

B) A 7.8-g (0.09 mole) sample of morpholine was added to a solution of 2.0 g (0.01 mole) of 4-piperidyl-2-sulfolene in 20 ml of methanol, and the mixture was heated at 60°C for 10 h. The resulting solution was evaporated, and the residue was crystallized from 50% aqueous acetone to give 2.7 g (98%) of VI. No melting-point depression was observed for mixtures of the products obtained in experiments A and B.

3,4-Dimorpholinylsulfolane (V). A 2.0-g (0.01 mole) sample of 4-morpholinyl-2-sulfolene and 8.7 g (0.1 mole) of morpholine were dissolved in 70 ml of methanol, and the solution was heated at 60°C for 20 h. It was then evaporated, and the residue was crystallized from 10% ethanol to give 2.6 g (90%) of a product with mp 167-168°C. Found: N 9.5; S 11.1%. $C_{12}H_{22}N_2O_4S$. Calculated: N 9.6; S 11.0%.

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SYNTHESIS OF ω, ω' -DIARYL-SUBSTITUTED 2,5-DIVINYLTHIOPHENES

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The phosphonate modification of the Wittig reaction was used to synthesize ω, ω' -diaryl-substituted 2,5-divinyldithiophenes that contain phenyl, 4-biphenyl, 2-naphthyl, 9-anthryl, and 2-thienyl groups, as well as functional substituted 2,5-distyryldithiophenes.

Vinyl derivatives of thiophene have found application as optical bleaches [1] and biologically active substances [2, 3]. These compounds, which include various chromophore groupings, may, like the analogous benzene derivatives [4], be of interest as effective luminophores.

We have synthesized ω, ω' -diaryl-substituted 2,5-divinyldithiophenes (DDVT) that contain phenyl, 2-naphthyl, 4-biphenyl, 9-anthryl, and 2-thienyl groups, as well as functional substituted 2,5-distyryldithiophenes (Table 1).

The arylthienylethylenes described in the literature were obtained by various methods [5, 6]. In particular, arylthienylethylenes were synthesized via the Wittig reaction both from formylthiophene [7] and from chloromethylthiophene [8]. However, a mixture of the cis and trans isomers is obtained in both cases.

For the synthesis of the DDVT we used the phosphonate modification of the Wittig reaction [9], which does not have this disadvantage; the reaction products are, as a rule, the trans isomers.

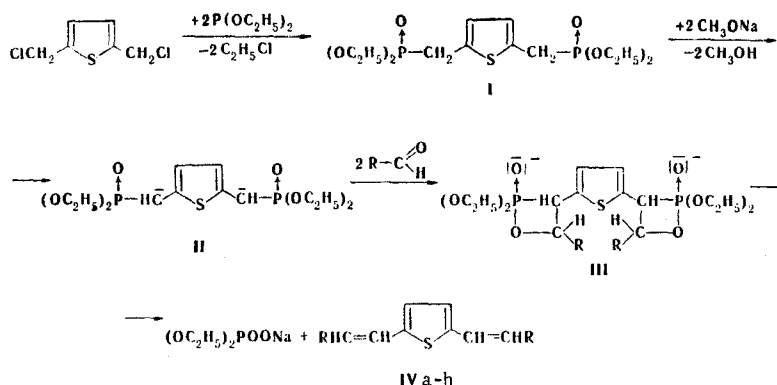
To obtain the DDVT we first used diethyl thiophenebis(methylenephosphonate) (I), since the use of 2,5-diformylthiophene as the starting compound would lead to complication of the synthesis and make it a multi-step process.

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TABLE 1. Characteristics of ω, ω' -Diaryl-Substituted 2,5-Di-
nylthiophenes

Compound	R	mp, °C	λ_{max} (in toluene), nm	$\epsilon \cdot 10^{-4}$	ν_{CH} , cm^{-1}	$\nu_{\text{C}=\text{C}}$, cm^{-1}	Found, %			Empirical formula	Calc., %			Yield, %
							C	H	S		C	H	S	
IVa	C ₆ H ₅	197	395	4,6	950	1620	83,2	5,4	10,9	C ₂₀ H ₁₆ S	83,3	5,5	11,1	30
IVb	2-C ₁₀ H ₇	247	405	4,78	945	1618	86,4	5,0	8,3	C ₂₈ H ₂₀ S	86,6	5,1	8,2	35
IVc	4-C ₁₂ H ₉	314	415	6,7	947	1627	87,3	5,2	7,2	C ₃₂ H ₂₄ S	87,3	5,4	7,3	40
IVd	9-C ₁₄ H ₉	283	420	2,5	953	1623	88,8	5,2	6,3	C ₃₆ H ₂₄ S	88,5	4,9	6,5	30
IVe	4-Cl-C ₆ H ₄	203	397	7,3	958	1618	67,1	3,8	8,8	C ₂₀ H ₁₄ SCl ₂	67,2	3,9	8,9	22
IVf	4-CH ₃ O-C ₆ H ₄	243	405	5,9	953	1605	76,0	5,5	8,9	C ₂₂ H ₂₀ O ₂ S	75,9	5,7	9,2	30
IVg	4-NO ₂ -C ₆ H ₄	275	435	4,6	950	1625	63,3	3,6	8,3	C ₂₀ H ₁₄ N ₂ O ₄ S	63,5	3,7	8,5	35
IVh	2-C ₄ H ₃ S	151	435	3,7	938	1620	63,9	3,8	32,0	C ₁₆ H ₁₂ S ₃	64,0	4,0	32,0	30

