and, conversely, similarly to solvent-wash all the di- form away from the mono- form, leaving the latter in a water solution. In the case of the octyl phosphoric acids it was found that the substitution of diethylene glycol for the water phase eliminated difficulty with emulsions and gave distribution coefficients of the right order of magnitude to give satisfactory separation of the two forms.

The distribution of the acids was followed by titrating aliquots of the phases potentiometrically with standardized base, using a Beckman Type G glass electrode *p*H meter. It was assumed throughout that no free phosphoric acid was present, so that the difference in titer between the two breaks of the curve could be taken to represent the amount of H_2RPO_4 present, and the difference between this quantity and the titer to the first break to represent the HR_2PO_4. Using this method, the values shown in Table I were obtained for the acid strengths of the commercial mixtures as purchased. The distribution coefficients of the acids between the various pairs of immiscible phases were then similarly obtained, and these are summarized in Table II.

TABLE I

COMPOSITION OF COMMERCIAL ALKYL PHOSPHORIC ACIDS

Phosphoric acid	Source	Concentrations, *M* H_2RPO_4	 HR_2PO_4
Ethyl-	Eastman	4.66	4.36
n-Propyl-	Eastman	4.36	3.15
n-Butyl-	Eastman	3.28	2.48
Isobutyl-	Monsanto	3.57	2.56
n-Amyl-	Monsanto	3.48	1.81
n-Octyl-	Monsanto	2.01	1.75

TABLE II

DISTRIBUTION OF ACIDS BETWEEN IMMISCIBLE PHASES

Phosphoric acid	Distribution coefficient (*E*) into solvents from water		
	Solvent	$E_{H_2RPO_4}$	$E_{HR_2PO_4}$
Ethyl-	*n*-Primary amyl alcohol	0.69	1.7
	Dibutyl carbitol	.14	0.51
n-Propyl-	*n*-Primary amyl alcohol	.86	5.4
	Dibutyl carbitol	1.4	1.2
n-Butyl-	*n*-Primary amyl alcohol	2.9	>1000?
	Dibutyl carbitol	2.1	39
	Dibutyl ether	0.66	15
Isobutyl-	Dibutyl ether	.54	11
n-Amyl-	Dibutyl ether	.72	6.2
n-Octyl-	Diethyl ether	42	~760
	Methyl isobutyl ketone	28	~106
n-Octyl-	Dibutyl ether	0.44[a]	7.0[a]

[a] Out of diethylene glycol rather than water.

For batch type washing, the most satisfactory separation is obtained when the HR_2PO_4 distribution coefficient is greater than 5, coupled with a corresponding *E* value of less than 1 for the H_2RPO_4 form. The use of counter-current column extraction techniques, however, should make separations feasible even though the two *E* values differ by a much smaller factor.

Using this technique, completely separated solutions of diethylphosphoric acid in *n*-amyl alcohol, dipropylphosphoric acid in isopropyl and dibutyl ethers, dibutylphosphoric acid in *n*-amyl alcohol and in dibutyl ether, diisobutylphosphoric acid in dibutyl ether, diamylphosphoric acid in dibutyl ether, dioctylphosphoric acid in dibutyl ether and monobutylphosphoric acid in water have all been prepared.

RADIATION LABORATORY
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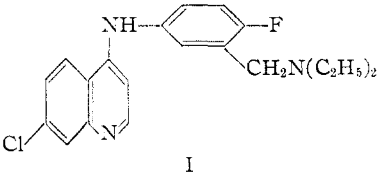
Synthesis of 2-Diethylaminomethyl-4-(7-chloro-4-quinolyl)-aminofluorobenzene Dihydrobromide

BY AUGUST SVEINBJORNSSON AND CALVIN A. VANDERWERF

In continuation of our studies on the replacement of amino and hydroxyl groups with the isosteric fluorine atom in medicinal agents of proved value, we have synthesized 2-diethylaminomethyl-4-(7-chloro-4-quinolyl)-aminofluorobenzene (I) the fluoro isostere of the antimalarial drug Camoquin [4-(7-chloro-4-quinolylamino)-α-diethyl-amino-*o*-cresol][1] in which the OH-group in Camoquin is replaced by a fluorine atom.



I

Of the various synthetic routes explored, the best method for the preparation of the desired compound involved the following steps: *o*-toluidine → *o*-fluorotoluene → *o*-fluorobenzoic acid → *o*-fluorobenzyl alcohol → *o*-fluorobenzyl bromide → 2-fluoro-5-nitrobenzyl bromide → 2-diethylaminomethyl-4-nitrofluorobenzene hydrobromide → 2-diethylaminomethyl-4-aminofluorobenzene dihydrobromide → dihydrobromide of I.

The antimalarial activity of I was found to be considerably less than that of Camoquin.

Experimental

Preparation of Known Intermediates.—*o*-Fluorotoluene was prepared in 60% yield by direct diazotization of *o*-toluidine in anhydrous hydrogen fluoride, followed by decomposition of the diazonium fluoride in refluxing hydrogen fluoride. The *o*-fluorotoluene was oxidized to *o*-fluorobenzoic acid in 75% yield by the general method of Clark and Taylor,[2] and the acid was reduced to *o*-fluorobenzyl alcohol in 81% yield by means of a 2.5 molar quantity of lithium aluminum hydride.[3] Treatment of the alcohol with anhydrous hydrogen bromide in benzene gave an 81% yield of the highly lachrymatory *o*-fluorobenzyl bromide.

2-Fluoro-5-nitrobenzyl Bromide.—To 200 ml. of fuming nitric acid (sp. gr. 1.5) at 0°, 25.0 g. (0.13 mole) of *o*-fluorobenzyl bromide was added dropwise with stirring. The mixture was then allowed to come to room temperature with stirring and poured onto ice. The yellow product which precipitated was filtered, washed with cold water, and recrystallized from ethanol to yield 25.0 g. (81%) of pure **2-fluoro-5-nitrobenzyl bromide**, m.p. 76.6–77.4°.

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(1) J. H. Burckhalter, F. H. Tendick, E. M. Jones, P. A. Jones, W. F. Holcomb and A. L. Rawlins, THIS JOURNAL, **70**, 1363 (1948).

(2) A. H. Blatt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 135.

(3) See R. F. Nystrom and W. G. Brown, THIS JOURNAL, **69**, 2548 (1947), for the general method.

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.

(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.

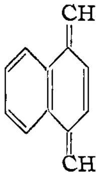
We find that the same scheme applies to the pyrolysis of 2,6-dimethylnaphthalene. The dimer was identified as 1,2-bis-(6-methyl-2-naphthyl)-ethane, m.p. 213–215°.

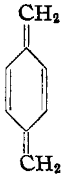
Anal. Calcd. for $C_{24}H_{22}$: C, 92.9; H, 7.1; mol. wt., 310. Found: C, 92.4; H, 6.95; mol. wt., 304.

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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(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
THE UNIVERSITY
MANCHESTER, ENGLAND
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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]

(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.