Phosphomolybdic Acid as a Catalyst for the Bulk Polymerization of Styrene[1]

By Jesse H. Day and Thomas A. Solak

While many catalysts have been used for the bulk polymerization of styrene, there is no mention in the literature of this use of phosphomolybdic acid. A large number of bulk polymerizations carried out at 30, 40 and 50° have shown phosphomolybdic acid to be an effective catalyst. Yields of polymer in excess of 80% were obtained in one hour at 40°. Molecular weights of the polymers were usually in the range 18,000–20,000.

At each temperature there appeared to be an optimum concentration of phosphomolybdic acid, the yield of polymer decreasing when this amount of phosphomolybdic acid was exceeded. Typical data are given in Table I. Each value is the average of 3 or more determinations.

Table I

Per cent. Polystyrene from Styrene Catalyzed by Phosphomolybdic Acid at 40° and at One Hour

% by wt. polymer	% by wt. phosphomolybdic acid
82	0.222
82	.332
86	.445
76	.656

The phosphomolybdic acid was apparently reduced to molybdenum blue, judging by the appearance of a blue solid in the polymer. This solid was easily removed by filtration after dissolving the polymer in benzene. Since phosphoric acid is well known as a catalyst for styrene polymerization, phosphomolybdic acid would be expected to act in the same way. However, it is the belief of the authors that a portion of the polymerization is brought about by the generation of free radicals by the oxidative action of the molybdenum.

The effectiveness of mixtures of phosphomolybdic acid and benzoyl peroxide as catalyst varied markedly with the weight ratio of phosphomolybdic acid to the peroxide. Polymer yields were relatively low, as were molecular weights, except when the ratio was in the range 1 to 1, 2 to 1. The best results were obtained with a ratio of phosphomolybdic acid to peroxide of 1.25.

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[1] This material is taken from a part of a thesis submitted by Thomas A. Solak in partial fullfillment of the requirements for the Master of Science degree at Ohio University, June, 1950.

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Some Reactions of 3-Pyridyllithium[1]

By Herbert E. French[2] and Kern Sears[3]

3-Pyridyllithium is conveniently prepared by the halogen–metal interchange between 3-bromopyridine and *n*-butyllithium,[4,5,6] but the reagent has found little use except in the preparation of nicotinic acid by carbonation,[4] which reaction has been used to prepare nicotinic acid labeled with carbon thirteen and fourteen in the carboxyl group.[7]

This paper describes the use of 3-pyridyllithium in the preparation of some pyridyl carbinols and some pyridyl ketones.

Attempts in the past to prepare 3-pyridylmagnesium bromide have met with failure,[8] but Proost and Wibaut[9] suggested it should be possible to use the entrainment method for its preparation as they did in the preparation of 2-pyridylmagnesium bromide. Low yields of the Grignard reagent were obtained from 3-bromopyridine by this method as was evidenced by its reaction with benzophenone to form a small amount of diphenyl-3-pyridylcarbinol.

Experimental

3-Pyridyllithium was prepared on both a 0.05 mole and a 0.2 mole scale by the method of Gilman and Spatz[4] from *n*-butyllithium prepared according to Stuckwish[10] and 3-bromopyridine prepared by the method of McElvain and Goese.[11]

Diphenyl-3-pyridylcarbinol.—Benzophenone (9.1 g.) in 20 ml. of dry ether was cooled just short of crystallization and was added rapidly to 0.05 mole of 3-pyridyllithium at −35 to −50°. After several hours, hydrochloric acid (30 ml., 10%) was added with cooling. The original tan precipitate dissolved and a precipitate of diphenyl-3-pyridylcarbinol hydrochloride was formed; yield 11.4 g. (76.5%). After recrystallization from very dilute hydrochloric acid with the aid of Norite, the white crystalline hydrochloride charred at 150–155°.

Anal. Calcd. for $C_{18}H_{16}ClNO$: neut. equiv., 297.7. Found: neut. equiv., 298.6.

The hydrochloride was dissolved in 200 ml. of dilute hydrochloric acid and made basic with concentrated ammonium hydroxide. The amorphous precipitate was stirred until solid. On crystallization from alcohol it formed needles melting sharply at 115°.

Anal. Calcd. for $C_{18}H_{15}NO$: C, 82.74; H, 5.97. Found: C, 82.45; H, 5.90.

Diphenyl-3-pyridylmethane.—Tschitschibabin's method of preparation of the two other isomeric diphenylpyridylmethanes[12] was used with slight modification. Diphenyl-3-pyridylcarbinol (4.45 g., 0.017 mole) in 10 ml. of glacial acetic acid and 3 ml. of concentrated hydrochloric acid was treated with 40% hydriodic acid (10 ml., 0.048 mole), boiled 2 minutes, and poured into 30 ml. of water containing 4 g. of sodium bisulfite. The mixture, made basic with 40% sodium hydroxide, was stirred until the oily layer was light yellow. The oil formed a waxy solid (4.35 g., theoretical yield, m.p. 70–75°) which was fractionally crystallized from petroleum ether "B" by slow evaporation. The yield was 50%, m.p. 76–77.5°.

