ethers containing iodine. The hydrochlorides were recrystallized from methanol, ethanol, methanol–ether, acetone, or ethyl acetate–ether.

The yields in the Williamson reactions averaged 25–35%. Low yields, sometimes below 5%, were obtained in several preparations involving dimethylaminoethyl chloride. Dialkylaminopropyl chlorides usually rendered the corresponding aryl ethers in yields of 50–90%. However, the optimum conditions have not been determined in all cases.

1-(2,4,5-Trichlorophenoxy)-2-*n*-butylaminoethane was prepared from *n*-butylaminoethyl chloride in an analogous manner. The yield was 18%.

2,4,5-Trichlorophenoxy Diethylaminomethane.—Diethylaminomethyl chloride hydrochloride was obtained in 81% yield by the direction of Prévost and de Mauny[4] and condensed with sodium 2,4,5-trichlorophenolate according to the procedure outlined above. The yield was 5%.

Chemical Analysis.—Most of the hydrochlorides listed in Table I were titrated in water or dilute alcohol solution with 0.05 *N* potassium hydroxide solution to a phenolphthalein end-point.

For several hydrochlorides, and water-insoluble derivatives, the total halogen content was determined by the method of Schwenk, Papa and Ginsberg,[7] using samples of 30–80 mg. and correspondingly small amounts of the required reagents. The silver nitrate and potassium thiocyanate solutions were 0.05 *N*. Reliable results were obtained on this semi-micro scale with most of the compounds; those derivatives analyzed for carbon, hydrogen or nitrogen did not give consistent halogen values by reduction with Raney nickel alloy.

Summary

A number of alkyl and dialkylaminoalkyl ethers of phenol and halogenated phenols with various substituents has been described. It has been found that nuclear iodine is not a prerequisite for the antitubercular action of such compounds.

(7) Schwenk, Papa and Ginsberg, *Ind. Eng. Chem., Anal. Ed.*, **15**, 576 (1943).

CHARLOTTESVILLE, VA.
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NOTES

Isolation of Rutin from *Hydrangea Paniculata*, Var. *Grandiflora Sieb.*

BY JAMES F. COUCH AND JOSEPH NAGHSKI

Rutin, 3,5,7,3′,4′-pentahydroxyflavone-3-rutinoside, has recently assumed some prominence in the treatment of increased capillary fragility associated with hypertension[1,2] and is promising as a remedy for certain other diseases resulting from capillary breakdown. Rutin has been found in thirty-three species of plants and is, thus, one of the most widely distributed of the glucosides. This paper reports the isolation and identification of rutin in the flowers of a common garden species of *Hydrangea*. Previous chemical examinations of the roots of white-flowered species of *Hydrangea* have been reported.[3,4,5] Hashimoto and Kawana[6] extracted the dried flowers of *H. paniculata* with benzene and obtained a phenolic substance, $C_9H_6O_3$, but they do not mention rutin. The presence of rutin in relatively large quantities in the flowers has not previously been reported.

Experimental.—Fresh blossoms (67.5 g., moisture, 83.6%) were digested with alcohol (300 ml.) for several hours. The solvent was removed from the filtered extract. The residue was freed from fats and resins with benzene and the insoluble matters were extracted with boiling water. On cooling and standing, 0.4 g. of rutin crystallized, m. p. 183–185°; raised by recrystallization from boiling water to 190–192°. A further crop, 0.05 g., was obtained by re-extracting the insoluble matters with boiling water; yield, 0.45 g. or 4.06% of the moisture-free plant.

Anal.[7] Calcd. for $C_{27}H_{30}O_{16}$: C, 53.10; H, 4.95. Found: C, 53.34; H, 5.09.

The substance gave the usual tests for the identification of rutin. These data were confirmed on a larger sample (1.6 kg.) of fresh flowers.

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(1) J. Q. Griffith, J. F. Couch and M. A. Lindauer, *Proc. Soc. Exp. Med. Biol.*, **55**, 228–229 (1944).

