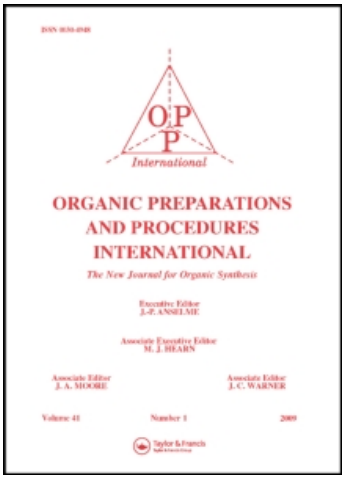

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3- AND 4-(BENZ[a]ANTHRACENYL)PHENYL-2-THIAZ0LINES AND 3- AND 4-(9-ANTHRACENYL)PHENYL-2-THIAZ0LINES. A NEW METHOD OF PREPARATION OF THIAZOLINES

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3- AND 4-(BENZ[a]ANTHRACENYL)PHENYL-2-THIAZOLINES AND 3- AND 4-(9-ANTHRACENYL)PHENYL-2-THIAZOLINES. A NEW METHOD OF PREPARATION OF THIAZOLINES[1]

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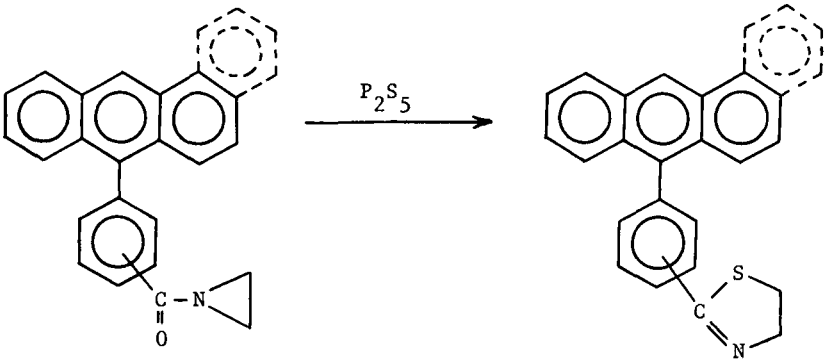
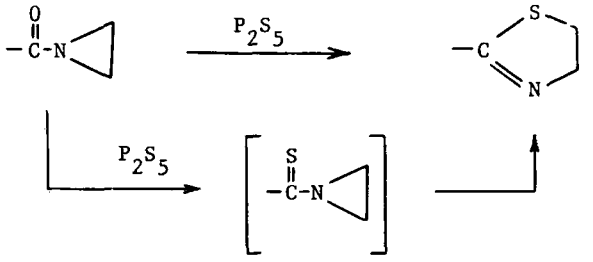
2-Thiazolines have previously been prepared by reaction of N-(2-thiolethyl)amides with phosphorus pentoxide or from N-(2-chloroethyl)amides by reaction with phosphorus pentasulfide.[3] We now report a one step method for the preparation of 2-thiazolines by reacting phosphorus pentasulfide with N-aroylaziridines, a method for preparing 2-thiazolines not previously reported. Since this reaction produces the 2-thiazolines in one step from the intermediate N-aroylaziridines and because of the high yields associated with this reaction, we have found it to be the method of choice for the preparation of 2-thiazolines.

The four thiazolines, 3- and 4-(7-benz[a]anthracenyl)phenyl-2-thiazolines (1 and 2), and 3- and 4-(9-anthracenyl)phenyl-2-thiazolines (3 and 4) were prepared in 70-77% yields by refluxing the four N-benzoylaziridines[4] 5, 6, 7 and 8, with excess phosphorus pentasulfide in toluene for three hours.



5, 6, 7 and 8 — 1, 2, 3 and 4

The reactions occurred rapidly, and the 2-thiazolines were formed from the N-aroylaziridines either by a one-step concerted type mechanism or by the formation of 1-thionylaziridine moieties which rapidly isomerize to the 2-thiazoline moieties under the conditions of the reaction. No evidence for



the presence of the 1-thionylaziridine moiety was obtained when the reaction times were varied from two hours down to one-half hour in one-half hour intervals.

