perchloric acid[4] and 0.5 g. of 5% palladium-on-charcoal (Wilkens-Anderson Co.). The still warm solution was shaken with hydrogen at 30–35 lb. pressure until 0.2 mole had been absorbed, about one hour. After removal of the catalyst the solution was heated to 75° and diluted with water until cloudy. Upon seeding and cooling, finally to 15°, the acid generally precipitated as an oil which later solidified. After drying *in vacuo* over solid sodium hydroxide the granular product weighed 20 g. It was dissolved in 130 ml. of petroleum ether (b. p. 60–70°) and treated with Norit to yield 19.8 g. (82.5%) of white needles, m. p. 74.5–75° (reported[3], 75°).

Four additional reductions were run as above and the reaction mixtures were combined and worked up to give the acid in 89% yield.

(4) The efficacy of perchloric acid in promoting hydrogenolysis was first recognized by Karg and Marcus, *Ber.*, **75**, 1850 (1942).

DEPARTMENT OF CHEMISTRY
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS RECEIVED JULY 19, 1946

2,5-Diamino-1,4-benzoquinones[1]

BY JOHN H. BILLMAN, DONALD G. THOMAS AND DAVID K. BARNES

The reaction of aromatic and aliphatic amines with 1,4-benzoquinone has long been known. Perhaps the most important incentive for the extensive study which has been made on this type of reaction is due to the close relationship between aromatic aminoquinones and dyes of commercial importance.[2] Since compounds of this type had not been examined for antimalarial activity, several of them have now been prepared by the following typical procedure.

2,5-Disulfapyridino-1,4-benzoquinone.—To a solution of 5 g. (0.04 mole) of 1,4-benzoquinone in 100 ml. of hot 95% ethanol was added 10.0 g. (0.04 mole) of sulfapyridine and one ml. of concentrated hydrochloric acid. The reaction proceeded smoothly and crystals precipitated when the solution was cooled. The product was filtered by suction and washed thoroughly with hot alcohol until the filtrate was almost colorless. The yield was 8 g. or 66%.

The following compounds were prepared and their antimalarial activity tested.

TABLE I

2,5-DIAMINO-1,4-BENZOQUINONES

Amine used	M. p.,[a] °C.	Mol. ratio quinone/amine	% Nitrogen Calcd.	% Nitrogen Found
Aniline	345	2/1		[b]
Ethanolamine	262	3/2		[c]
β-Phenylethylamine	208	3/1	8.09	8.02
p-Anisidine	300	1/1	8.00	8.09
Sulfapyridine	218–220	1/1	13.82	14.09

[a] Determined on a Maquenne block, uncorrected decomposition points. [b] Previously prepared by Willstätter and Majima, *Ber.*, **43**, II, 2591 (1910). [c] Previously prepared by Kansas and Inagawa, *J. Pharm. Soc. Japan*, **58**, 347–352 (1938).

CHEMICAL LABORATORY
INDIANA UNIVERSITY
BLOOMINGTON, INDIANA RECEIVED JUNE 28, 1946

(1) This work was done under a contract, recommended by the Committee on Medical Research, between the Office of Scientific Research and Development and Indiana University at Bloomington, Indiana.

(2) Suida and Suida, *Ann.*, **416**, 113 (1918).

(*p*-Halogenophenyl)-trimethylsilanes

BY CHARLES A. BURKHARD

(*p*-Chlorophenyl)-trimethylsilane and (*p*-bromophenyl)-trimethylsilane have been prepared by the following reaction.

$$(CH_3)_3SiCl + p\text{-}XC_6H_4MgBr \longrightarrow p\text{-}(CH_3)_3SiC_6H_4X + MgBrCl$$

Grüttner and Krause[1] have prepared the corresponding triethyl compounds and (*p*-chlorophenyl)-tri-*n*-propylsilane by reaction of the alkyl Grignard reagent with the corresponding *p*-halogenophenyltrichlorosilane.

(*p*-Chlorophenyl)-trimethylsilane.—*p*-Chlorophenylmagnesium bromide was prepared by the reaction of 382 g. of *p*-chlorobromobenzene with 50 g. of magnesium turnings in 700 ml. of anhydrous ether. To this was added dropwise with stirring 220 g. of chlorotrimethylsilane. The solution was kept at reflux to ensure complete reaction. The compound was recovered by rectification; yield 305 g., 83%, b. p. 119–120° (50 mm.), d^{20}_4 1.0282, $n^{20}D$ 1.5128.

Anal.[2] Calcd. for $C_9H_{13}SiCl$: Cl, 19.20. Found: Cl, 19.3.

(*p*-Bromophenyl)-trimethylsilane.—*p*-Bromophenylmagnesium bromide was prepared by the reaction of 177 g. of *p*-dibromobenzene with 18.8 g. of magnesium turnings in 300 ml. of anhydrous ether. To this was added 81 g. of chlorotrimethylsilane with stirring. The solution was kept under reflux to ensure complete reaction. The compound was recovered by rectification; yield 90.5 g., 53%; b. p. 146–148° (50 mm.), d^{20}_4 1.2197, $n^{20}D$ 1.5302.

Anal. Calcd. for $C_9H_{13}SiBr$: Br, 34.87. Found: Br, 34.2.

(1) Grüttner and Krause, *Ber.*, **50**, 1559 (1917).

(2) The author is indebted to Dr. E. W. Balis and Mr. L. B. Bronk for analyses.

RESEARCH LABORATORY
GENERAL ELECTRIC CO.
SCHENECTADY, N. Y. RECEIVED JUNE 27, 1946

The Preparation of Mercaptans from Alcohols[1]

BY ROBERT L. FRANK AND PAUL V. SMITH

The preparation of isothiouronium salts by the direct action of thiourea and halogen acids on alcohols, first recorded by Stevens[2] and developed by Johnson and Sprague,[3,4] is herein further described as a step in the synthesis of mercaptans (I–III).

$$ROH + H_2NCSNH_2 + HX \longrightarrow$$

I

$$RSC(=NH)NH_2 \cdot HX \xrightarrow{NaOH} RSH$$

II III

Our experiments comparing hydrochloric and hydrobromic acids in this reaction have shown a great advantage in the use of the latter for making primary mercaptans. *n*-Dodecyl mercaptan, for

(1) This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

(2) Stevens, *J. Chem. Soc.*, **81**, 79 (1902).

(3) Johnson and Sprague, THIS JOURNAL, **58**, 1348 (1936).

(4) Sprague and Johnson, *ibid.*, **59**, 1837 (1937).