Anal. Calcd. for $C_7H_5O_2NFBr$: C, 35.9; H, 2.1; N, 6.0. Found: C, 35.9; H, 2.1; N, 6.0.

Permanganate oxidation of the product gave in 67% yield a single acid whose m.p. (137.2–138.0°) was not depressed by admixture with an authentic sample of 2-fluoro-5-nitrobenzoic acid, prepared by the method of Slothouwer.[4]

2-Diethylaminomethyl-4-nitrofluorobenzene Hydrobromide.—In a typical run made according to the general directions of Burckhalter, *et al.*,[1] for the preparation of α-alkylamino-4-nitro-*o*-cresols from α-chloro-4-nitro-*o*-cresol, 22.0 g. (0.094 mole) of 2-fluoro-5-nitrobenzyl bromide and 14.6 (0.2 mole) of diethylamine gave 19.0 g. (66%) of pure product, m.p. 162° (dec.).

Anal. Calcd. for $C_{11}H_{15}N_2O_2F \cdot HBr$: C, 43.0; H, 5.2; N, 9.1. Found: C, 42.9; H, 5.2; N, 9.3.

2-Diethylaminomethyl-4-(7-chloro-4-quinolyl)-aminofluorobenzene Dihydrobromide.—A suspension of 18.0 g. (0.059 mole) of 2-diethylaminomethyl-4-nitrofluorobenzene hydrobromide in 50 ml. of absolute ethanol was reduced at a hydrogen pressure of 40 lb. in the presence of platinum oxide catalyst. The resulting mixture was filtered and the filtrate treated with a slight excess of alcoholic hydrogen bromide. Then 11.9 g. (0.06 mole) of 4,7-dichloroquinoline was added and the mixture heated on a steam-bath for 2 hours. The mixture was cooled and ether added until precipitation of the crude product was complete. Recrystallized from methanol, the pure 2-diethylaminomethyl-4-(7-chloro-4-quinolyl)-aminofluorobenzene dihydrobromide, m.p. 203.8° (dec.), weighed 19.0 g. (60%).

Anal. Calcd. for $C_{20}H_{21}N_3ClF \cdot 2HBr$: C, 46.2; H, 4.4; N, 8.1. Found: C, 46.1; H, 4.7; N, 7.9.

Acknowledgment.—These studies were aided by a contract between the Office of Naval Research, Department of the Navy, and the University of Kansas.

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[4] J. H. Slothouwer, *Rec. trav. chim.*, **33**, 324 (1914).

DEPARTMENT OF CHEMISTRY
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LAWRENCE, KANSAS

RECEIVED AUGUST 21, 1950

New Derivative of Dinaphthylethane

BY M. SZWARC AND A. SHAW

Previous studies of the pyrolysis of toluene and its derivatives[1,2,3,4] have demonstrated that the initial decomposition of these compounds is represented by the equation

$$C_6H_5CH_3 \longrightarrow C_6H_5CH_2 + H\cdot$$

Benzyl radicals (or their derivatives) dimerize, and this process accounts for the presence of dibenzyl (or its derivatives) among the products of pyrolysis. We have found recently[5] that the pyrolysis of 1- and 2-methylnaphthalenes takes place according to the same scheme to yield 1,2-bis-(1-naphthyl)-ethane, m.p. 162–163°, reported[6] 162–163°, picrate m.p. 204–205°, reported[7] 205°, and 1,2-bis-(2-naphthyl)-ethane, m.p. 182–184°, reported[8] 182–183°, picrate m.p. 198°, reported[8] 198°, respectively.

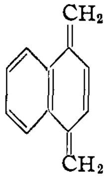
We find that the same scheme applies to the pyrolysis of 2,6-dimethylnaphthalene. The dimer was identified as 1,2-bis-(6-methyl-2-naphthyl)-ethane, m.p. 213–215°.

Anal. Calcd. for $C_{24}H_{22}$: C, 92.9; H, 7.1; mol. wt., 310. Found: C, 92.4; H, 6.95; mol. wt., 304.

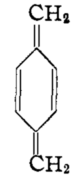
Its picrate melts at 210°.

