IV* by action of sodium or potassium carbonate takes place in aqueous formaldehyde to yield directly 5-nitro-2-vinylfuran in a 80–92% yield. The great advantage of this procedure is that the overall temperature maximum does not exceed 30–40°C at which 5-nitro-2-vinylfuran is stable enough.

We checked the influence of isolation of the respective intermediates *II* to *V* on the yields. The most pure product *VI* was obtained from pure *IV*. The total conversion of *VI* was shown to be 20–30% (calculated on the starting furfuryl alcohol), the yield of the individual intermediates being: $I \rightarrow II$ 50%, ref.[4], $II \rightarrow III$ 75%, ref.[5], $IV \rightarrow \rightarrow V \rightarrow VI$ 80–92%. The isolation of *V* is not necessary, since the *in situ* reaction from *IV* to *VI* gives 5-nitro-2-vinylfuran in a 80–92% yield. The yields were observed to decrease when *V* was isolated, because the ylide *V* is not sufficiently stable for

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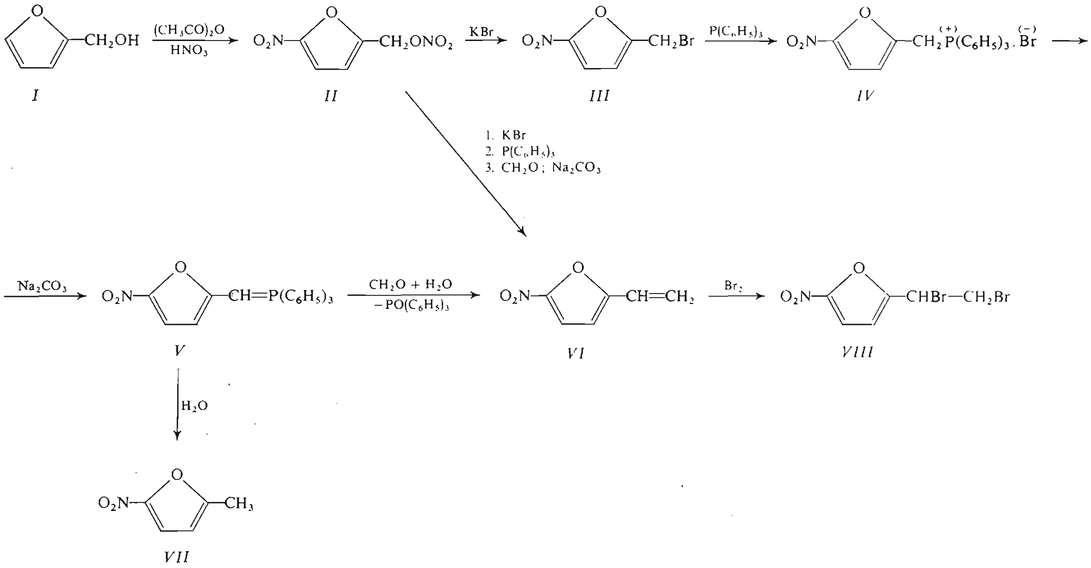
CH₂OH
(CH₃CO)₂O
HNO₃
O₂N
CH₂ONO₂
KBr
CH₂Br
P(C₆H₅)₃
CH₂P(C₆H₅)₃.Br
(+)
(−)
I
II
III
IV
1. KBr
2. P(C₆H₅)₃
3. CH₂O ; Na₂CO₃
Na₂CO₃
CH=P(C₆H₅)₃
CH₂O + H₂O
−PO(C₆H₅)₃
CH=CH₂
Br₂
CHBr—CH₂Br
V
VI
VIII
H₂O
CH₃
VII
O

SCHEME 1

a longer time and hydrolyses to 5-nitro-2-methylfuran, the formation of which was not observed during the direct conversion of *IV* to *VI in situ*. When the reaction was carried out by a shortened procedure (*I* to *II* and *II* to *VI*, Scheme 1) a decrease in conversion *I* → *VI* by 50% occurred.

5-Nitro-2-vinylfuran is a yellow cotton-like crystalline compound, which was obtained in this reaction (Scheme 1) in a highly pure state; it is stable enough in an inert atmosphere at −15−25°C. A sample stored at this condition for half a year undergoes a slight decomposition (c. 10%). In the air at room temperature it polymerizes to give a transparent polymer. The easiness of polymerization and the high reactivity of the activated double bond offers a big deal of possibilities for preparation of polymers and for 5-nitro-2-furylethylation of nitrogen and sulfur containing compounds.