EXPERIMENTAL[5]

2-Thiazolines. General Procedure.- In a 500 ml flask equipped with a mechanical stirrer, a mixture of 0.008 mole of N-benzoylaziridine (5, 6, 7 or 8)[4] and 3.6 g (0.016 mole) of phosphorus pentasulfide in 100 ml of toluene was refluxed for 3 hr. (After 15 min the bottom of the flask was coated with a viscous red oil). The mixture was then cooled to room temperature, the solvent decanted from the red oil and concentrated to give a yellow solid. The solid was dissolved in 100 ml of THF-100 ml of 10% sodium hydroxide, this solution was poured back into the reaction flask with the red oil, and the mixture stirred at room temperature for 1 hr. The THF layer was then separated, the aqueous layer saturated with sodium chloride and extracted twice with 50 ml portions of THF. The THF layers were combined, washed successively with 75 ml water, 75 ml 10% sodium bicarbonate, twice with 75 ml water, and the THF layer was then dried over sodium sulfate. The dried solution was filtered, concentrated, and the resulting pale red oil dissolved in 25 ml of benzene and passed through a silica gel column using 500 ml of benzene as eluant. The eluted benzene was concentrated and the resultant material (solid or oil) was recrystallized.

TABLE I

Elemental Analysis for Polycyclic 2-Thiazolines

C'mpd.	Formula	% Calcd.				% Found			
		C	H	N	S	C	H	N	S
1	$C_{27}H_{19}NS$	83.24	4.93	3.59	8.23	83.37	4.97	3.58	8.07
2	$C_{27}H_{19}NS$	83.24	4.93	3.59	8.23	83.06	4.90	3.56	8.22
3	$C_{23}H_{17}NS$	81.37	5.06	4.13	9.45	81.37	5.09	3.89	9.37
4	$C_{23}H_{17}NS$	81.37	5.06	4.13	9.45	81.25	4.83	4.13	9.26

TABLE II

Physical Data for Polycyclic 2-Thiazolines

C'mpd.	Recrystallization Solvent	Yield (%)	Mp (°C)	Nmr (δ, $CDCl_3$)
1[a]	benzene-ethanol (95%) (7:3)	71	173-174	5.0-4.0 (m, 15, ArH), 1.8 (t, 2, CH_2), 1.4 (t, 2, CH_2).
2[b]	chloroform-ethanol (100%)[c] (7:3)	75	211-213	5.0-4.0 (m, 15, ArH), 2.45 (t, 2, CH_2), 1.85 (t, 2, CH_2).
3[d]	ethanol (100%)	70	126-128	4.6-4.0 (m, 13, ArH), 2.45 (t, 2, CH_2), 1.85 (t, 2, CH_2).
4[e]	chloroform-ethanol (95%) (7:3)	77	215-217	4.6-4.0 (m, 13, ArH), 2.5 (t, 2, CH_2), 1.9 (t, 2, CH_2).

[a]White spherical crystals. [b]White needles. [c]Two recrystallizations were required. [d]Light yellow needles. [e]Yellow crystals.

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2. a) Present address: Northeast Louisiana State College, Department of Chemistry, Monroe, Louisiana 71201; b) Abstracted from the Ph.D. Thesis of M.P.R., Nov. 1969; c)To whom inquiries should be sent.

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5. The nmr data were obtained on a 10% deuterated chloroform solution from a Varian A-60 spectrometer. Line positions are recorded as ppm from internal tetramethylsilane (δ scale). The chromatography columns were 1 1/2 in. in diameter and 11 in. in length, and were wet packed with Baker's Silica Gel, powder, "Suitable for Chromatographic Use," with benzene, and were eluted with benzene. All melting points are corrected.

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