TABLE I

QUINOLYL DODECYL SULFIDES

Haloquinoline	Dodecyl sulfide	Yield, %	M. p., °C.	Color	Formula	S Analyses, % Calcd.	S Analyses, % Found
5-Nitro-6-chloro-	5-Nitro-6-quinolyl	80	44–5°	Yellow	$C_{21}H_{30}O_2N_2S$	8.56	8.50
5-Nitro-6-chloro-8-acetamido-	8-Amino-5-nitro-6-quinolyl	93	89.5–90.5	Orange	$C_{21}H_{31}O_2N_3S$	8.23	8.30
6-Methoxy-2-chloro-4-methyl-	6-Methoxy-4-methyl-2-quinolyl	70	71–72	Cream	$C_{23}H_{35}ONS$	8.58	8.70
4,7-Dichloro-	7-Chloro-4-quinolyl	87	59–60	White	$C_{22}H_{30}NSCl$	8.80	8.90

TABLE II

AMINOQUINOLYL DODECYL SULFIDES

Nitro derivative	Amino derivative	Yield, %	M. p., °C.	Formula	S Analyses, % Calcd.	S Analyses, % Found
5-Nitro-6-quinolyl	5-Amino-6-quinolyl[a,b]	76	59–60	$C_{21}H_{32}N_2S$	9.30	9.02
8-Acetamido-5-nitro-6-quinolyl	8-Acetamido-5-amino-6-quinolyl	80	77–78	$C_{23}H_{35}ON_3S$	7.98	6.97[c]

TABLE III

ACETAMIDOQUINOLYL DODECYL SULFIDES

Amine	Acetamide	M. p., °C.	Color	Formula	S Analyses, % Calcd.	S Analyses, % Found
5-Amino-6-quinolyl	5-Acetamido-6-quinolyl	121–122	White	$C_{23}H_{34}ON_2S$	8.29	8.21
8-Amino-5-nitro-6-quinolyl	8-Acetamido-5-nitro-6-quinolyl	67–68	Yellow	$C_{23}H_{33}O_3N_3S$	7.42	7.29
8-Acetamido-5-amino-6-quinolyl	5,8-Diacetamido-6-quinolyl	126–127	Cream	$C_{25}H_{37}O_2N_3S$	..[d]	..

[a] This amine would not form a derivative with salicylaldehyde or acetonylacetone. [b] The dihydrochloride melted at 156–157°. Calcd. for $C_{21}H_{34}N_2Cl_2S$: S, 7.67. Found: S, 7.67. [c] This amine could not be purified, but the acetamido derivative gave the correct analysis. [d] Calcd. for $C_{25}H_{37}O_2N_3S$: N, 9.48. Found: N, 9.48.

A series of substituted quinolyl dodecyl sulfides was prepared from activated chloroquinolines and sodium dodecyl mercaptide in methyl cellosolve. The quinoline compounds used were 5-nitro-6-chloroquinoline,[2] 5-nitro-6-chloro-8-acetamidoquinoline,[3] 4,7-dichloroquinoline[4] and 6-methoxy-2-chlorolepidine.[5] The nitroquinolyl sulfides were then reduced to the amino derivatives and these, in turn, were acetylated to the acetamido derivatives.

These compounds were tested against tuberculosis; reports on their activities will be published elsewhere. The authors are grateful to Parke, Davis and Co. for arranging for the tests, and to William Meikle for assistance.

Experimental

Quinolyl Dodecyl Sulfides.—The general method of preparation was to add a solution of sodium dodecyl mercaptide in methyl cellosolve to the chloroquinoline in hot methyl cellosolve.[6] The mixture was refluxed for an hour, cooled, poured into 200 ml. of water, acidified with acetic acid, filtered, and the precipitate recrystallized from methanol.

Aminoquinolyl Dodecyl Sulfides.—The nitroquinolyl dodecyl sulfides were reduced with hydrogen and Raney nickel in absolute ethanol. Recrystallization was not necessary. The amines were yellow solids.

Acetamidoquinolyl Dodecyl Sulfides.—The acetamido derivatives were prepared by heating the amine and acetic anhydride in glacial acetic acid. The mixture was poured into water, filtered and recrystallized from absolute ethanol.

