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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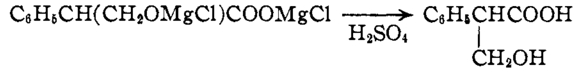
The Preparation of Tropic Acid

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

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

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



$$C_6H_5CH(CH_2OMgCl)COOMgCl \xrightarrow[H_2SO_4]{} C_6H_5\underset{\substack{|\\ CH_2OH}}{C}HCOOH$$

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).

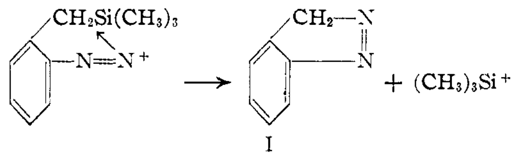
Aminoaryltrialkylsilanes

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.



I

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).

TABLE I

	Aminophenyltrimethylsilanes							Acetyl derivatives		
	B.p. (10 mm.)	$n^{20}\text{D}$	$d^{20}{}_4$	M_D (obsd.)	M_D (calcd.)	Si, % Calcd.	Si, % Found	M.p., °C.	Si, % Calcd.	Si, % Found
Ortho	101	1.5388	0.952	54.38	54.45	16.98	16.99	130–130.5	13.53	13.70
Meta[a]	111	1.5362	.947	54.44	54.45	16.98	16.96	114–115	13.53	13.83
Para	113	1.5393	.947	54.73	54.45	16.98	16.57	169–170	13.53	13.72

[a] It must be kept in mind that the nitro compound here was adjudged to be only 95% pure.

	β-Naphthol coupling products							
	M.p., °C.	Si, % Calcd.	Si, % Found	N, % Calcd.	N, % Found	Yield, %	Color	Crystallizing solvent
Meta	94–95	8.76	8.68	8.74	8.95	58	Red needles	Acetic acid
Para	94–95	8.76	8.48	8.74	8.94	50	Red-orange	Acetic acid

TABLE II

	Aminobenzyltrimethysilanes							Acetyl derivatives		
	B.p. (10 mm.)	$n^{20}\text{D}$	$d^{20}{}_4$	M_D (obsd.)	M_D (calcd.)	Si, % Calcd.	Si, % Found	M.p., °C.	Si, % Calcd.	Si, % Found
Ortho	114	1.5345	0.939	59.41	59.01	15.66	15.47	117–117.5	12.69	12.40
Para	119	(m.p. 33.5–34°)		...	...	15.66	15.85	132–133	12.69	12.84

	β-Naphthol coupling products							
	M.p., °C.	Si, % Calcd.	Si, % Found	N, % Calcd.	N, % Found	Yield,[a] %	Color	Crystallizing solvent
Ortho	97–98	8.39	8.15	8.38	8.31	12	Orange	Acetic acid
Para	126–127	8.39	8.25	8.38	8.82	19	Red	Acetic acid

[a] It is entirely possible that these yields can be improved since the optimum conditions were not investigated.

p.s.i. After absorption of the calculated amount of hydrogen, the catalyst was removed by filtration through a layer of Celite and the alcohol was removed by distillation. The residual amine was fractionally distilled through an efficient column at 10 mm. pressure. All amines were initially clear colorless liquids, but darkened on standing. The properties of these amines are given in Tables I and II.

The reduction of *o*-nitrophenyltrimethylsilane required careful control, in order to avoid excessive cleavage to give aniline. By carrying out the reduction in 95% ethanol, wrapping the reduction bottle in damp cloths, and terminating the reduction as soon as the calculated amount of hydrogen was absorbed, it was possible to obtain an 83% yield of *o*-aminophenyltrimethylsilane, with minor amounts of aniline and tarry pot residue.

The reduction of *m*-nitrophenyltrimethylsilane (95% pure)[1] and *p*-nitrophenyltrimethylsilane was carried out with no unusual precautions to give 75–85% yields of *m*-aminophenyltrimethylsilane and *p*-aminophenyltrimethylsilane, respectively. Very small amounts of aniline and tars were formed.