The synthesis was accomplished via the scheme



As a consequence of the electron-acceptor effect of the thiophene ring [10], replacement of the benzene ring by a thiophene ring facilitates the formation of the diethyl thiophenebis(methylenephosphonate) carbanion (II).

The negative charge in carbanion II is delocalized to a greater extent than in the case of the participation of the benzene ring. The decrease in the nucleophilicity of II, on the one hand, decreases the rate of its attack on the carbonyl carbon atom, whereas, on the other hand, it will promote an increase in the polarization of the $\text{P} \rightarrow \text{O}$ bond. The step involving the formation of four-membered intermediate III and its subsequent decomposition to give the olefin and a phosphinic acid salt is facilitated as the electrophilicity of the phosphorus atom increases.

Thus I forms a stable carbanion, and, as is well known [11], in this case the step involving the formation and decomposition of the four-membered ring is the rate-determining step.

The structure of the compounds obtained is confirmed by data from their IR spectra. An intense band of out-of-plane deformation vibrations of the CH bond of a trans-ethylene group ($\nu_{\text{CH}} = 938\text{--}958 \text{ cm}^{-1}$) appears in the IR spectra. The bands of the stretching vibrations of the double bonds ($\nu_{\text{C}=\text{C}} = 1605\text{--}1627 \text{ cm}^{-1}$) are of low intensity, which is characteristic for symmetrical systems with a double bond that is only slightly polarized. When methoxy and nitro groups are introduced in the para position of the terminal phenyl groups of 2,5-distyrylthiophene, the intensity of the band increases significantly, and this constitutes evidence for an increase in the polarity of the $\text{C}=\text{C}$ bond.

The compounds obtained were characterized by their UV absorption spectra in toluene; they contain one intense band at 395–435 nm (ϵ 25,000–73,000).

Thus, the phosphonate modification of the Wittig reaction can be successfully used for the synthesis of vinyl derivatives of thiophene.

EXPERIMENTAL

The absorption spectra of 10^{-4} - 10^{-5} mole/liter solutions of the compounds in toluene were measured with an SF-4A spectrophotometer. The IR spectra of KBr pellets were measured with a UR-20 spectrometer at 700-4000 cm^{-1} (with NaCl and LiF prisms).

Diethyl Thiophenebis(methylenephosphonate) (I). A mixture of 41 g (0.37 mole) of bis(chloromethyl)thiophene, 77 ml (0.45 mole) of triethyl phosphite, and 150 ml of dry p-xylene was refluxed for 10 h, after which the p-xylene was removed by vacuum distillation to give 85 g (97%) of I as a red oil.

2,5-Distyrylthiophene (IVa). Sodium methoxide (a solution of 1.5 g of sodium in the minimum amount of absolute methanol) was added in portions to a solution of 10 g (0.025 mole) of I in 40 ml of dimethylformamide (DMF), and the mixture was allowed to stand for 15 min. A solution of 5.5 g (0.05 mole) of benzaldehyde in 15 ml of DMF was then added, and the mixture was allowed to stand for another 15 h. The resulting precipitate was removed by filtration and an additional amount of the reaction product was isolated from the filtrate by the addition of water. The product was purified by two crystallizations with activated charcoal from cyclohexane and subsequent chromatography of a solution in benzene on aluminum oxide to give 2.2 g (30%) of a yellow powder with mp 197°C. Compounds IVb-h were similarly synthesized (Table 1).

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CONDENSED HETEROAROMATIC SYSTEMS THAT INCLUDE A THIOPHENE RING

36.* NEW COMPLEXING AND CHELATE COMPOUNDS OF THE BENZO[b]- THIOPHENE SERIES WITH SELENIUM AS THE DONOR

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New complexing compounds, viz., 2-formylbenzo[b]thiophene-3-selenol and 3-formylbenzo[b]thiophene-2-selenol, and some derivatives involving the selenium atom and the formyl group, as well as complexes of divalent nickel and copper based on them, were obtained. The tautomerism of the isomeric formylthiopheneselenols was studied by means of IR spectroscopy, and it was shown that 3-formylbenzo[b]thiophene-2-selenol, in contrast to 2-formylbenzo[b]thiophene-3-selenol, exists in the form of a mixture of two tautomers.

* See [1] for communication 35.

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