The results are given in Tables I, II and III.

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A New Synthesis of 2,4-Dihydroxyquinoline

BY E. H. HUNTRESS AND J. BORNSTEIN

A recent review[1] of 4-hydroxyquinolines prompts us to report a synthesis of 2,4-dihydroxyquinoline from isatin, giving better results by simpler procedure than prior methods.

The most widely used method for the preparation of 2,4-dihydroxyquinoline has been the treatment of the esters of N-acetylanthranilic acid with sodium metal in toluene or xylene.[2,3,4] Although Camps[2] reported 60% crude yield, subsequent investigators[2,3,4] (including ourselves) have been unable to obtain more than 28–40%.

Reaction of isatin with chloroacetyl chloride gave N-(chloroacetyl)-isatin which on refluxing with aqueous potassium hydroxide, followed by acidification of the reaction mixture with hydrochloric acid, precipitated 2,4-dihydroxyquinoline with the simultaneous evolution of carbon dioxide.

Experimental

N-(Chloroacetyl)-isatin.—Isatin (10 g., 0.068 mole) was vigorously refluxed with chloroacetyl chloride (70 ml., 100 g., 0.89 mole) for five hours. The dark brown reaction mixture was cooled for two hours in an ice-bath

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(2) Kindly furnished by Mrs. Martha Mackin.

(3) Gilman and co-workers, THIS JOURNAL, **68**, 1577 (1946).

(4) Surrey and Hammer, *ibid.*, **68**, 115 (1946).

(5) Prepared by directions of Dr. K. N. Campbell, The University of Notre Dame, South Bend, Indiana.

(6) 5-Nitro-6-chloroquinoline yielded only a small amount of the sulfide by this procedure. It was found desirable to stir the solution of the reactants at room temperature for two hours or more before heating.

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(1) Reitsema, *Chem. Revs.*, **43**, 43 (1948).

(2) Camps, *Arch. Pharm.*, **237**, 689–691 (1899).

(3) Ashley, Perkin and Robinson, *J. Chem. Soc.*, 388 (1930).

(4) Brooker and Smith, THIS JOURNAL, **59**, 72 (1937).

and the precipitate filtered. The filtrate was saved and the solid washed twice with 20 ml. portions of ether and air-dried. The N-(chloroacetyl)-isatin (10.0 g., 66%) consisted of fine-golden-yellow needles, m. p. 210–211° cor., suitable for use without additional purification. The reaction filtrate was replenished with fresh chloroacetyl chloride (10 ml.) and the run repeated with additional isatin (10 g.) giving more equally pure product (12.0 g., 78%). For analysis the N-(chloroacetyl)-isatin was recrystallized from ethyl acetate.

Anal. Calcd. for $C_{10}H_6O_3NCl$: C, 53.71; H, 2.71; N, 6.26; Cl, 15.85. Found: C, 53.32; H, 2.91; N, 6.41; Cl, 15.79.

On recrystallization from methanol the yellow N-(chloroacetyl)-isatin separated with one mole of solvent as fine, *colorless* needles, m. p. 83.0–83.5° cor.

Anal. Calcd. for $C_{11}H_{10}O_4NCl$: C, 51.68; H, 3.95; N, 5.48; Cl, 13.88. Found: C, 51.52; H, 4.09; N, 5.46; Cl, 14.02.

2,4-Dihydroxyquinoline.—Into 150 ml. of an aqueous boiling solution of potassium hydroxide (5.0 g., 0.09 mole) was added all at once 5.0 g. (0.022 mole) of yellow N-(chloroacetyl)-isatin. The straw-colored solution was refluxed for two hours and then cooled to room temperature. On acidification of the reaction mixture with concentrated hydrochloric acid a cream-colored solid separated which was filtered and washed three times with 10-ml. portions of cold water. The crude yield was 2.0–2.5 g., 56–70%. From the filtrate small amounts of isatin were isolated. The 2,4-dihydroxyquinoline was purified by dissolving in the minimum amount of 10% sodium carbonate solution, filtering, boiling the filtrate with Darco for five minutes, filtering, and then reacidifying. On recrystallizing from methanol the compound separated as fine, colorless needles; m. p. 352–354° cor., recorded m. p. 355°.[5]

Anal. Calcd. for $C_9H_7O_2N$: C, 67.08; H, 4.38; N, 8.69. Found: C, 67.21; H, 4.63; N, 8.65.