EXPERIMENTAL

Melting points were determined on a Kofler block, infrared spectra were recorded with a UR-20 (Zeiss, Jena) spectrophotometer in $CHCl_3$. Ultraviolet spectra were measured with a UV VIS (Zeiss, Jena) apparatus in methanol. The ^{1}H-NMR spectra were taken in deuteriochloroform with a Tesla BS 487 C instrument operating at 80 MHz and 25°C with tetramethylsilane as an internal reference substance. 5-Nitro-2-furfuryl nitrate (*II*) was prepared according to[4], 5-nitro-2-furfuryl bromide (*III*) according to[2] and 5-nitro-2-furfuryltriphenylphosphonium bromide (*IV*) according to[5].

5-Nitro-2-vinylfuran (*VI*)

A. A 10% solution of Na_2CO_3 (10 ml) was dropwise added to 5-nitro-2-furfuryltriphenylphosphonium bromide (4·67 g, 10 mmol) in 40% formaldehyde (40 ml) at 25°C. The rate of addition was determined by temperature and change in colouration of the solution from purple-red to deepbrown. After addition of the base the solution was stirred for 2 h at room temperature and extracted three times with ether (150 ml total). The organic layer was evaporated under diminished pressure and the residue chromatographed on alumina (neutral), hexane, heptane and light petroleum being the eluents. Yield 1·25 g (90%), m.p. 49−51°C (hexane). IR spectrum (cm^{-1}): 1025, 1335, 1362, 1503, 1531, 1611, 2870, 2935. ^{1}H-NMR spectrum (δ, ppm): 6·46 (H_3); 7·27, $J_{3,4} = 3·7$ Hz (H_4); 5·52 (H_A); 6·01 (H_B); 6·54, $J_{AB} = 1·2$ Hz, $J_{AX} = 10·8$ Hz, $J_{BX} = 17·6$ Hz (H_X). For $C_6H_5NO_3$ (139·1) calculated: 10·07% N; found: 9·92% N.

B. The condensed procedure *II* → *VI*: 5-Nitro-2-furfuryl nitrate (*II*) (75 g, 40 mmol), NaBr (82 g) and benzene (200 ml) were refluxed while stirred for 4−5 h. The mixture was then cooled to 30°C, triphenylphosphine (100 g) in benzene (100 ml) was added under stirring, heated to 60°C for 2−3 h and cooled to 30°C. Formaldehyde (40%, 200 ml) was added to this suspension and under continuous stirring 20% aqueous Na_2CO_3 (500 ml) was added in 50 ml instalments and 15 min intervals. The mixture was stirred for additional 1h, the organic layer was separated, the solvent removed *in vacuo* (at 30−35°C bath temperature) and the residue purified using a short alumina column and suction pump (eluent hexane, heptane and light petroleum). Yield 12−17 g (21−30%), m.p. 48−51°C (hexane).

5-Nitro-2-methylfuran (*VII*)

A. The title compound was obtained as a by-product during generation of the ylide *V* in an aqueous-organic medium in a 10—30% yield.

B. Aqueous Na_2CO_3 (10%, 10 ml) was added to a mixture consisting of 5-nitro-2-furfuryltriphenylphosphonium bromide (4·7 g, 10 mmol) in water (10 ml) and ethyl formate (90 ml) at 25°C; the temperature was then risen to 50°C while stirred for 3—4 h. The organic layer was separated, the solvent distilled off and the residue chromatographed on silica gel (150—250 mesh, eluent benzene). Yield 0·75 g, (60%), m.p. 43—45°C (benzene), (ref.[6] 43·5°C). ^1H-NMR spectrum (δ, ppm): 6·20 (H_3); 7·19, $J_{3,4} = 3 \cdot 7$ Hz (H_4); 2·44 (CH_3).

1-(5-Nitro-2-furyl)-1,2-dibromoethane (*VIII*)

This compound was obtained according to[1] in 85—90% yield; m.p. 55—57°C (hexane). ^1H-NMR (δ, ppm): 7·05 (H_3); 7·32, $J_{3,4} = 3 \cdot 7$ Hz (H_4); 3·96 (H_A); 4·13 (H_B); 5·23, $J_{AB} = 10 \cdot 2$ Hz, $J_{AX} = 6 \cdot 3$ Hz, $J_{BX} = 10 \cdot 0$ Hz (H_X).

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