Anal. Calcd. for $C_{30}H_{25}O_7N_3$: N, 7.9. Found: N, 8.1.

It is interesting to note that the pyrolysis of 1,4-dimethylnaphthalene results in the formation of quinono-hydrocarbon (A),[9] which is a homolog of a similar compound (B) produced in the pyrolysis of *p*-xylene.[10]



A



B

One could expect that a similar compound would be produced in the pyrolysis of 2,6-dimethylnaphthalene, but that is not the case.

These pyrolyses have been carried out in a flow system essentially similar to that described previously by one of us.[1] The decomposition was investigated at temperatures of about 800°, pressures of the order of 5–10 mm., and times of contact of the order 0.5–1 sec. Due to the low volatility of these compounds it was necessary to heat electrically the tubes and taps composing this section of the apparatus, through which the compounds investigated were introduced into the reaction vessel. The dimers formed in the pyrolysis crystallized on the walls of a tube leading from the reaction vessel. This tube was maintained at a temperature of about 50° which was sufficiently high to prevent crystallization of the undecomposed methylnaphthalenes present in the gas phase. The dimers collected in the tube were subsequently dissolved in the appropriate solvents and purified by crystallization.

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[1] M. Szwarc, *Nature*, **160**, 403 (1947); *J. Chem. Phys.*, **16**, 128 (1948).

[2] M. Szwarc and J. S. Roberts, *ibid.*, **16**, 609 (1948).

[3] J. S. Roberts and M. Szwarc, *ibid.*, **16**, 981 (1948).

[4] M. Szwarc and J. S. Roberts, THIS JOURNAL, **70**, 2831 (1948).

[5] A. Shaw and M. Szwarc, unpublished results.

[6] P. Schorigin, *Ber.*, **59**, 2512 (1926).

[7] W. Friedmann, *ibid.*, **49**, 281 (1916).

[8] W. Friedmann, *ibid.*, **49**, 1354 (1916).

[9] M. Szwarc, *J. Polymer Sci.*, in press; summary in *J. Polymer Sci.*, June, 1950.

[10] M. Szwarc, Discussions Faraday Soc., No. 2, 46, 1947.

CHEMISTRY DEPARTMENT
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RECEIVED SEPTEMBER 18, 1950

Preparation and Purification of Potassium Ferrate. VI

BY G. W. THOMPSON,[1] L. T. OCKERMAN[2] AND J. M. SCHREYER

Numerous investigators[3,4,5] have reported wet methods for the preparation of solutions and impure crystalline samples of potassium ferrate(VI).

A procedure for the preparation of pure potassium ferrate(VI) has been reported by Schreyer.[6]

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[1] Richfield Oil Corp., Bakersfield Laboratory, Bakersfield, Calif.

[2] Deceased April 11, 1950.

[3] E. F. Fremy, *Compt. rend.*, **12**, 23 (1841); **14**, 424 (1842).

[4] L. Moser, *J. prakt. Chem.*, [21] **56**, 425 (1897).

[5] L. Losana, *Gazz. chim. ital.*, **55**, 468 (1925).

[6] J. M. Schreyer, Thesis, "Higher Valence Compounds of Iron," Oregon State College, Corvallis, Oregon, 1948.

This procedure involved the oxidation of hydrous ferric oxide suspended in 8 *M* potassium hydroxide by bubbling chlorine gas through the solution which was maintained at a temperature of 50–55°. This procedure was laborious and gave low yields.

Hrostowski and Scott[7] reported the preparation of 96.9% potassium ferrate by an analogous method, except that they utilized sodium hypochlorite as an oxidizing agent and precipitated potassium ferrate from the solution of sodium ferrate by addition of solid potassium hydroxide until saturation was attained. Yields were reported from 10 to 15% of the theoretical.

Experimental

Preparation of Potassium Ferrate.—Preparations of samples of potassium ferrate were made using the methods of Schreyer[6] and Hrostowski and Scott.[7]

Additional preparations of potassium ferrate were made by the hypochlorite method except that hydrous ferric oxide was formed by the addition of ferric nitrate, rather than ferric chloride, to concentrated sodium hypochlorite solutions. The oxidation took place almost immediately at room temperature in contrast to the 50–55° temperature necessary with the ferric chloride–sodium hypochlorite method. Although no purification of the samples was carried out, yields were determined analytically by the arsenite–bromate method.[8] The results are shown in Table I.

