TABLE I

POLYMERIZATION OF STYRENE

Catalyst	Run	Catalyst Concentration Moles/liter	Catalyst Concentration Ml.	Catalyst Medium	Polymerization Medium	Polymerization Medium Ml.	Ml. Styrene	Time	Temp.	Crystallinity[a,b]	Inherent Viscosity[a]	Yield G.	Yield %
Triphenylmethylpotassium	1	0.19	30	Hexane	Hexane	200	30	7 hr.	Reflux	High	1.3	1.5	5.5
	2	0.19	30	Hexane	Hexane	200	30	18 hr.	Reflux	High	0.79	21.0	7.7
	3	0.19	30	Hexane	Hexane	200	30	2 wk.	40°	Medium	2.76	15.0	55.5
	4	0.19	5	Hexane	...	...	5	5 days	25°	High	1.61	3.5	78.0
	5	0.53	30	Hexane	...	...	30	5 days	25°	Medium	0.93	24.0	89.0
	6	0.53	60	Hexane	...	...	30	2 days	25°	High	0.96	9.5	35.2
	7	0.19	30	Hexane	Benzene	200	30	8 hr.	Reflux	Nil	0.19	14.0	51.7
	8	0.19	30	Hexane	Benzene	200	30	18 hr.	Reflux	Nil	0.2	26.3	97.5
Diphenylcyclohexylmethylpotassium	9	0.5	30	Hexane	Hexane	200	30	8 days	40°	High	0.68	24.0	88.8
Diphenylmethylpotassium	10	0.8	15	Hexane	Hexane	200	30	3 days	40°	Medium	0.48	22.6	84.0
	11	0.8	30	Hexane	...	...	30	3 days	40°	Low	0.32	27.0	100.0
1,1-Diphenylethylpotassium	12	0.1	30	Hexane	Hexane	100	30	4 days	25°	Nil	1.41	7.0	25.9
Benzylpotassium	13	0.66	5	Toluene	Hexane	200	30	1 day	28°	Nil		19.0	70.0
	14	0.66	10	Toluene	Hexane	200	30	15 min.	25°	Nil	1.0	27.0	100.0
Triphenylmethylsodium	15	0.96	20	Ether	Hexane	200	30	14 days	25°	Nil	0.24	23.0	88.8
Sodium hydride	16	10 g.		...	Hexane	200	30	72 hr.	25°	Nil	0.88	24.3	90.0
Potassium amide	17	0.2		Hexane	Hexane	100	30	24 hr.	25°	Nil	0.29	5.0	18.5
Potassium	18	0.1		Hexane	Hexane	200	30	60 days	25°	Nil	2.45	5.0	18.0

[a] Viscosity and crystallinity measurements were made as described previously.[2] [b] The samples of polymers were crystallized by immersion in boiling heptane for 16 hr.

Pyridinaldazines

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Although 2-pyridinaldazine was described as long ago as 1915,[3] and in spite of a widespread interest in the physiological properties of various pyridine aldehyde derivatives,[4-11] we have been unable to locate any later reference to the azines of the pyridine aldehydes.[12]

As part of a fungicidal study,[13] we have prepared 2-, 3- and 4-pyridinaldazine in alkaline media using the convenient method of *Organic Synthesis* for benzalazine.[14] In each case the yield was excellent (over 90%). Azine formation under these conditions is not conventional and to check the generality of this procedure we have prepared the known 1-naphthaldazine,[15] 2,2′-dichlorobenzalazine,[16] and 3,3′-dinitrobenzalazine[17] in similar yield.

EXPERIMENTAL[18]

2-Pyridinaldazine. 4.6 g. (0.43 mole) of pyridine-2-carboxaldehyde was added dropwise to a solution of 2.4 g. (0.185 mole) of hydrazine sulfate in 180 ml. of water and 25 ml. of concentrated ammonium hydroxide with vigorous stirring at room temperature. Stirring was continued for 3 hr. The yellow product which had separated was recrystallized from aqueous methanol to give 4.1 g. of the azine

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(8) F. E. Anderson (to Nepera Chemical Co.), U. S. Patent **2,782,201** (Feb. 19, 1957).

