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Three simple routes for the synthesis of thieno[2,3-*b*]quinoxalines are described.

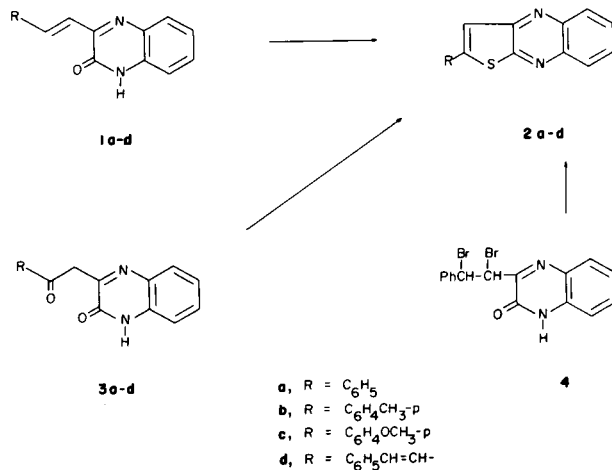
J. Heterocyclic Chem., **19**, 699 (1982).

Condensed thiophenes are structurally (1) and biologically (2-6) interesting compounds. As a part of a project directed towards the synthesis of fused thiophenes as a part of heterocyclic tricyclic array, we report here synthetic approaches to thieno[2,3-*b*]quinoxalines.

The recently reported one step conversion of **1a-c** into **2a-c** by the action of phosphorus pentasulfide in pyridine (7) has been applied to 3-(4-phenyl-1,3-butadienyl)-2-oxo-1,2-dihydroquinoxaline (**1d**). The product obtained was shown to be 2-styrylthieno[2,3-*b*]quinoxaline (**2d**). Although this interesting synthesis accomplishes three reactions in one step [thiation, cyclization and aromatization (7,8)], the yield in most cases ranges from 30-40%.

In searching for a more efficient synthesis of **2** we examined the possible conversion of 3-acylmethylquinoxalines **3**, readily available by condensing α,γ -dioxoacids or esters with *o*-phenylenediamine (9), into **2**. Thus the action of phosphorus pentasulfide in pyridine on compounds **3a-d** yielded compounds **2a-d** efficiently in 90-95%.

Compound **2a** has also been obtained by the action of phosphorus pentasulfide on the dibromo derivative **4** readily obtainable by bromination of **1a** with bromine in acetic acid (10). Thus offering a third avenue for the synthesis of compounds **2**, however the yield was very low (10%).



EXPERIMENTAL

All melting points are uncorrected. The uv spectra were measured in 2-propanol, with Unicam spectrophotometer model SP 1750. The ir spectra were recorded with a Unicam SP 1200 infrared spectrophotometer. The pmr spectra were determined on Varian A-60A and EM-360 60 MHz nmr spectrometer.

3-(4-Phenyl-1,3-butadienyl)-2-oxo-1,2-dihydroquinoxaline (**1d**).

A mixture of cinnamylidenepyruvic acid (30 mmoles) and *o*-phenylenediamine (30 mmoles) in acetic acid (20 ml) was boiled and left overnight at room temperature. The yellow precipitate was collected and

Table

Thieno[2,3-*b*]quinoxaline (**2a-d**)

Products (a)	Mp °C	Yield %	Formula (Mol wt)	Analysis %			
				C	H	N	S
2a	185	92	C ₁₆ H ₁₀ N ₂ S (262.33)	73.26	3.84	10.68	12.22
	(Ethanol)			73.10	3.90	10.50	12.40
2b	216	90	C ₁₇ H ₁₂ N ₂ S (276.35)	73.89	4.37	10.13	11.60
	(AcOH)			74.10	4.20	10.30	11.50
2c	207	95	C ₁₇ H ₁₂ N ₂ SO (292.35)	69.84	4.13	9.58	10.97
	(toluene)			69.70	4.20	9.60	11.10
2d	222	94	C ₁₈ H ₁₂ N ₂ S (288.38)	74.97	4.19	9.71	11.12
	(toluene)			75.10	3.90	9.50	11.30

(a) Compounds **2a-d** prepared by different procedures were found to be identical (mixed mp and ir spectra). Additional data are: **2a**: uv (2-propanol): λ max 285, 375 nm; ¹H-nmr (deuteriochloroform): δ 7.1-8.2 ppm (m); **2b**: uv (2-propanol): λ max 295, 385 nm; ¹H-nmr (deuteriochloroform): δ , 2.33 (s, 3H, CH₃); 7.15-8.2 ppm (m, 9H); **2d**: uv (2-propanol): λ max 310, 400 nm; ¹H-nmr (deuteriochloroform): δ , 7.15-8.12 ppm (m).

recrystallized from DMF as yellow crystals of **1d**, mp 263-265° (yield ca. 67%).

Anal. Calcd. for C₁₈H₁₄N₂O: C, 78.81; H, 5.14; N, 10.21. Found: C, 78.70; H, 5.30; N, 10.20.

2-Styrylthieno[2,3-*b*]quinoxaline **2d** from **1d**.

A solution of **1d** (10 mmoles) and phosphorus pentasulfide (20 mmoles) in pyridine (30 ml) was heated under reflux for 6 hours, diluted with water, the solvents were decanted leaving an oily residue which was extracted with chloroform (100 ml), dried and concentrated to 20 ml then poured over ethanol (40 ml) and cooled. The precipitate was collected and recrystallized from toluene into yellow needles of **2d**, mp 222-223° (yield ca. 31%). Analysis, uv and nmr are given in the Table; ir (potassium bromide) 3150, 3125, 3100, 3020 and 1625 cm⁻¹.

Preparation of Thieno[2,3-*b*]quinoxalines **2a-d** from 3-Acylmethyl-2-oxo-1,2-dihydroquinoxalines **3a-d**.

The appropriate acylmethylquinoxaline **3a-d** (10 mmoles) and phosphorus pentasulfide (10 mmoles) in pyridine (30 ml) were heated under reflux for 6 hours and left at room temperature overnight. The precipitated crystals were collected, washed with water then ethanol and dried. The yield, mp, analysis, uv and nmr are given in the Table.

2-Phenylthieno[2,3-*b*]quinoxaline (**2a**) from the Dibromide **4**.

The dibromide **4** (10 mmoles) and phosphorus pentasulfide (10 mmoles) in pyridine (30 ml) was heated under reflux in several ex-

periments from 1-6 hours. Under all conditions the product **2a** was isolated as above in 8-12% yield.

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