The reduction of *o*-nitrobenzyltrimethylsilane was found to take place very slowly, requiring 20 to 50 hours to obtain complete reduction. A maximum yield of 90% of *o*-aminobenzyltrimethylsilane was obtained from 39 g. of the nitrosilane in 50 ml. of absolute ethanol.

The reduction of *p*-nitrobenzyltrimethylsilane proceeded in a normal manner, requiring about 4 to 8 hours and giving about 85% yields of *p*-aminobenzyltrimethylsilane.

Acylation of Aminosilanes.—Small portions (0.5 g.) of the amines were dissolved in 3 to 5 ml. of acetic anhydride, with slight cooling. After solution was complete, 20 to 30 ml. of water was added and the mixture was cooled in an ice-bath. The waxy solids obtained were crystallized from hot petroleum ether (90–100°). Virtually quantitative yields of the acetyl derivatives were obtained, with properties as shown in Tables I and II.

Diazotization of Aminosilanes and Coupling with β-Naphthol.—The following procedure is typical of that employed in the diazotization and coupling of the amines.

Weighed portions (4 to 12 g.) of the aminosilanes were added to a mixture of 50 to 100 g. of crushed ice and a slight excess of dilute hydrochloric acid. In all cases the amine hydrochloride separated as a white solid. A dilute ice cold solution of the calculated amount of sodium nitrite was added rapidly (2 to 5 min.) with vigorous stirring. Most of the precipitated hydrochloride reacted in a short time, giving an orange diazonium solution. The solution darkened rapidly and formed dark tarry material. Within 10 min. of the start of the reaction, the diazonium solution was filtered rapidly through a glass wool plug into a cold dilute solution of the calculated amount of β-naphthol, containing a slight excess of sodium hydroxide. This reaction mixture was stirred rapidly and red solid particles separated usually along with dark tarry material. After about 20 min., acetic acid was added, if required, to give a slightly acid solution, and the product was filtered. The red gummy solid was dissolved in a small amount of benzene and poured into a chromatographic column, packed with activated alumina and Celite (50–50 by volume). The silicon-containing dye was collected in the first red area carried through the column by the benzene used as the elution solvent. Subsequent fractions obtained from the column contained mixtures of cleavage products, tars and unreacted β-naphthol. The product was crystallized from acetic acid, containing small amounts of water. Properties and yields of the azo compounds are given in Tables I and II.

Several attempts to obtain a coupling product from the ortho amine were not successful.

Action of Nitrosyl Chloride on *o*-Aminobenzyltrimethylsilane.—An ethereal solution of 25.6 g. (0.14 mole) of *o*-aminobenzyltrimethylsilane was cooled to −10° in an ice-salt-bath. With mechanical stirring, a cold solution of 9.6 g. (0.15 mole) of nitrosyl chloride in ether was added through a condenser cooled with Dry Ice. Addition was carried out slowly, the reaction mixture becoming orange and cloudy and finally forming black tar. After reaction was complete, the ether and any unreacted nitrosyl chloride were removed by vigorous suction with a water-pump. Ice cold water was added and one portion of the black solution resulting was added to boiling water in an attempt to form the phenol. The remainder of the diazonium solution was added to a solution of excess potassium iodide. Steam distillation of both portions of the reaction gave small amounts of dark oil and some yellow solid. Distillation of the organic material from either phase of the reaction gave no identifiable material other than this solid. Combination of the solid from both phases gave 2.7 g. (16%) of indazole, m.p. 147–148°, identified by an undepressed melting point with an authentic sample.[3]

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[3] See *Org. Syntheses*, **20**, 73 (1940).

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The Ethanolysis of Allyl Benzenesulfonate

BY CLARENCE G. BERGSTROM AND SAMUEL SIEGEL

In connection with another investigation[1] information on the kinetics of the ethanolysis of allyl

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[1] C. G. Bergstrom and S. Siegel, THIS JOURNAL, **73**, 145 (1951).