(2) J. F. Couch and C. F. Krewson, United States Department of Agriculture, Mimeograph Circular AIC-52, July, 1944.

(3) C. S. Bondurant, *Am. J. Pharm.*, **59**, 122–124 (1887).

(4) A. G. Leubert, *ibid.*, **70**, 550–552 (1898).

(5) H. J. M. Schroeter, *ibid.*, **61**, 117–118 (1889).

(6) A. Hashimoto and T. Kawana, *J. Pharm. Soc. Japan*, **55**, 183–186 (1935); *C. A.*, **29**, 5112 (1935).

(7) C and H determinations by C. L. Ogg.

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sym-Tetraphenylethane from DDT and Related Compounds[1]

BY ELMER E. FLECK, ROBERT K. PRESTON AND H. L. HALLER

During an investigation of the effect of various solvents on the dehydrochlorination of 1-trichloro-2,2-bis-(*p*-chlorophenyl)-ethane (known as DDT),[2] it was noted that an abnormal reaction took place in the presence of anhydrous aluminum chloride and benzene. When one mole of anhydrous aluminum chloride was used with a large

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(1) Some of the work reported was done under a transfer of funds, recommended by the Committee on Medical Research, from the office of Scientific Research and Development to the Bureau of Entomology and Plant Quarantine. Article not copyrighted.

(2) Fleck and Haller, THIS JOURNAL, **66**, 2095 (1944).

excess of benzene, approximately two moles of hydrogen chloride was evolved. Since the apparent reaction was of the Friedel–Crafts type, the following experiment was carried out:

A solution of 35 g. of DDT (m. p. 107–108°) in 200 ml. of dry benzene was stirred vigorously at room temperature while 13 g. of anhydrous aluminum chloride was added during the course of twenty-five minutes. Rapid evolution of hydrogen chloride occurred while the first part of the aluminum chloride was being added, but little or no gas evolution was noted during addition of the last third. There was no appreciable increase in the temperature of the reaction mixture. Stirring was continued for one hour. The black reaction mass was diluted with ice water and then transferred to a separatory funnel. The reddish-orange benzene solution was shaken with water until the washings were neutral to congo red. The benzene solution was allowed to stand in the ice box, and the prisms that separated were recrystallized from benzene to a constant melting point of 210–212.°

Anal. Calcd. for $C_{26}H_{22}$: C, 93.37; H, 6.63. Found: C, 93.65; H, 6.79.[3]

No depression in melting point could be observed when this material was mixed with *sym*-tetraphenylethane.[4] Both samples gave a faint yellow color when tested with tetranitromethane.

The benzene mother liquor was concentrated to a volume of about 100 ml. and a second crop of *sym*-tetraphenylethane was obtained. The filtrate was steam-distilled, and the distillate was separated from the water and fractionated. After the benzene had distilled, 1.1 g. of chlorobenzene distilled at 128–130°, $n^{19}\text{D}$ 1.5238.

The mother liquor from a second run was concentrated to about 30 ml. after the *sym*-tetraphenylethane had been removed. After it had stood in the ice box for several months, large diamond-shaped crystals were obtained. These crystals were removed mechanically from the brick-red residue and recrystallized from *n*-pentane to a constant melting point of 87–88°. No depression in melting point could be observed when this product was mixed with 1,1-dichloro-2,2-bis-(*p*-chlorophenyl)-ethylene.[5]

Approximately the same per cent. yield of *sym*-tetraphenylethane was obtained when the experiment was repeated with 3.5 g. of DDT (m. p. 108–109°) obtained by three recrystallizations from alcohol.

In order to determine whether the *sym*-tetraphenylethane was a reaction product of DDT or an impurity, several compounds related to DDT were treated as above, 0.01 mole being used in each case.

1,1-Dichloro-2,2-bis-(*p*-chlorophenyl)-ethane gave a red solution when aluminum chloride was added. With the addition of water this color faded, and the resulting colorless solution yielded *sym*-tetraphenylethane.

