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Synthesis of Distyryl Derivatives of Five-Membered Heterocycles

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Although 1,4-distyrylbenzene was first reported by Kauffmann (1) almost half a century ago and much interest has centered around the spectral and fluorescent properties of this compound, the analogous distyryl heterocyclic compounds are unknown.

We wish to report the synthesis of 2,5-distyrylfuran, 2,5-distyrylthiophene, and 1-methyl-2,5-distyrylpyrrole (IIIa-c), according to the reaction scheme indicated. Phosphonate condensation with diethyl benzylphosphonate and the heterocyclic aldehyde gave the monostyryl compounds; Vilsmeier formylation of the latter gave the corresponding heterocyclic aldehydes (IIa-c); and phosphonate condensation with diethyl benzylphosphonate converted these to the distyryl compounds.

The phosphonate condensation reaction, originally reported by Horner and co-workers (2), was carried out in dimethylformamide solution by using one mole of sodium methoxide as the base (3). The styryl heterocyclic compounds in Table I were prepared in this manner. Upon reaction with the Vilsmeier complex (4) prepared from phosphorus oxychloride and dimethylformamide, the 2-styryl heterocycles (Ia-c) gave the corresponding heterocyclic aldehydes (IIa-c), listed in Table II. In each case, sub-

stitution in the open alpha-position of the hetero ring was confirmed by the infrared absorption spectrum (see Experimental section). Vilsmeier formylation of 2-styrylthiophene has been reported (5) and has been shown to give 5-styryl-2-thiophenecarboxaldehyde.

The ultraviolet absorption maxima for the monostyryl heterocycles (Ia-c) and distyryl heterocycles (IIIa-c) are tabulated in Table III. The long-wavelength band of the 2-styryl heterocycles (Ia-c) shows the expected shift of absorption maximum (6), $NCH_3 > S > O$, in accordance with the predicted ability of the hetero atom to donate its unshared *p*-electrons to the π system. In the distyryl heterocycles (IIIa-c), the long-wavelength band is displaced considerably to longer wavelength. Interestingly enough, the absorption maximum of this band occurs at the same wavelength in each of the distyryl heterocycles. This is because the molecule is symmetrical and the hetero atom is a side-chain substituent and is not at the end of the conjugated system.

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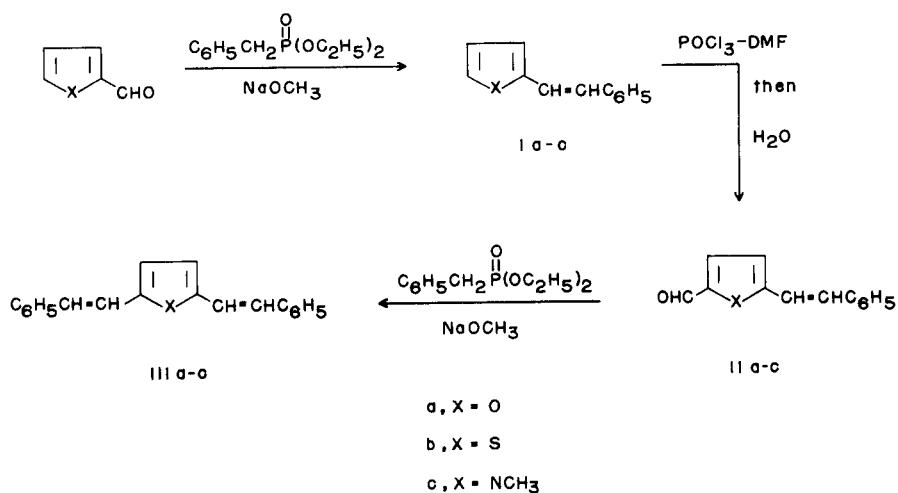


TABLE I
Preparation of Styryl Heterocycles VIA the Phosphonate Condensation Reaction

No.	Olefin	Yield %	M. p., °C	Recrystallization Solvents	Empirical Formula	Elemental Analysis		
						Calcd./Found		
						C	H	N or S
Ia	2-Styrylfuran (a)	88	54-55	Methanol	C ₁₂ H ₁₀ O			
Ib	2-Styrylthiophene (a)	77	112-113	Ethanol	C ₁₂ H ₁₀ S			
Ic	1-Methyl-2-styrylpyrrole	66	73.5-75	Methanol	C ₁₃ H ₁₃ N	85.2 85.3	7.15 6.9	7.65 7.5
IIIa	2,5-Distyrylfuran	87	144-145.5	Ethanol	C ₂₀ H ₁₆ O	88.2 87.9	5.9 6.0	
IIIb	2,5-Distyrylthiophene	66	196-198	Acetonitrile-benzene	C ₂₀ H ₁₆ S	83.3 83.5	5.6 5.8	
IIIc	1-Methyl-2,5-distyrylpyrrole	45	192.5-193.5	Carbon tetrachloride	C ₂₁ H ₁₉ N	88.4 88.2	6.7 6.8	4.9 4.7

(a) For previous synthesis and melting points, see ref. (3).

