166–167°,[10] 167–168°[11]). A mixture melting point of this material with an authentic sample was not depressed.

Indene reactions. The dark oil from a typical run was extracted with hot glacial acetic acid; upon cooling a colorless crystalline material separated from the acetic acid solution. The solid was washed with a mixture of acetic acid and methanol and recrystallized from glacial acetic acid to yield *2-indanylphosphonic acid,* m.p. 195–196° (reported[12] m.p. 196°). The infrared spectrum (Nujol mull) of this material was identical to that of an authentic sample of 2-indanylphosphonic acid.

The dark material remaining after acetic acid extraction was further extracted with ether. Evaporation of the ethereal solution yielded a solid which was recrystallized from ether to yield *2-(1-indanyl)-indene* (14–31%), m.p. 56–57° (reported[5] m.p. 57–58°). The identity of this material was confirmed by comparison of infrared spectra and lack of mixture melting point depression with an authentic sample of 2-(1-indanyl)-indene.

The ether insoluble material remaining after the isolation of 2-(1-indanyl)-indene was extracted with 20% aqueous potassium hydroxide. The basic extract was acidified with sulfuric acid and filtered (60°); upon cooling, a crystalline material precipitated. Recrystallization of this material from a mixture of benzene and petroleum ether gave *3-isochromanone* (8–21%), m.p. 81–83° (reported m.p. 81–83°,[4] 83°[3]). The identity of this product was confirmed by infrared and mixture melting point methods. No 3-isochromanone was detected when an indene/phosphorous acid reaction was conducted in a nitrogen atmosphere.

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[10] J. O. Clayton and W. L. Jensen, *J. Am. Chem. Soc.,* **70,** 3880 (1948).

[11] R. Graf, *Chem. Ber.,* **85,** 9 (1952).

[12] E. Bergmann and A. Bondi, *Ber.,* **63,** 1158 (1930).

4-Fluoro- and 3,4-Difluorobenzoic Acids: An Isomorphic Pair

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We recently had occasion to prepare 3,4-difluorotoluene (I). As a proof of structure, the material was oxidized to the known 3,4-difluorobenzoic acid (II). We should like to record our observations with this acid and 4-fluorobenzoic (III).

The product obtained on oxidation of I, when crystallized from toluene, melted at 184–185°.[1] The melting point of III is 184–186°. The melting point of a mixture of the oxidation product with an authentic sample of III was 183–184°. The neutral equivalent of the oxidation product was determined to be 158 (theory for II, 158). The neutral equivalent of the authentic sample of III was determined to be 142.8 (theory, 140). A fluorine analysis of the oxidation product gave a value consistent with its formulation as 3,4-difluorobenzoic acid. These data suggested an isomorphic relationship between II and III.

J. W. Turley of Dow's Spectroscopy Laboratory obtained single-crystal x-ray diffraction photographs of the two acids and indicated them to be isomorphic crystals with the following unit cell constants:

4-Fluorobenzoic	3,4-Difluorobenzoic
a = 26.64 Å	a = 26.96 Å
b = 6.421 Å	b = 6.529 Å
c = 3.835 Å	c = 3.795 Å
B = 109.9°	B = 101.5°
Space group Pz/N	Space group Pz/N

EXPERIMENTAL

2-Fluoro-5-methylaniline. 3-Bromo-4-fluorotoluene (75.6 g.), ammonium hydroxide (220 g., 27.5% NH_3) and cuprous oxide (6.5 g.) were charged to a stainless steel bomb. The bomb was agitated by rocking and heated at 175–180° for a period of 5 hr. The cooled reaction mixture was filtered through a supercel filter pad to remove catalyst and sludge. The sludge was washed with ether and the filtrate extracted with ether. The combined ether layers were extracted with dilute hydrochloric acid until no more color went into the aqueous phase. Unreacted 3-bromo-4-fluorotoluene was recovered from the ether. The aqueous phase was made alkaline with 20% sodium hydroxide. The dark oil which separated was taken up in ether and the aqueous phase was extracted with ether several times. The combined ether extracts was dried over anhydrous magnesium sulfate overnight. The solvent was removed by distillation and the residual liquid was distilled under reduced pressure. The fraction boiling 80–86°/11 was collected. This amounted to 30.9 g. or 61.8% of the theoretical. The literature reports a b.p. of 88–90/17 mm.[2]

2-Fluoro-5-methylbenzenediazonium fluoborate. 2-Fluoro-5-methylaniline (37.1 g.) was dissolved in a mixture of 100 ml. of fluoboric acid (48–50%) and 100 g. of ice. With stirring and while maintaining the temperature below 10°, a solution of 21.0 g. of sodium nitrite in 35 ml. of water was added slowly. A precipitate formed as the reaction proceeded. The mixture was stirred at 0° for 0.5 hr. after the nitrite solution had been added. The salt was collected by filtration, washed with 50 ml. of 5% fluoboric acid, 50 ml. of ice-cold absolute methanol and then with several portions of anhydrous ether. The product was air dried for several hours and finally kept in a vacuum desiccator over calcium chloride overnight. There was obtained 60.0 g. of pale tan solid, decomposing at 140–145° (vigorous evolution of gas). Yield, 90.2%.

3,4-Difluorotoluene. 2-Fluoro-5-methylbenzenediazonium fluoborate (60.0 g.) was placed in a 500 ml. three necked flask, fitted with a thermocouple, stirrer, and air condenser. The air condenser was connected downward to a cold water condenser by means of an adapter carrying a thermometer. 1,2,4-Trichlorobenzene (250 ml.) was added to the reaction flask and, with vigorous stirring, heating was begun. A white gas began to evolve at 100°. As this initial reaction subsided, the temperature was again raised slowly and evolution of gas was again apparent at 140°. The temperature was slowly raised as the reaction proceeded until the temperature at the top of the air condenser had reached 195°. The reaction was stopped by cooling. The material which had collected in the receiver connected to the cold water condenser was dried over calcium chloride overnight and distilled through a short Vigreaux column. The fraction

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[1] J. T. Minor and C. A. Vanderwerf, *J. Org. Chem.,* **17,** 1429 (1952) report a m.p. of 119.2–120.1 for the hydrate of this compound (0.5 H_2O).