TABLE I

COMPARISONS OF YIELDS OF POTASSIUM FERRATE BY DIFFERENT METHODS OF SYNTHESIS

Salts of iron	Oxidizing agent	Yield in grams	Purity, %	Theoretical yield, %
$FeCl_3 \cdot 6H_2O$[a]	Cl_2	8.36	15.46	7.0
25 g.		5.27	16.81	4.8
		10.38	14.72	8.3
$FeCl_3 \cdot 6H_2O$[b]	NaOCl	6.90	67.21	25.3
25 g.		10.74	52.46	30.7
		9.64	74.71	39.3
$Fe(NO_3)_3 \cdot 9H_2O$	NaOCl	12.13	51.20	50.6
25 g.		10.43	63.40	53.9

[a] Method of Schreyer. [b] Method of Hrostowski and Scott.

Purification.—Previous methods of purification removed chloride impurities by taking advantage of the fact that a portion of this impurity remained in the saturated potassium hydroxide solution from which the potassium ferrate had been precipitated. Brönsted's data[9] show a pronounced increase in the solubility of both potassium chloride and potassium nitrate as the potassium hydroxide molarity is decreased. The solubility at 20° of potassium ferrate in various concentrations of potassium hydroxide was determined by the recommended total iron method.[8] An impure K_2FeO_4 sample was selected in order to simulate the conditions encountered during actual purifications by means of the reprecipitation method. The chloride ion present in the solutions of known potassium hydroxide concentrations saturated with potassium ferrate was determined by the Mohr method.[10] The concentration of potassium ferrate in these solutions was determined by the total iron method.[8] Results are shown in Table II. These data indicate that the precipitation of the bulk of the dissolved potassium ferrate would be accomplished by making the solution 11 *M* in potassium hydroxide, but the major part of the potassium chloride impurity as well as the potassium nitrate would still be in solution. Brönsted[9] reports that the solubility of potassium chloride in 10.95 *M* potassium hydroxide is 20.35 g./l.

TABLE II

CONCENTRATION OF POTASSIUM CHLORIDE AND POTASSIUM FERRATE IN AQUEOUS SOLUTIONS OF POTASSIUM HYDROXIDE

Sample number	KOH, m./l.	KCl, g./l.	Saturated K_2FeO_4, g./l.
1	6.15	23.8	13.35
2	6.86	23.6	11.80
3	7.60	23.3	8.81
4	8.22	22.9	7.52
5	9.41	21.6	5.06
6	10.92	20.4	3.02
7	11.55	17.2	2.66
8	13.03	12.4	2.09
9	14.58	..	1.80

Combined Preparation and Purification of Potassium Ferrate.—A combined preparation and purification process is advantageous in that mechanical losses are minimized and less time is consumed in drying and washing the reaction products. The following procedure is recommended.

Thirty grams of sodium hydroxide is dissolved in 75 ml. of water and the cooled solution is chlorinated with vigorous stirring while maintaining the temperature under 20°. Chlorination is continued until the weight of the solution has increased by 20 g. Seventy grams of solid sodium hydroxide is added slowly with stirring, permitting the temperature to rise as high as 25–30° to aid solution of the sodium hydroxide; finally, the mixture is cooled to 20°. The precipitated sodium chloride is removed by filtration through a fritted glass filter.

To the alkaline hypochlorite solution at 25–30°, 25 g. of ferric nitrate is added slowly. The temperature is maintained at 30° while saturating with sodium hydroxide. The mixture is then filtered with suction through a coarse fritted glass filter.

The filtrate of sodium ferrate is transferred to a 250-ml. beaker placed in a 20° water-bath and 100 ml. of saturated potassium hydroxide solution is added with stirring. Stirring is continued for 5 minutes, finally, filtering through a fritted glass filter of medium porosity. The filtrate is discarded.

The precipitate is leached on the filter with 4 or 5 successive 10-ml. portions of 3 *M* potassium hydroxide solutions. The liquid is drawn each time through the filter into 50 ml. of chilled saturated potassium hydroxide solution. The residue remaining on the filter has a light gray cast and is discarded.

