2-FORMYL-5-NITROTHIOPHENE AS A REAGENT FOR PHOSPHORANES

SYNTHESIS OF NITROTHIOPHENE ANALOGS OF CHALCONE

V. N. Listvan

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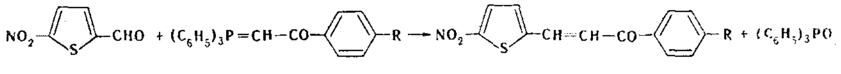
2-Formyl-5-nitrothiophene has high reactivity with respect to phosphoranes, with which it reacts quantitatively to give 1-aryl-3-(5-nitro-2-thienyl)propenones. The reaction can be used for the qualitative detection of phosphoranes.

In 1961, Venter, Giller, and co-workers [1] used the Wittig reaction for the synthesis of α,β-unsaturated and polyene compounds in the 5-nitrofuran series with the aid of acetyl- and ethoxycarbonylmethylenetriphenylphosphoranes and 5-nitroformylfurans. We tested the action of 2-formyl-5-nitrothiophene on several α-ketophosphoranes. It is known [2] that the Wittig reaction is, as a rule, carried out by prolonged heating. 2-Formyl-5-nitrothiophene proved to be so reactive that bright-yellow 5-nitrothiophene analogs of chalcone (I-IV) crystallized in quantitative yields from mixtures of it with phosphoranes in alcohol or benzene even after a few minuts at room temperature. Chalcones in considerably lower yields were obtained by condensation of 2-formyl-5-nitrothiophene with acetophenones [3]. In the presence of phosphoranes, the method that we discovered is simple to accomplish and has a number of obvious advantages for the synthesis of some 5-nitrothiophene derivatives.



I R = H, II R = CH$_3$; III R = Br; IV R = C$_6$H$_5$

It is known that the Wittig reaction with stable phosphoranes generally leads to trans-alkenes [2]. Products I-IV apparently also have trans structures, inasmuch as their IR spectra contain bands at 980-985 cm^{-1} (out-of-plane vibrations of C—H bonds of trans-disubstituted conjugated ethylenes [4]). The IR spectra of I-IV also contain the characteristic bands of C = O groups (1663-1667 cm^{-1}) and conjugated C = C bonds (1604-1607 cm^{-1}). The $\nu_{C=C}$ band is more intense than the $\nu_{C=O}$ band ($\nu_{C=O}/\nu_{C=C}=0.8-0.9$), which indicates a cisoid orientation of these groups relative to one another [5-8] and was used for the establishment of the conformations of α,β-unsaturated ketones [9-12]. The difference between $\nu_{C=O}$ and $\nu_{C=C}$ (Δ ν) [9, 12], which is 51-70 cm^{-1} for some sym-cis derivatives [12], is also used to prove that the compounds belong to the sym-cis or sym-trans series. In our case, Δ ν ranges from 57 to 63 cm^{-1}, and thus they also should be assigned to the sym-cis series, according to this criterion.

TABLE 1. 1-Aryl-3-(5-nitro-2-thienyl)propenones I-IV

Compound	R	mp, °C	Empirical formula	Found, %		Calc., %		IR spectrum, cm^{-1}			
				N	S	N	S	$\nu_{C=O}$	$\nu_{C=C}$	$\nu_{s}NO_2$	$\nu_{=C-H}$
I	H	180—181*	$C_{13}H_9NO_3S$	5,2	—	5,4	—	1665	1607	1342	980
II	Me	189—190	$C_{14}H_{11}NO_3S$	5,2	11,4	5,1	11,7	1666	1606	1344	980
III	Br	227—228	$C_{13}H_8BrNO_3S$	4,2	9,3	4,1	9,5	1667	1604	1348	985
IV	Ph	236—237	$C_{19}H_{13}NO_3S$	4,1	9,2	4,2	9,6	1663	1606	1342	982

*According to [3], this compound has mp 181°.

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One's attention is drawn to the most intense bands at 1342-1348 cm^{-1}. They correspond to symmetrical vibrations of an NO_2 group [5], particuarly one bonded to the furan ring [13]. However, there are indications [10] that the ν_{sNO_2} bands may coincide with the frequencies of the thiophene ring, and this possibly also explains their high intensity. It is imperative to note the fact that the IR spectrum of I coincides with the published spectrum [10].

The reaction of phosphoranes with 2-formyl-5-nitrothiophenes proceeds with coloring of the solutions and the formation of yellow precipitates, and it can therefore be recommended for the qualitative detection of phosphoranes and, possibly, for their quantitative determination.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-10 spectrometer.

1-Aryl-3-(5-nitro-2-thienyl)propenones. (I-IV). Equimolecular amounts (5 mmole) of the phosphorane and 2-formyl-5-nitrothiophene were dissolved in the minimum volume of benzene, and the solutions were mixed. The mixture immediately became yellow, and chalcones I-IV crystallized in a few minutes. The major portions of the substances precipitated in 30 min. After 3 h, the precipitate was removed by filtration and washed with benzene. A small amount of chalcone remained in the benzene solution. We were also able to isolate it by evaporating the benzene and treating the solid residue, which consists mainly of triphenylphosphine oxide, with alcohol. When this was done, the triphenylphosphine oxide dissolved, and I-IV remained in the precipitate. They were recrystallized from benzene. Data for I-IV are indicated in Table 1.

The triphenylphosphine oxide formed in the reaction was precipitated from the alcohol solution by the addition of water and was crystallized from ligroin. The yields of the oxide (mp 158°) were 80-90%.

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