

Table I. Aldoxine Derivatives

Compound	% Yield	M.P., ° C.	% C		% H	
			Found	Calcd.	Found	Calcd.
4-Pyridinecarboxaldehydoxyamidoxime	36	104-105	47.03	47.06	4.73	4.57
2-Pyridinecarboxaldehydoxyamidoxime	73	101-102	46.70	47.06	5.00	4.57
4-Pyridinecarboxaldehydeazidoxime	43	168-169	44.30	44.17	3.28	3.07
2-Pyridinecarboxaldehydeazidoxime	85	123-124	45.78	44.17	3.55	3.07
^a Dichlorosalicylaldehydeazidoxime	60	162-164	34.48	34.01	1.87	1.63
					% Cl ^a	
					28.80	28.74

The pyridinecarboxaldehyde derivatives reported as azidoximes have a weak infrared band at 4.67μ and are believed to be the azides rather than the isomeric tetrazoles (1).

LITERATURE CITED

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Substituted Aziridines: Preparation and Properties

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The synthesis and characterization of a number of previously unreported substituted aziridines is described. Known methods were used for the preparation of these compounds.

A NUMBER OF substituted aziridines were synthesized for use in a study of the ring opening reaction by various active hydrogen compounds. A series of aziridines was desired in which the N and C substituents were varied in order to ascertain the effect of structure upon ring opening. Those aziridines which were synthesized for this study and which are not previously reported in the literature are given in Table I.

In general the method of Bestian was utilized for the preparation of the *N*-acyl, sulfonyl and phosphoryl aziridines (1). Likewise the 1-aziridine-carboxylate ester IV and the nitrophenyl compounds XI and XIII were prepared from the chloroformate and the nitrophenyl chlorides respectively.

EXPERIMENTAL

Reaction of Acid Halides with Aziridines. Reactions were done in benzene or in ether, and triethylamine was used as the acceptor for the hydrogen chloride formed. In general, a solution of the aziridines and triethylamine in benzene was added slowly to a benzene solution of the acid halide. The reaction mixture was cooled externally and the rate of addition was such that the temperature did not exceed 15° . The reaction mixture was stirred at room temperature for 1-2 hours and filtered. The filtrate was washed rapidly with water, dried over magnesium sulfate and the solvent was removed under vacuum. Crude yields were generally above 85 per cent. The products were distilled under vacuum and yields of pure material were generally between 50 and 80 per cent. When the washing step was omitted, products

sometimes polymerized on attempted distillation because of the triethylamine hydrochloride present.

When 2,4-dinitrochlorobenzene and picryl chloride were used, it was necessary to heat the mixture at 70° to effect reaction. The solids were recrystallized from benzene-petroleum ether mixtures.

Reaction of Isocyanates with Aziridines. A benzene solution of the aziridine was added slowly to a cold (15°) solution of the isocyanate in benzene. The reaction mixture was stirred at 25° for 4 hours and the solvent removed under vacuum. The crude product was distilled under vacuum. Yields were somewhat lower (30 to 40 per cent) than for the other compounds (see Table I).

Assay for the aziridine ring was done by the method of Durbetaki with minor changes in solvent to fit the solubility of the particular aziridine (2).

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Table I. Preparation and Properties of Substituted Aziridines

	Yield %	B.P., ° C./Mm.	n_D^{25}	Carbon		Hydrogen		Aziridine (Equiv./100 g.)	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
I. $C_4H_9SO_2N(CH_2)_2$	56	60/0.025	1.4635	44.15	44.44	8.03	8.37	0.61	0.61
II. $C_4H_9CON(CH_2)_2$	55	36/0.02	1.4422	66.14	66.45	10.24	10.65	0.79	0.79
III. $C_4H_9NHCON(CH_2)_2$	30	92/0.08	1.4662	59.16	59.47	9.86	9.88
IV. $C_4H_9OCON(CH_2)_2$	76	52/0.56	1.4316	58.72	59.98	9.15	9.71	0.69	0.65
V. $(C_4H_9)_2PON(CH_2)_2$	44	95/0.01	1.4659	59.09	59.06	10.91	11.21	0.49	0.51
VI. $(C_6H_5)_2PON(CH_2)_2$	53	120-21.5°	...	69.12	68.46	5.80	6.10	0.41	0.41
VII. $(C_6H_5O)_2PON(CH_2)_2$	100 ^{b,c}	...	1.5517	61.09	62.39	5.13	5.50	0.36	0.34
VIII. $C_4H_9SO_2N(CH_2)_2CH_2CH_3$	83	91/0.3	1.4580	47.43	47.37	8.53	8.52	0.56	0.58
IX. $C_4H_9CON(CH_2)_2CH_2CH_3$	60	46/0.08	1.4326	61.12	61.00	9.62	9.76	0.62	0.62
X. $C_4H_9NHCON(CH_2)_2CH_2CH_3$	34	74/0.045	1.4612	61.54	62.02	10.26	10.59	0.64	0.73
XI. $2,4,6-(NO_2)_3C_6H_2-N(CH_2)_2CH_2CH_3$	41	133-35°	...	40.31	40.31	3.01	3.13	0.37	0.39
XII. $C_6H_5SO_2N(CH_2)_2CH_2CH_3$	90 ^b	61.3-63°	...	54.80	54.75	5.62	5.75	0.51	0.52
XIII. $2,4-(NO_2)_2C_6H_3-N(CH_2)_2CH_2CH_3$	95 ^b	96.5-98°	...	48.43	48.26	4.06	4.18	0.45	0.45
XIV. $C_6H_5CON(CH_2)_2CH_2CH_3$	83	56/0.045	1.5446 ^d	74.55	74.75	6.83	7.12	0.62	0.59
XV. $C_6H_5NHCON(CH_2)_2CH_2CH_3$	91	65-66.5°	...	68.16	68.78	6.87	7.10	0.56	0.53
XVI. $(C_4H_9)_2PON(CH_2)_2CH_2CH_3$	28	99/0.03	1.4625 ^d	60.83	60.70	11.06	11.06	0.46	0.46
XVII. $(C_4H_9O)_2PON(CH_2)_2CH_2CH_3$	97	100/0.3	1.4394 ^d	53.01	53.29	9.63	10.24	0.40	0.37
XVIII. $(C_6H_5)_2PON(CH_2)_2CH_2CH_3$	89	102-3.5°	...	70.00	69.92	6.27	6.01	0.39	0.37
XIX. $(C_6H_5O)_2PON(CH_2)_2CH_2CH_3$	67	135/0.05	1.5464 ^d	62.26	62.37	5.57	5.65	0.35	0.34
XX. $C_4H_9CON(CH_2)_2CH_2C_2H_5$	83	70/0.15	1.4401	69.63	69.81	11.04	11.56	0.62	0.60
XXI. $C_4H_9CON(CH_2)_2C(CH_3)_2$	70	60/1	1.4396	69.63	69.62	11.04	11.22	0.64	...
XXII. $C_4H_9CON(CH_2)_2CH_2C_4H_9$	70	60/0.08	1.4445	72.13	72.48	11.48	11.61	0.55	0.55
XXIII. $2-NO_2C_6H_4CON(CH_2)_2CH_2CH_3$	98 ^b	76-78°	...	58.25	58.28	4.85	5.18	0.48	0.48

^aUncorrected melting point. ^bCrude yield. ^cPolymerized on attempted distillation. ^dMeasured at 20°.