Anal.[9] Calcd. for $C_6H_{13}O_2N$; C, 54.94; H, 9.99; N, 10.68. Found: C, 55.00, 55.16; H, 9.81, 9.75; N, 10.56, 10.55.

Acknowledgment. The authors wish to express their appreciation for the financial assistance of the U. S. Atomic Energy Commission and the U. S. Public Health Service.

DEPARTMENT OF ANIMAL HUSBANDRY AND
SCHOOL OF VETERINARY MEDICINE
UNIVERSITY OF CALIFORNIA
DAVIS, CALIF.

(9) Analysis by the College of Chemistry, Univ. of Calif., Berkeley, Calif.

Crystallizable Polystyrene. II. Polymerization of Styrene with Triphenylmethyl Potassium and Related Compounds

JACK L. R. WILLIAMS, THOMAS M. LAAKSO, AND WILLIAM J DULMAGE

Received October 9, 1957

In preceding publications[1,2] the preparation of crystallizable polystyrene with Alfin-type catalysts was reported. The present work deals with the extension of the organometallic catalysts for the polymerization of styrene to include alkali metal derivatives of triphenylmethane and related compounds. Triphenylmethylpotassium, diphenylcyclohexylmethylpotassium, and diphenylmethylpotassium have been found to produce crystallizable polystyrene, having the same range of crystallizability as the polymers prepared using the Alfin catalyst. The highest degree of crystallizability comparable to that produced by the Alfin catalysts was obtained by use of triphenylmethylpotassium. 1,1-Diphenylethylpotassium, benzylpotassium, triphenylmethylsodium, sodium hydride, potassium amide, and potassium gave noncrystallizable polystyrene. Table I contrasts the results obtained when styrene was polymerized using the above catalysts.

In accord with previous observations using the Alfin catalysts,[1,2] polymerizations with triphenylmethylpotassium conducted in a benzene medium, produced high yields of noncrystallizable polystyrene. The heterogeneous isotactic polymerization system was thus converted to a homogeneous nonisotactic polymerization since benzene acted as a solvent for triphenylmethylpotassium. A hexane medium, however, provided the required heterogeneous system, facilitating isotactic polymerization.

(1) J. L. R. Williams, J. VanDenBerghe, W. J. Dulmage, and K. R. Dunham, *J. Am. Chem. Soc.*, **78**, 1260 (1956).
(2) J. L. R. Williams, J. VanDenBerge, K. R. Dunham, and W. J. Dulmage, *J. Am. Chem. Soc.*, **79**, 1716 (1957).

EXPERIMENTAL

Polymerizations. The polymerizations and crystallizations were carried out as previously described.[1]

Catalysts. The catalysts were bottled under dry nitrogen with self-sealing caps and were dispensed by means of hypodermic syringes and needles.

Triphenylmethylpotassium. Triphenylmethylpotassium was prepared according to the method of Levine, Baumgarten, and Hauser.[3] The triphenylmethylpotassium was transferred to a hexane suspension by removal of ether by distillation. The hexane suspension was transferred from the reaction flask by nitrogen pressure and was stored in a bottle capped with a self-sealing cap.

Diphenylmethylpotassium. Diphenylmethylpotassium was prepared in ether solution according to the method of Yost and Hauser.[4] The ether was subsequently replaced with hexane.

Benzylpotassium. Benzylpotassium was prepared from chlorobenzene and potassium in a toluene medium, according to the procedure of Gilman, Pacivitz, and Baine.[5]

Potassium amide. Potassium amide was prepared in liquid ammonia.[3] The liquid ammonia was replaced by hexane.

Diphenylcyclohexylmethylpotassium. Diphenylcyclohexylmethylpotassium was prepared according to the directions of Ziegler and Schnell,[6] with some modifications. The potassium compound was prepared using diphenylcyclohexylchloromethane (m.p. 83–84°) which was prepared from the carbinol *via* acetyl chloride. Diphenylcyclohexylchloromethane was treated with potassium amide, according to the directions used for the preparation of diphenylmethylpotassium.[4] Diphenylcyclohexylacetic acid was obtained in 92% crude yield by the carbonation of diphenylmethylcyclohexylpotassium and melted at 202–203° upon recrystallization from acetic acid. This melting point is in agreement with that obtained by Ziegler and Schnell[6] by carbonation of the diphenylcyclohexylmethylpotassium which they obtained by reaction of potassium on diphenylcyclohexylcarbinol methyl ether. The catalyst was transferred to hexane solution as already described.

1,1-Diphenylethylpotassium. 1,1-Diphenylethylene[7] was reduced to 1,1-diphenylethane with sodium ethylate, according to the directions of Klages.[8] 1,1-Diphenylethylpotassium was prepared by essentially the same method as that used for diphenylmethylpotassium. However, in this case, hexane was used in place of ether since 1,1-diphenylethane was soluble in hexane. 1,1-Diphenylpropionic acid obtained by carbonation of the potassium salt was obtained in 94% crude yield and melted at 171–172° on crystallization from benzene. This melting point is in agreement with that obtained by Ziegler and Schnell[6] on carbonation of 1,1-diphenylethylpotassium which they obtained by the action of potassium on 1,1-diphenylethylcarbinol methyl ether.

Potassium. A 0.1-g. piece of freshly cut potassium was used. The polymer grew outward from the surface of the potassium.

COMMUNICATION NO. 1921
RESEARCH LABORATORIES
EASTMAN KODAK CO.
ROCHESTER 4, N. Y.

(3) R. Levine, E. Baumgarten, and C. R. Hauser, *J. Am. Chem. Soc.*, **66**, 1231 (1944).
(4) R. S. Yost and C. R. Hauser, *J. Am. Chem. Soc.*, **69**, 2325 (1947).
(5) H. Gilman, H. A. Pacivitz, and O. Baine, *J. Am. Chem. Soc.*, **62**, 1518 (1940).
(6) K. Ziegler and B. Schnell, *Ann.*, **437**, 227 (1924).
(7) *Org. Syntheses*, **Coll. Vol. I**, 226 (1948).
(8) A. Klages, *Ber.*, **35**, 2647 (1902).

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

FREDERICK J. ALLAN[1] AND G. GRAHAM ALLAN[2]

Received October 10, 1957

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

(1) To whom enquiries should be addressed.

(2) Present address: Electrochemicals Department, E. I. du Pont de Nemours and Co., Wilmington, Del.

(3) C. Harries and G. H. Lenart, *Ann.*, **410**, 101 (1915).

(4) H. Kewitz, I. B. Wilson, and D. Nachmansohn, *Arch. Biochem. Biophys.*, **64**, 456 (1956) No. 2.

(5) J. Klosa, *Arch. Pharm.*, **289**, 196 (1956) No. 4.

(6) H. H. Fox (to Hoffman-La Roche Ltd.), Canadian Patent **533,124** (Nov. 13, 1956).

(7) S. Archer and M. E. Auerbach (to Sterling Drug Co.), U. S. Patent **2,775,598** (Dec. 25, 1956).

(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.