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
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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).

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(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
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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).

example, was prepared in 77–90% yield from *n*-dodecyl alcohol, thiourea and 48% hydrobromic acid after seven hours of reaction; use of hydrochloric acid gave only 24% yield after twenty-eight hours.

The best procedure was as follows: In a 1-liter, three-necked round-bottomed flask fitted with a stirrer and a reflux condenser were placed 0.50 mole of the appropriate alcohol, 0.50 mole of thiourea and 1.50 moles of hydrogen bromide as 48% hydrobromic acid (double these amounts of thiourea and hydrobromic acid were used for making hexamethylene and decamethylene dithiols). The mixture was refluxed for nine hours with stirring. A solution of 60 g. (1.5 moles) of sodium hydroxide in 600 ml. of water was then added; a stream of nitrogen was passed over the surface of the liquid; and the mixture was refluxed without stirring for two hours. The layers were separated, and the acidified aqueous layer was extracted with three 50-ml. portions of ether. The ethereal extracts and original organic layer were combined, dried over calcium sulfate (Drierite), and fractionally distilled through a 12-inch helix-packed column.

The yields of several mercaptans obtained by this means are as follows: *n*-butyl, 91%; isobutyl, 56%; *n*-hexyl, 71%; *n*-octyl, 73%; *n*-dodecyl, 77%[5]; cetyl, 64%[5]; benzyl, 72%; β-phenylethyl, 70%; hexamethylene, 63%; decamethylene, 48%; *s*-butyl, 64%; cyclohexyl, 19%; 2-octyl, 59%. The purity of the products was established by comparison of the boiling points and refractive indices with the best data given in the literature.

Yields of mercaptans from alcohols by this method are as good as those from the alkyl bromides, so that the intermediate step of converting the alcohol to the bromide can advantageously be eliminated.

As is also found in the reaction between alkyl halides and thiourea, the yields are best for primary and poorest for tertiary mercaptans due to the tendency toward olefin formation in the latter types. The experiments of Sprague and Johnson[4] have shown that for mercaptans such as cyclohexyl or *t*-butyl the best procedure would be to use hydrochloric acid instead of hydrobromic and resort to long reaction periods. The reaction failed in attempts to prepare allyl mercaptan, *t*-butyl mercaptan, triphenylmethyl mercaptan, and *p*-nitrothiophenol, using hydrobromic acid.

It is reasonable to suppose that the course of the reaction to form the isothiouronium salts (I–II) involves the intermediate formation of an alkyl halide. On the other hand, it is possible that the hydroxyl group of the alcohol (I) may be directly replaced by the S-isothiouronium group. The available evidence indicates that both mechanisms may obtain. For example, the difference in reaction rates using hydrochloric and hydrobromic acids favors the former; one would not expect such a difference if these act only in their capacity as acids rather than as reagents to replace the alcoholic hydroxyl group by halogen. A further experiment, however, shows that the intermediate halide is not absolutely necessary: *n*-octyl mercaptan was obtained by refluxing with stirring 65 g. (0.50 mole) of *n*-octyl alcohol, 38 g. (0.50 mole) of thiourea, and 77 g. (0.75 mole) of concentrated sulfuric acid for nine hours. The mixture was then worked up with alkali in the same manner as described above. The yield of *n*-octyl mercaptan, not obtained completely free from *n*-octyl alcohol, was judged by refractive indices to be 5.1%. It was identified through its addition product with benzalacetophenone, m. p. 46.5–47°; mixed m. p. with an authentic sample of β-*n*-octylmercapto-β-phenylpropiophenone, 46.5–47.2°. The authentic sample was prepared by refluxing 1.0 g. (0.048 mole) of benzalacetophenone and 0.7 g. (0.048 mole) of *n*-octyl mercaptan in 3.0 ml. of 95% ethanol for one-half hour. The product separated on cooling; one recrystallization from 95% ethanol gave white needles, m. p. 47.5–48°.

(5) In the preparation of higher mercaptans such as dodecyl and cetyl, oxidation of some product to the disulfide is unavoidable; in these two cases were also obtained yields of 22 and 35% of the respective disulfides.