TABLE II
Aldehydes Prepared by Vilsmeier Formylation of Styryl Compounds Ia-c

No.	Aldehyde	Yield %	M. p., °C	Recrystallization Solvents	Empirical Formula	Elemental Analysis		
						Calcd./Found		
						C	H	N or S
IIa	5-Styryl-2-furan-carboxaldehyde	93	63.5-64	Pet. ether-THF	C ₁₃ H ₁₀ O ₂	78.75 78.6	5.1 5.3	
IIb	5-Styryl-2-thiophene-carboxaldehyde	87	83-85 (a)	Cyclohexane	C ₁₃ H ₁₀ OS	72.9 72.6	4.7 4.8	15.0 15.0
IIc	1-Methyl-5-styryl-2-pyrrolecarboxaldehyde	47	82.5-85	Cyclohexane	C ₁₄ H ₁₃ NO	79.6 79.8	6.2 6.1	6.65 6.5

(a) Lit. (5) m. p. 84°.

TABLE III
Ultraviolet Absorption of Styryl Heterocycles (mμ)

No.	Compound	Solvent	λ max (ε)
Ia	2-Styrylfuran	Methanol	315 (32,000), 232 (8,200), 225 (7,850)
Ib	2-Styrylthiophene	Methanol	323 (27,700), 229 (10,000),
Ic	1-Methyl-2-styrylpyrrole	Methanol	337 (21,000), 237 (9,800)
IIIa	2,5-Distyrylfuran	Ethanol	379 (38,500), 281 (21,650), 273 (22,000), 234 (14,300)
IIIb	2,5-Distyrylthiophene	Methanol	380 (32,000), 274 (12,000), 266 (11,700), 239 (16,350)
IIIc	1-Methyl-2,5-distyrylpyrrole	Methanol	379 (37,250), 244 (15,250)

EXPERIMENTAL

Melting points cited in the tables are for the analytical sample and are corrected. Ultraviolet spectra were obtained on a Cary Model 11 Recording Spectrophotometer. Infrared spectra were obtained in potassium bromide on a Perkin-Elmer Infracord.

Diethyl benzylphosphonate and 2-furaldehyde were obtained from Distillation Products Industries, Division of Eastman Kodak Company; 2-thiophenecarboxaldehyde and 1-methyl-2-pyrrolicarboxaldehyde were obtained from the Aldrich Chemical Company. Sodium methoxide was obtained from the Fisher Scientific Company.

Preparation of Styryl Heterocycles (Table I).

These compounds were prepared by the general procedure previously described (3). Diethyl benzylphosphonate (0.050 mole) and sodium methoxide (0.050-0.055 mole) were combined in dimethylformamide (30-60 ml.) in a flask fitted with a drying tube. The heterocyclic aldehyde (0.050 mole) in dimethylformamide (20-45 ml.) was added, with stirring and cooling, to maintain the reaction temperature at 25-40°. After standing for 30-60 minutes, the reaction mixture was treated with 1-2 volumes of cold water and the precipitated olefin was collected on a filter and slurried with water. The resulting olefins were quite pure and for most purposes required no further purification.

Preparation of 5-Styryl-2-heterocyclic Carboxaldehydes (Table II).

The Vilsmeier reagent was prepared at approximately 20°, by adding phosphorus oxychloride (0.10-0.20 mole) to dimethylformamide (100-200 ml.), the latter functioning as reagent and solvent. Addition of the styryl heterocyclic compound (0.10 mole) Ia-c, with stirring, which usually resulted in an exothermic reaction, was followed by brief

heating in a warm water bath or standing overnight at room temperature. The reaction mixture was decomposed by the cautious addition (with cooling) of 10% sodium hydroxide solution, and the precipitated aldehyde was collected on a funnel, slurried with water, and air-dried. The aldehydes were sufficiently pure for the subsequent reaction and did not require recrystallization. The infrared absorption spectrum of each of the aldehydes showed strong absorption in the regions 690-700 cm^{-1} and 750-770 cm^{-1} (monosubstituted phenyl) (7a), 800-820 cm^{-1} (1,4-substituted aromatic) (7b), and 960-980 cm^{-1} (trans CH=CH out of plane bending) (7c), as well as carbonyl absorption at 1660-1675 cm^{-1} . These spectra are consistent only for substitution of the formyl group into the alpha-position of the hetero ring.

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