(9) H. B. König and H. A. Offe (to Fabriken Bayer A.G.), German Patent **1,008,294** (May 16, 1957).

(10) W. Wilde, British Patent **776,118** (June 5, 1957).

(11) F. J. Allan, G. G. Allan, and J. B. Thomson, *J. Org. Chem.*, **23**, 112 (1958).

(12) After this note had been prepared, the Abstracts of Papers of the 132nd Meeting of the American Chemical Society, New York, Sept. 8–13 (1957), appeared which contain an abstract (12N, paragraph 32) concerning complexes of 2-pyridinaldazine with iron (II) and nickel (II) by W. J. Stratton and D. H. Busch.

(13) Details of which we hope to publish later elsewhere.

(14) *Org. Syntheses*, **Coll. Vol. II,** page 395.

(15) M. L. Rousset, *Bull. soc. chim. France* [3], **17**, 304 (1897).

(16) Th. Curtius and H. Pauli, *Ber.*, **34**, 849 (1901).

(17) Th. Curtius and A. Lublin, *Ber.*, **33**, 2462 (1900).

(18) Melting points are uncorrected.

(yield 91%) as long golden yellow blades, m.p. 151–152°. Lit.[3] m.p. 149°.

Anal. Calcd. for $C_{12}H_{10}N_4$: C, 68.55; H, 4.80; N, 26.65. Found: C, 68.63; H, 4.63; N, 26.40.

The following five azines were similarly prepared.

3-Pyridinaldazine, golden yellow prismatic needles (4.1 g., yield 91%) from aqueous methanol, m.p. 148–149°. A specimen on admixture with 2-pyridinaldazine melted at 126–128°.

Anal. Calcd. for $C_{12}H_{10}N_4$: C, 68.55; H, 4.80; N, 26.65. Found: C, 68.45; H, 4.69; N, 26.45.

4-Pyridinaldazine, golden yellow needles (4.15 g., yield 92%) from aqueous methanol, m.p. 192–193°.

Anal. Calcd. for $C_{12}H_{10}N_4$: C, 68.55; H, 4.80; N, 26.65. Found: C, 68.60; H, 4.91; N, 26.35.

1-Naphthaldazine, yellow needles (3 g., yield 90%) from acetone-methanol, m.p. 155–156°. Lit.[15] m.p. 152°.

2,2'-Dichlorobenzalazine, long yellow needles (2.6 g., yield 87%) from methanol, m.p. 150–151°. Lit.[16] m.p. 143–145°.

3,3'-Dinitrobenzalazine, yellow blades (2.9 g., yield 89%) from acetic acid, m.p. 196–197°. Lit.[17] m.p. 194°.

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Preparation of 2-Cyanotetrahydropyran[1]

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Although substituted 2-cyanotetrahydropyrans have been reported in the literature, they have been prepared either by addition of hydrogen cyanide to substituted dihydropyrans[3] or by reaction of appropriate acroleins and vinyl cyanides[4] in reactors at moderate pressure. There appeared to be no simple laboratory procedure for 2-cyanotetrahydropyran which was needed for other research. Accordingly the metathesis of 2-bromotetrahydropyran with metal cyanides has been partly evaluated as a method of synthesis.

2-Bromotetrahydropyran[5] solutions were treated in toluene with cuprous, mercuric, potassium, and silver cyanides in the manner reported for open chain, α-chloro ethers.[6] Maximum conversions were obtained in experiments at 20–30°. None of the desired product was formed when potassium cyanide was used and the yield was only 12% from cuprous cyanide. However, silver and mercuric cyanides gave 27–30% yields of 2-cyanotetrahydropyran.

The compound was characterized by hydrolysis in 63% yield to tetrahydropyran-2-carboxylic acid[7] and by reaction with benzylmagnesium chloride to form 2-(phenylacetyl)tetrahydropyran.