Anal. Calcd. for $C_{18}H_{15}N$: C, 88.13; H, 6.16. Found: C, 87.81; H, 6.22.

Diethyl-3-pyridylcarbinol.—Diethyl ketone (4.3 g.) in 20 ml. of dry ether was cooled to −30° and added quickly to 0.05 mole of 3-pyridyllithium. The mixture was treated with 10% hydrochloric acid and the two layers separated. The acid layer was made basic with ammonium hydroxide and extracted with ether. The ether extract was dried over sodium sulfate and distilled; diethyl-3-pyridylcarbinol distilled at 156–157.5° (15 mm.). Sobecki reported the boiling point of the same compound prepared by another method as 152.5° (24 mm.).[13] The yield was 4.3 g. (52.1%).

The picrate was prepared in and recrystallized from alcohol; m.p. 112–113° as recorded in the literature.[13]

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[1] From the thesis submitted by Mr. Sears in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Missouri.

[2] Deceased.

[3] Harding College, Searcy, Arkansas.

[4] Gilman and Spatz, This Journal, **62**, 446 (1940).

[5] Spatz, *Iowa State College J. of Sci.*, **17**, 129 (1942).

[6] Spatz and Gilman, *Proc. Iowa Acad. of Sci.*, **47**, 262 (1940).

[7] Murray, Forman and Langham, *Science*, **106**, 277 (1947).

[8] Harris, *Iowa State College J. of Sci.*, **6**, 425 (1932).

[9] Proost and Wibaut, *Rec. trav. chim.*, **59**, 973 (1940).

[10] Stuckwish, *Iowa State College J. of Sci.*, **18**, 92 (1943).

[11] McElvain and Goese, This Journal, **65**, 2231 (1943).

[12] Tschitschibabin and Benewolenskaja, *Ber.*, **61**, 551 (1929).

[13] Sobecki, *Ber.*, **41**, 4103 (1908).

TABLE I

3-PYRIDYL ARYL KETONES

3-Pyridyl ketones	Yields, g.	Yields, %	M.p., °C.	B.p.,[g] °C.	Analyses, % Calcd. C	Analyses, % Calcd. H	Analyses, % Found C	Analyses, % Found H
Phenyl	22.3	60.9	32–34[a,b]	139–142				
m-Tolyl	4.1	41.9	37–38[c]	148–150	79.17	5.62	79.01	5.77
p-Tolyl	5.1	52.4	78.0–78.5[c,d]	175–176				
p-Chlorophenyl	1.7	15.6	88–89[e]	150–153	66.12	3.71	66.19	3.95
2-Naphthyl	3.8	32.5	77.8[e,f]	197–200	82.40	4.72	82.91	4.85

[a] Unrecrystallized. [b] The m.p. of 3-pyridyl phenyl ketone has been given as 39°.[14] [c] From benzene–petroleum ether "A." [d] This agrees with the literature value.[15] [e] From alcohol. [f] "3-Pyridyl naphthyl ketone" has been described as a brown tar.[14] [g] The boiling points were determined at 2 mm. pressure except for 3-pyridyl *p*-tolyl ketone which was determined at 6 mm.

1,3-Diphenyl-3-(3-pyridyl)-propanone-1.—Benzalacetophenone (10.4 g.) was treated with 3-pyridyllithium in the usual way, and the mixture decomposed with dilute hydrochloric acid, which produced a brown tar. The tar and the acid layer were both made basic with ammonium hydroxide and extracted quickly with ether. The ether extract started depositing a light yellow solid at once (2 g., 10%). The solid was white when crystallized from alcohol and melted at 190.5–191.5°. Analysis in the Grignard machine seemed to indicate one carbonyl per mole of compound, so tentatively it is assumed that 1,4-addition had occurred.

Anal. Calcd. for $C_{20}H_{17}NO$: carbonyl, 9.76. Found: carbonyl, 9.76.

The compound crystallized from benzene with one molecule of benzene of crystallization; m.p. (in a preheated block) 220–221°.

Anal. Calcd. for $C_{20}H_{17}NO \cdot C_6H_6$: C, 85.43; H, 6.38. Found: C, 85.50, 85.53; H, 6.23, 6.35.

No picrate nor chloroplatinate could be prepared from the above compound.