The identity of the 2,4-dihydroxyquinoline was confirmed by means of its nitroso derivative, m. p. 208° dec., uncor. (recorded 208°[6]), which melted at the same temperature when mixed with an authentic sample, In addition, the (mono) acetyl derivative was prepared; m. p. 215.0–215.5° uncor. (recorded 214–215°[3]), mixed melting point with authentic sample was 215.0–215.5° uncor.

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(5) Niementowski, *Ber.*, **40**, 4289 (1907).

(6) Baeyer and Homolka, *ibid.*, **16**, **2216** (1883); *cf.* **Meyer**, Heimann, *Compt. rend.*, **203**, 335–337 (1936).

DEPARTMENT OF CHEMISTRY
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The Synthesis of Boron Trichloride

BY DALLAS T. HURD

A well known and convenient method for preparing small amounts of boron trichloride or boron tribromide comprises passing boron trifluoride gas over aluminum chloride or aluminum bromide.[1] I recently have found that a reaction may occur at elevated temperatures between aluminum chloride and boric oxide to produce boron trichloride.

Experimental.—120 grams of anhydrous boric acid and 440 g. of aluminum chloride were ground together and placed in a steel pressure vessel. The reaction mixture was heated at 350° for sixteen hours. The bomb then was cooled and the gaseous reaction product was bled off and caught in a trap held at −80°. The collected product was a clear colorless liquid boiling at 12° (reported boiling point of boron trichloride +12.5°). This material fumed in moist air, reacting with the moisture to produce white solid boric acid. A small amount of the liquid was dissolved in water to give a solution which, when tested with silver nitrate, gave a strong test for chloride.

The total amount of product collected was 30 g. or about 7.5% yield based on a complete conversion of boric oxide to boron trichloride.

It also was observed that a molten mixture of boric oxide and calcium chloride at 800–900° evolved boron trichloride very slowly and became more viscous, precipitating an infusible residue in the magma. This solid residue was treated with water after it was cool and a strongly alkaline solution resulted, indicating a conversion of some of the calcium chloride to calcium oxide.

Discussion.—The low yields of boron trichloride are ascribed to: (1) the reaction between aluminum chloride and boric oxide to form aluminum oxide and boron trichloride may be an equilibrium reaction which did not go to completion in the sealed bomb; and/or (2) part of the boric oxide may become bound chemically as aluminum borate by reaction with the aluminum oxide as this material is formed. It is noteworthy that attempts to prepare boron trichloride by a reaction of sodium borate or tetraborate with aluminum chloride were unsuccessful at reaction temperatures up to 350°.

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(1) Gamble, Gilmont and Stiff, THIS JOURNAL, **62**, 1257 (1940).

Reactions of Polyhaloparaffins with Grignard Reagents. 1,1,1-Trichloropentane

BY CORLISS R. KINNEY AND WILLIAM L. SPLIETHOFF

Binaghi[1] has shown that chloroform and carbon tetrachloride react readily with ethylmagnesium bromide, but that gaseous reduction products are formed for the most part. We have reëxamined the reaction from the point of view of controlling its course for the production of tri- and tetrasubstituted paraffins. However, even at −78°, using the less reactive *n*-butylmagnesium chloride, and carrying the halide into the reaction flask vaporized in a stream of dry nitrogen, a vigorous reaction occurs and the products are largely gaseous.

On the other hand, the reaction may be controlled to a certain extent by using the inverse Grignard technique. Thus, adding *n*-butylmagnesium chloride to a solution of carbon tetrachloride in ether gives a small yield of the first step in the reaction, 1,1,1-trichloropentane. The new compound loses hydrogen chloride at about 140° but could be vacuum distilled without decomposition. This thermal instability further indicates activity of the vicinal chlorine atoms. No attempt was made to treat this compound with additional Grignard reagent, but instead the more available 1,1,1-trichloroethane was investigated. This compound, like chloroform, gave largely

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(1) Binaghi, *Gazz. chim. ital.*, **52**, II, 132–138 (1922); **53**, 879 (1923).