EXPERIMENTAL

2-Cyanotetrahydropyran. A solution of 85 g. (1.0 mole) of 2,3-dihydro-4*H*-pyran in 300 ml. of dry toluene was maintained at −10 to 0° while a stream of hydrogen bromide was added with stirring until 73 g. (0.90 mole) had been absorbed. The 2-bromotetrahydropyran so obtained was used for the preparation of the 2-cyano compound since attempts to isolate the halopyran by vacuum distillation resulted in decomposition.[8]

The toluene solution was added dropwise with stirring to a suspension of 252 g. (1.0 mole) of mercuric cyanide in 200 ml. of dry toluene in an exothermic reaction that was kept at 20–25°. After 2 hr. the mixture was filtered and the filtrate was washed with water, dried, and distilled to give 21–30 g. (21–30%) of 2-cyanotetrahydropyran, b.p. 90–92°/18 mm., n_D^{25} 1.4430.

In a similar way, 40 g. (0.30 mole) of silver cyanide added over 30 min. to 51 g. (0.31 mole) of the bromopyran in 200 ml. of dry toluene at 25–30° gave 9.0 g. (27%) of 2-cyanotetrahydropyran, b.p. 77–83°/16 mm., n_D^{24} 1.4455.

Anal. Calcd. for C_6H_9ON: C, 64.85; H, 8.16; N, 12.60. Found: C, 65.15; H, 8.16; N, 12.63.

Reaction of equimolar amounts of 2-bromotetrahydropyran and cuprous cyanide in a similar manner at 20–25° gave 12% of product, b.p. 75–79°/15 mm., n_D^{25} 1.4422, provided the reaction mixture was washed with 10% ammonium hydroxide before distillation.

2-Tetrahydropyrancarboxylic acid. A mixture of 55.6 g. (0.50 mole) of 2-cyanotetrahydropyran was boiled for 7 hr. with 40.0 g. (1.00 mole) of sodium hydroxide in 200 ml. of water. The alkaline solution was extracted with three 50-ml. portions of ether and exactly neutralized with one equivalent of hydrochloric acid. Ether extraction in a liquid-liquid extractor and distillation of the ether extract gave 41 g. (63%) of 2-tetrahydropyrancarboxylic acid, b.p. 142–145°/20 mm., n_D^{25} 1.4620.

Anal. Calcd. for $C_6H_{10}O_3$: C, 55.37; H, 7.75; neut. equiv., 130. Found: C, 55.50; H, 7.82; neut. equiv. 129.

The acid was further characterized by conversion to phenacyl 2-tetrahydropyrancarboxylate, m.p. 74–76°.

Anal. Calcd. for $C_{14}H_{16}O_4$: C, 67.72; H, 6.50. Found: C, 67.92; H, 6.65.

2-(Phenylacetyl)tetrahydropyran. A solution of 16.8 g. (0.15 mole) of 2-cyanotetrahydropyran in 100 ml. of ether was added dropwise to the Grignard reagent prepared from 7.2 g. (0.30 mole) of magnesium and 38 g. (0.30 mole) of benzyl chloride in 400 ml. of anhydrous ether. One hour after addition was complete, hydrolysis with ice and dilute hydrochloric acid and distillation of the dried ether layer gave 13 g. (42%) of 2-(phenylacetyl)tetrahydropyran, b.p. 155–165°/3–4 mm., n_D^{25} 1.5241. An analytical sample was obtained as a fraction, b.p. 140–141°/3 mm., n_D^{25} 1.5218.

Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.54; H, 8.00.

This product was further characterized as the 2,4-dinitrophenylhydrazone, m.p. 139–142°.

(1) Abstracted from the senior thesis of Kenneth Yorka, De Paul University, 1955. Preliminary experiments were conducted by A. M. Laurinaitis.

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(8) 2-Chlorotetrahydropyran made the same way can be distilled although occasionally rapid decomposition may occur.