The filtrate is transferred to a 250-ml. beaker and 50 ml. of chilled, saturated potassium hydroxide solution is added. Any solid potassium ferrate remaining in the filter flask is washed out with a few ml. of saurated potassium hydroxide solution. The final solution is approximately 11 *M* in potassium hydroxide. The solution is stirred for 5 minutes and is filtered through fritted glass of medium porosity.

The precipitate remaining on the filter is washed with 10 ml. of benzene. After three to five 20-ml. portions of 95% ethyl alcohol are drawn through the filter, the precipitate is transferred to a beaker containing 1000 ml. of 95% ethyl alcohol and stirred for 20 minutes. This washing is repeated three times. The precipitate is removed by filtration and dried by drawing 50 ml. of ethyl ether through the filter. During this drying operation, a calcium chloride tube is used to protect the potassium ferrate from the moisture of the atmosphere. Suction is continued for 20 minutes and final drying is accomplished by the use of a vacuum desiccator. Dry potassium ferrate is stable and should be kept in a desiccator.

Numerous samples were prepared by this method. Results of analysis, using the chromite method[11] gave yields of 44.1 to 76.4% of theory, and purities from 92.34 to 96.3% K_2FeO_4. These maximum yields were obtained when using centrifugation instead of filtration during the preparation.

If it is desirable to obtain a sample of greater purity than

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[7] Hrostowski and Scott, *J. Chem. Physics*, **18**, 105 (1950).

[8] Schreyer, Ockerman and Thompson, *Anal. Chem.*, **22**, 691 (1950).

[9] Brönsted, THIS JOURNAL, **42**, 1448-1454 (1920).

[10] Pierce and Haenisch, "Quantitative Analysis," John Wiley and Sons, Inc., New York, N. Y., 1940, p. 258.

[11] Schreyer, Ockerman and Thompson, *Anal. Chem.*, in publication.

those prepared by the procedure recommended above, the sample is subjected to an additional reprecipitation from 6 *M* potassium hydroxide solution. In this Laboratory, such additional purifications of samples obtained by the recommended procedure gave products ranging in purity from 98.5 to 99% potassium ferrate, as analyzed by the chromite method,[11] although a great reduction in the quantity of potassium ferrate resulted.

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RECEIVED AUGUST 9, 1950

Phosphorus Oxychloride in the Preparation of Ketimines

BY ARTHUR W. WESTON AND R. J. MICHAELS, JR.

It has been found that phosphorus oxychloride is an excellent agent for promoting the formation of anils derived from 2-thienyl aryl and 2-thienyl alkyl ketones. Recently Hartough[1] reported that propyl 2-thienyl ketone yielded 28% of the Schiff base when condensed with aniline in the presence of iodine. However, by adding a small amount of phosphorus oxychloride to a refluxing solution of the reactants we were able to isolate 88% of the desired condensation product. Similarly, an improved yield of N-phenyl methyl 2-thienyl ketimine[1] resulted when phosphorus oxychloride was used. High yields were obtained with the other thienyl ketones employed.

The use of phosphorus oxychloride is particularly indicated for the 2-acylthiophenes which form insoluble complexes[1] with zinc chloride, a commonly employed condensing agent, and for other compounds that are sensitive to zinc chloride.

In addition, it was observed that benzophenone, which does not condense directly with aniline, readily produced the anil when these reactants were treated with phosphorus oxychloride. On the other hand, the condensation of acetophenone with aniline was complicated by the formation of both acetophenone anil and dypnone anil. The latter product is to be expected in view of the tendency of acetophenone to undergo molecular condensation in the presence of acid. It is interesting to note, however, that the isostere, methyl 2-thienyl ketone, yielded little or no self condensation product under the same reaction conditions.

The addition of 0.5 cc.[2] of phosphorus oxychloride to a mixture of 0.25 mole of ketone and 0.3 mole of aniline was sufficient to ensure complete condensation, except in the case of phenyl 2-thienyl ketone. In this instance it was necessary to use twice the quantity of catalyst in order to obtain a good yield of N-phenyl phenyl 2-thienyl ketimine. In all condensations a slight excess of aniline was employed to compensate for the material removed by salt formation.