Anal.[6] Calcd. for $C_{22}H_{30}OS$: C, 77.91; H, 8.53. Found: C, 77.80; H, 8.22.

Further experiments of interest in comparing the chlorine and bromine derivatives in this reaction are as follows: A mixture of 65 g. (0.50 mole) of *n*-octyl alcohol and 254 g. (1.50 moles) of 48% hydrobromic acid were refluxed in a 1-liter, round-bottomed flask for nine hours. It was then extracted with two 50-ml. portions of ether, dried over calcium sulfate (Drierite), and fractionally distilled through a 12-inch helix-packed column to give 79 g. (82%) of *n*-octyl bromide, b. p. 93° (20 mm.); $n^{20}D$ 1.4520. The same procedure, using 150 ml. (1.80 moles) of concentrated hydrochloric acid, resulted in the recovery of 62 g. (95%) of *n*-octyl alcohol, b. p. 96–97°; $n^{20}D$ 1.4290.

A similar procedure, using 48.5 g. (0.65 mole) of *n*-butyl alcohol, 49.5 g. (0.65 mole) of thiourea, 194 ml. (2.30 moles) of concentrated hydrochloric acid, and a nine-hour reaction period, followed by the addition of 92 g. (2.30 moles) of sodium hydroxide in 500 ml. of water and refluxing for three hours, gave a 41-g. (85%) recovery of *n*-butyl alcohol, b. p. 117°; $n^{20}D$ 1.3988. Inclusion of 313 g. (2.30 moles) of pulverized zinc chloride in this reaction mixture gave on distillation 30 g. (50%) of *n*-butyl chloride, b. p. 77°; $n^{20}D$ 1.4002. No *n*-butyl mercaptan was obtained.

Thus both the replacement of hydroxyl by halogen and of halogen by the S-isothiouronium group, assuming this reaction course, are influenced by the choice of halogen acid.

(6) Microanalysis carried out by Mr. Howard Clark.

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Some Heterocyclic Acetic Acids in Plant Hormone Tests

BY HENRY GILMAN AND S. AVAKIAN

In extension of studies on polynuclear hetero types, some acetic acid derivatives of dibenzofuran, dibenzothiophene, phenoxathiin and carbazole have been prepared for plant hormone tests.

Experimental

2-Dibenzofurylacetic Acid.—This compound has been prepared by three different procedures.[1,2]

1. Arndt–Eistert Reaction.—Five and one-half g. (0.026 mole) of 2-dibenzofurancarboxylic acid was refluxed for forty-five minutes with an excess of thionyl chloride. After removing the excess thionyl chloride by distillation, the residual acid chloride was crystallized from benzene as colorless needles, m. p. 103–104°; yield 5.6 g. (93%).

Anal. Calcd. for $C_{13}H_7O_2Cl$: Cl, 15.22. Found: Cl, 15.03.

To an ether solution of diazomethane obtained from 15 g. (0.146 mole) of nitrosomethylurea was added 5 g. (0.022 mole) of 2-dibenzofurancarboxylic acid chloride and the solution was allowed to stand overnight. After removal of the ether and recrystallization from benzene–ligroin there was obtained an 86% yield of yellow crystals of diazomethyl 2-dibenzofuryl ketone, m. p. 126–127°.

Anal. Calcd. for $C_{14}H_8O_2N_2$: N, 11.86. Found: N, 12.02.

To a stirred and refluxed solution of 2.5 g. (0.01 mole) of diazomethyl 2-dibenzofuryl ketone in 50 cc. of dioxane was added 13 cc. of concentrated ammonium hydroxide and then 3 cc. of a 10% solution of silver nitrate. After heating and stirring for one hour, the hot solution was filtered from the silver oxide and shaken with cold water. The precipitated crude 2-dibenzofurylacetamide was obtained

(1) Arndt and Eistert, *Ber.*, **68**, 200 (1935).
(2) Fieser and Kilmer, THIS JOURNAL, **62**, 1354 (1940).