1-Trichloro-2,2-diphenylethane and 1-trichloro-2-(*p*-chlorophenyl)-2-(*o*-chlorophenyl)-ethane yielded *sym*-tetraphenylethane.

1,1-Dichloro-2,2-bis-(*p*-chlorophenyl)-ethylene did not yield *sym*-tetraphenylethane.

Where *sym*-tetraphenylethane was isolated, the yield was about 10% of the theoretical in all cases except in that of 1,1-dichloro-2,2-bis-(*p*-chlorophenyl)-ethane, when a 25% yield resulted.

When chlorobenzene was substituted for benzene in the reaction, no *sym*-tetraphenylethane could be isolated.

It is therefore evident that the use of benzene and aluminum chloride gives rise to a number of competing reactions. Besides the dehydrohalogenation reaction a dechlorination or "halogen migration"[6] occurs. These reactions are accompanied by formation of unidentified colored material.

The catalytic elimination of hydrogen chloride is much more difficult from 1,1-dichloro-2,2-bis-(*p*-chlorophenyl)-ethane than from the corresponding trichloromethyl derivative.[2] This may account for the high yield of *sym*-tetraphenylethane in this case.

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(3) Analysis by W. F. Barthel.

(4) Norris, Thomas and Brown, *Ber.*, **43**, 2940 (1910).

(5) Zeidler, *ibid.*, **7**, 1181 (1874).

(6) Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1941, p. 692.

Ethynyllithium Compounds by Halogen–Metal Interconversions

BY HENRY GILMAN AND A. H. HAUBEIN

It was shown recently,[1] incidental to the development of an improved procedure for the quantitative analysis of alkyllithium compounds, that benzyl chloride underwent a halogen–metal interconversion reaction with ethyllithium.

$$C_6H_5CH_2Cl + C_2H_5Li \longrightarrow C_6H_5CH_2Li + C_2H_5Cl$$

This reaction was significant as decisive experimental evidence for the formation of an RLi compound from an alkyl chloride by the interconversion reaction.[2] However, because of the extremely small yield of benzyllithium in this reaction, it was desirable to get confirmatory evidence with an RCl compound like phenylethynyl chloride.

We first showed that phenylethynyl bromide underwent a smooth interconversion with *n*-butyllithium to give, subsequent to carbonation, an 87% yield of phenylpropiolic acid.

$$C_6H_5C{\equiv}CBr + n\text{-}C_4H_9Li \xrightarrow[[H_2O]]{[CO_2]} C_6H_5C{\equiv}CCO_2H$$

From phenylethynyl chloride the yield of phenylpropiolic acid was 20%. The reaction, of course, is not intended for synthetic purposes inasmuch as phenylethynyllithium is most readily prepared from phenylacetylene.

Vinyllithium would be a highly useful tool for the introduction of the vinyl group, particularly in studies concerned with pharmacologically active compounds derived from nitrogen heterocycles like pyridine and quinoline. It was shown earlier[3] that β-bromostyrene and *n*-butyllithium, when allowed to react in petroleum ether and then carbonated, gave a 23% yield of *trans*-cinnamic acid. This suggested the possibility of preparing vinyllithium by a corresponding reaction with vinyl bromide. However, acetylenedicarboxylic acid was formed. One of the mechanisms for this reaction may be like that suggested for the formation of phenylpropiolic acid when β-bromostyrene is treated with *n*-butyllithium[3] or phenyllithium,[2] in diethyl ether: namely, a lateral metalation followed by the loss of lithium bromide.

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(1) Gilman and Haubein, THIS JOURNAL, **66**, 1515 (1944).

(2) Wittig and Witt, *Ber.*, **74**, 1474 (1941). This article describes a series of interesting experiments on the reaction of phenyllithium with carbon tetrachloride, benzotrichloride, benzyl chloride, benzohydryl chloride, triphenylmethyl chloride, and β-chlorostyrene.

(3) Gilman, Langham and Moore, THIS JOURNAL, **62**, 2327 (1940).