1,3-Diphenyl-1-(3-pyridyl)-propanol-1.—Benzylacetophenone (10.5 g.) was added as a solid to an equivalent of 3-pyridyllithium. The product was worked up as for diphenylpyridylcarbinol except that the hydrochloride could not be recrystallized. The free base crystallized easily from benzene; m.p. 118.5–119°. There was an indefinite second m.p. at about 100° which was observed in a preheated block. The yield was 7.6 g. (52.4%).

Anal. Calcd. for $C_{20}H_{19}NO$: C, 82.96; H, 6.63. Found: C, 83.43, 83.45, 83.49; H, 6.85, 6.72, 6.77.

The chloroplatinate was prepared in and recrystallized from a mixture of two parts alcohol and one part 6 *N* hydrochloric acid. The salt formed light orange needles; m.p. 211–212° (dec.).

Anal. Calcd. for $C_{40}H_{40}Cl_6N_2O_2Pt$: C, 48.57; H, 4.09; Pt, 19.74. Found: C, 48.92; H, 4.32; Pt, 19.76.

1-(3-Pyridyl)-cyclohexanol.—Cyclohexanone (19.6, 0.2 mole) in 50 ml. of ether was added to an equivalent of pyridyllithium at −40° in the usual way. The mixture was decomposed with 10% hydrochloric acid. The acid layer was removed and made basic with ammonium hydroxide and the product extracted with ether. A tan solid (24.5 g., 69.2%) was left after evaporation of the ether. This was decolorized in alcohol with Norite but was recrystallized from a benzene–petroleum ether "A" mixture with about 50% loss. The compound formed pure white plates melting at 89–90°.

Anal. Calcd. for $C_{11}H_{15}NO$: C, 74.55; H, 8.63. Found: C, 74.61, 74.54; H, 8.64, 8.67.

The picrate was prepared in benzene and recrystallized from alcohol. It formed fine dark yellow needles melting at 166–167°.

3-Pyridyl Ketones.—The ketones containing the pyridyl radical were prepared by the following procedure. The aromatic nitrile (0.05 mole, except for benzonitrile which was used in runs four times as large) dissolved in dry ether (20 ml., or more when the solubility of the nitrile was low) was cooled to −35°, when crystallization could be avoided, and was added rapidly to an equivalent of 3-pyridyllithium at −35 to −50°. The orange reaction mixture was treated with 10% hydrochloric acid (30 ml.) and the two layers separated. The ether layer was extracted with 25% hydrochloric acid (25 ml.). The combined acid layers were boiled, cooled and made basic with 40% sodium hydroxide. The product was extracted with ether, dried and distilled. The physical constants and analyses of the ketones are listed in Table I.

3-Pyridylmagnesium Bromide.—3-Bromopyridine (5 ml.) was converted to the Grignard reagent by the entrainment method using 4 ml. of ethyl bromide as an auxiliary halide. After spontaneous refluxing had stopped, the mixture was warmed, allowed to stand, and treated with benzophenone (15 g.). The product was worked up by the usual procedure and yielded a small amount of diphenyl-3-pyridylcarbinol, identical in m.p. and mixed m.p. with the same carbinol prepared above.

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[14] Wolfenstein and Hartwich, *Ber.*, **48**, 2043 (1915).

[15] Just, *Monatsh.*, **18**, 452 (1897).

Aromatic Reductive Debromination with a Glycol-alkali Mixture

BY HENRY GILMAN, DONALD L. ESMAY AND ROBERT K. INGHAM

Hydroxy-substituted dibenzofurans have been prepared from the corresponding bromo- derivatives by oxidation of the Grignard compounds[1] and by alkali fusion in the presence of a catalyst in an autoclave.[2,3] The first method gives low yields, and the second procedure, although it gives improved yields, is inconvenient. An experiment was conducted to determine if high temperatures and a catalyst were sufficient to bring about the latter reaction through the use of a high boiling solvent such as triethylene glycol, thus obviating the necessity of a bomb. A related procedure was carried out by Thirtle[4] in a reaction between 2-bromopyridine and potassium hydrosulfide. It was found, however, that the bromine atom was replaced by a hydrogen atom rather than by an hydroxyl group. The reductive debromination was found to take place with 2-bromodibenzofuran, 2,8-dibromodibenzofuran, and 2,8-dibromodibenzothiophene. The isolation of 2-bromodibenzofuran when diethylene glycol was used as the reaction medium for 2,8-dibromodibenzofuran indicates that the reaction proceeds stepwise. When ethanol was employed as the solvent, no reductive debromination occurred un-

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[1] Gilman, Bywater and Parker, THIS JOURNAL, **57**, 885 (1935).

[2] Gilman and Van Ess, *ibid.*, **61**, 1365 (1939).

[3] I. G. Farbenind. A.-G., German Patent 606,350 [*C. A.*, **29**, 1434 (1935)].

[4] Thirtle, THIS JOURNAL, **68**, 342 (1946).