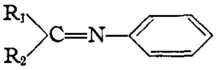
If the phosphorus oxychloride added at the start of the reaction proved to be inadequate, more could be added later without impairing the yield, as illustrated in the experimental section. An amount of concentrated hydrochloric acid, sirupy phosphoric acid, or a mixture of the two equivalent to the quantity of phosphorus oxychloride employed gave inferior results in the preparation of N-phenyl methyl 2-thienyl ketimine. With benzophenone and aniline, comparable results were realized when the phosphorus oxychloride was replaced by phosphorus oxybromide, phosphorus trichloride or phosphorus pentachloride. Phosphorus pentoxide was not effective, indicating that a halogen-containing catalyst is probably required.

Experimental

N-Phenyl Ethyl 2-Thienyl Ketimine.—A mixture of 27.9 g. (0.30 mole) of aniline, 35 g. (0.25 mole) of ethyl 2-thienyl ketone[3] and 0.5 cc. (0.0055 mole) of phosphorus oxychloride in 150 cc. of toluene was refluxed overnight in a flask equipped with a reflux condenser and a conventional water separator. At the end of this time, the theoretical amount (4.5 cc.) of water had been collected. After the reaction mixture was filtered to remove the aniline salt which had separated, the toluene was removed under reduced pressure and the residue distilled. There was obtained 10.2 g. of forerun followed by 40.4 g. (75%) of product, b.p. 133° at 1 mm., n^{24}D 1.6347.

N-Phenyl Phenyl 2-Thienyl Ketimine.—By refluxing a mixture of 47 g. (0.25 mole) of phenyl 2-thienyl ketone,[4] 27.9 g. (0.30 mole) of aniline and 0.5 cc. (0.0055 mole) of phosphorus oxychloride for 17 hours, 2 cc. of water was liberated. After the addition of another 0.5 cc. (0.0055 mole) of phosphorus oxychloride along with 4.7 g. (0.05 mole) of aniline to combine with the acid subsequently formed, the mixture was again refluxed overnight. The theoretical amount of water (4.5 cc.) had then been liber-

TABLE I

N-PHENYL KETIMINES 

R_1	R_2	B.p. °C.	Mm.	M.p., °C.	Yield,[g] %	Formula	Nitrogen, %[h] Calcd.	Found
2-Thienyl	Methyl	137–138	1.5	69–70[a,b]	68	$C_{12}H_{11}NS$	6.96	6.87
2-Thienyl	Ethyl	130–133	1.0	[c]	75	$C_{13}H_{13}NS$	6.51	6.42
2-Thienyl	*n*-Propyl	130–132	0.8	[d]	88	$C_{14}H_{15}NS$	6.11	6.04
2-Thienyl	Phenyl	158–162	1.7	123–124[b]	80	$C_{17}H_{13}NS$	5.32	5.35
Phenyl	Phenyl	160–163	0.8	113–114[e,f]	86	$C_{19}H_{15}N$	..	..

[a] Reported (ref. 1) m.p. 69–70°. [b] Crystallized from absolute alcohol. [c] n^{24}D 1.6347. [d] n^{25}D 1.6199; reported (ref. 1) b.p. 128–130 at 1 mm. [e] C. M. Rosser and J. J. Ritter, THIS JOURNAL, 59, 2179 (1937), report m.p. 113–114°. [f] Crystallized from acetone. [g] In most instances, some of the original ketone was recovered so that the yields are actually higher than reported. [h] We are indebted to Mr. E. F. Shelberg and members of the Microanalytical Department for these microanalyses.

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[1] H. D. Hartough, THIS JOURNAL, 70, 1282 (1948).

[2] The importance of this quantity was not determined but it was noted that the use of appreciably smaller amounts of the agent lowered the yield considerably.

[3] H. D. Hartough and A. I. Kosak, THIS JOURNAL, 69, 3099 (1947).

[4] The phenyl 2-thienyl ketone and methyl 2-thienyl ketone were furnished through the courtesy of Dr. G. A. Harrington of the Socony-Vacuum Oil Company.