Parrod reported imidazole and 4(5)-(*D-arabino*)-tetrahydroxybutaneimidazole as the products. The chromatograms indicate that fair quantities of 4(5)-hydroxymethylimidazole and two other diazo reacting substances were obtained as well.

Chromatograms have been made of many other complex materials, such as deproteinized liver fractions, the products of the action of L-aminoacid oxidase on DL-histidine, and culture filtrates from *Neurospora* and *Penicillium* histidineless mutants, with good separation of imidazoles and reproducible colors and R_f values.

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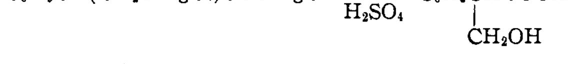
The Preparation of Tropic Acid

BY F. F. BLICKE, HAROLD RAFFELSON AND BOHDAN BARNA

It has been found that tropic acid, which is required for the synthesis of atropine and certain synthetic medicaments, can be obtained very conveniently, and in good yield, by the addition of formaldehyde to the Ivanov reagent[1] prepared from phenylacetic acid and isopropylmagnesium chloride

$$C_6H_5CH_2COOH + 2(CH_3)_2CHMgCl \longrightarrow C_6H_5CH(MgCl)COOMgCl + 2C_3H_8$$

$$\underset{\text{(Ivanov reagent)}}{C_6H_5CH(MgCl)COOMgCl} + CH_2O \longrightarrow$$



$$C_6H_5CH(CH_2OMgCl)COOMgCl \xrightarrow[H_2SO_4]{} C_6H_5\underset{\displaystyle CH_2OH}{\underset{|}{C}H}COOH$$

Magnesium (97.3 g.) and 2 liters of anhydrous ether were placed in a 5-liter, 3-necked flask fitted with a stirrer, dropping funnel and a 2-ft. reflux condenser. About 2 cc. of ethyl bromide and 10 cc. of isopropyl chloride were added, and the mixture was warmed to initiate the reaction. Isopropyl chloride (330 g.) was then added, dropwise, at such a rate that the mixture refluxed. After all of the chloride had been added, the mixture was refluxed for one-half hour.

Phenylacetic acid (240 g.), dissolved in 2 liters of dry benzene, was added to the stirred solution at such a rate that the mixture refluxed. After the addition was completed, the material was refluxed (about 12 hours) until no more gas was evolved. Since a large volume of propane was evolved during and after the addition of the phenylacetic acid, this operation should be carried out in a hood or the gas should be passed through a tube which carries it out of the laboratory.

The mixture was cooled in an ice-bath, and the dropping funnel was replaced by the side-arm of a distillation flask. The side-arm was made of wide glass tubing and was bent at a right angle. The horizontal section of the side-arm should be about 6 inches long and the vertical section should be long enough so that after it has been inserted into the reaction flask the end of the side-arm is about 1 inch above the surface of the stirred liquid. Paraformaldehyde (140 g.) (Mallinckrodt), which had been dried for two days in a desiccator over phosphorus pentoxide, was placed in the distillation flask which was heated in an oil-bath at 180–200°. The formaldehyde was carried into the vigorously-stirred mixture by a slow stream of dry nitrogen. The latter operation required from three to three and one-half hours. The reaction mixture was then poured into a mixture of 300 cc. of concd. sulfuric acid and 3 liters of finely crushed ice which had been placed in a 2-gal. crock, and the mixture was stirred for one-half hour. The solid material was removed by filtration, the organic layer separated, and the aqueous layer, and also the filtered solid, were placed in the original reaction flask. The mixture was warmed on a steam-bath for one-half hour, or until most of the solid had disappeared, then thoroughly cooled, filtered, and extracted with three 300-cc. portions of ether. The ether extracts and the organic layer were combined, and the solvents were removed under reduced pressure until the volume in the distillation flask had been reduced to about 500 cc. The mixture was then cooled for 12 hours, the precipitated tropic acid filtered, the filtrate concentrated to one-half of its original volume, cooled and more tropic acid removed by filtration. The crude tropic acid was heated with 500 cc. of benzene to dissolve unchanged phenylacetic acid, cooled, filtered, and washed with a small amount of cold benzene. The air-dried acid melted at 116–117°; yield 207–245 g. (71–83%).

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[1] D. Ivanov and S. Spassov, *Bull. soc. chim.*, [4] **49**, 19 (1931).

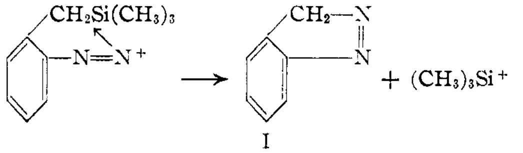
Aminoaryltrialkylsilanes

BY ROBERT A. BENKESER AND PHILIP E. BRUMFIELD

The successful isolation and identification of the isomeric nitro compounds from phenyltrimethylsilane and benzyltrimethylsilane[1] has provided a convenient approach to the preparation and study of the corresponding amines. Very few reports[2] of such amines are found in the literature, probably because compounds of this type suffer easy fission of their aromatic carbon–silicon bond which renders their preparation rather difficult. This tendency for cleavage of the silicon group becomes especially pronounced in acidic media, when the amine group is situated on the aromatic nucleus either *ortho* or *para* to the silicon. The instability of these aromatic silanes to strong acid renders the so-called "wet" reductions of the corresponding nitro compounds rather difficult since these procedures normally employ an acidic medium. In the work herein reported low pressure hydrogenation over a Raney nickel catalyst was found quite satisfactory for obtaining the aminosilanes. These compounds can be acetylated in the usual manner with little or no cleavage of the silicon group.

Five of these amines (*o*-aminophenyltrimethylsilane excepted) were diazotized and then coupled with β-naphthol to yield the corresponding azo compound. The formation of considerable amounts of tar *during* the diazotization indicated that the diazonium salts were unstable.

During the diazotization and subsequent reaction of *o*-aminobenzyltrimethylsilane there was isolated a 16% yield of indazole (I). This product can be explained if one assumes an intramolecular displacement of the trimethylsilyl group.



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Experimental

Aminosilanes.—Weighed portions of up to 50 g. of the nitrosilanes[1] obtained from phenyltrimethylsilane and benzyltrimethylsilane were dissolved in 95% or absolute ethanol and reduced with hydrogen over Raney nickel. A Parr hydrogenator was used, with maximum pressures of 60

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[1] R. A. Benkeser and P. E. Brumfield, THIS JOURNAL, **73**, 4770 (1951).

[2] See F. S. Kipping and N. W. Cusa, *J. Chem. Soc.*, **79**, 1088 (1935); also B. N. Dolgov and O. K. Panina, *J. Gen. Chem.*, **18**, 1129 (1948), *C. A.*, **43**, 1737 (1949); and R. F. Fleming, U. S. Patent 2,386,452 (1945).