[2] Ng. Ph. Buu-Hoï and Ng. D. Xuong, *J. Chem. Soc.,* 386 (1953).

boiling at 100–120° was redistilled through an 8-inch vacuum jacketed glass helices packed column and the fractions boiling at 110–112° (I), and 112–113° (II) were collected. Fraction I had n_D^{24} 1.4475, while Fraction II gave n_D^{24} 1.4473. Yield, 18.7 g. (41.9%).

Anal. Calcd. for $C_7H_6F_2$: C, 65.63; H, 4.72; F, 29.66. Found: C, 65.89; H, 4.22; F, 30.21.

3,4-Difluorobenzoic acid. 3,4-Difluorotoluene (0.9 g.) was oxidized to the corresponding acid according to procedure 32B in "Identification of Organic Compounds," 2nd edition, Shriner and Fuson, John Wiley & Sons, p. 164. The product, recrystallized from toluene, melted at 184–185° and had a neutral equivalent of 158 (theory, 158).

Anal. Calcd. for $C_7H_4F_2O_2$: F, 24.03. Found: F, 23.72.

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Addition of Silicon Hydrides to Olefinic Double Bonds. IV. The Addition to Styrene and α-Methylstyrene

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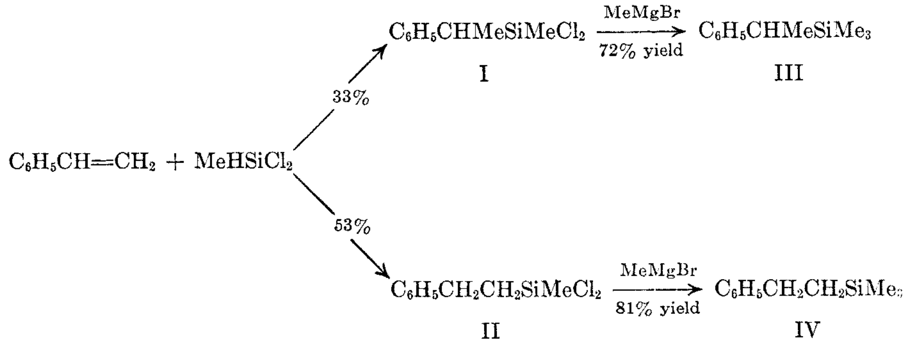
Styrene with methyldichlorosilane in the presence of platinized carbon has recently[1] been described as giving only (2-phenylethyl)methyldichlorosilane. Careful experiments repeated several times now indicate two isomeric products form with either platinized carbon or chloroplatinic acid. The two products are the 1- and the 2-phenylethylmethyldichlorosilane in a ratio of approximately 33 to 53. The mixture has physical properties very nearly coinciding with those previously reported[1] as those of 2-phenylethylmethyldichlorosilane.

Careful distillation separated the isomers which were methylated to form obviously different derivatives (see Table I).



The structure of IV was confirmed by the agreement of its physical properties with those of an authentic sample prepared from trimethylchlorosilane and 2-phenylethylmagnesium bromide.[1,2] The NMR proton spectra of I, II, III, and IV were consistent with the structures assigned.[3]

From these data we conclude that styrene forms two adducts. However, experiments indicated that only one product formed with α-methylstyrene under the same conditions. Only one product (V) was detected by distillation. This product was methylated to form apparently pure VI (2-phenylpropyl)trimethylsilane as judged by distillation, gas liquid phase chromatography and by a NMR proton spectrum. The spectrum clearly showed the presence of phenyl, $SiCH_3$, —CH_2—, and —$CHCH_3$— groups.

Methylcyclosiloxanes $(MeHSiO)_n$ react very well with α-methylstyrene in the presence of chloroplatinic acid to form nearly quantitative yields of (2-phenylpropyl)methylcyclosiloxanes. The structure of these was established by the NMR proton spectra and also in one case by converting the adduct to VI by way of (2-phenylpropyl)methyldifluorosilane and methylmagnesium bromide.

Hydrolysis of (2-phenylpropyl)methyldichlorosilane gave a polysiloxane mixture from which was isolated a cyclic trimer (VII). The trimer (VII) was also isolated as the most volatile product formed in the alkaline depolymerization of the adduct obtained with 1,3,5,7,9-pentamethylcyclopentasiloxane.

sym-Tetramethyldisiloxane gave an 81% yield of 1,3-bis(2-phenylpropyl)tetramethyldisiloxane (IX) and trichlorosilane gave 67% (2-phenylpropyl)trichlorosilane (X). These products were assigned their structures largely on the basis of their NMR proton spectra. All of the adducts had spectra clearly indicative of (2-phenylpropyl) structures free of any detectable impurities.

EXPERIMENTAL

Styrene and methyldichlorosilane. Styrene (921 g., 8.85 mol.), *t*-butylcatechol (0.1 g.) and 8 × 10^{-5} mol. of chloroplatinic acid (added as a 0.06*M* solution in dioxane ethanol) was heated to 90° in a 3-l., three necked flask equipped with an addition funnel, reflux condenser, and thermometer Methyldichlorosilane (1120 g., 9.73 mol.) was added during 2 hr. so that the heat of reaction maintained the mixture between 90 and 130°. Distillation then gave: (I), 642 g.,

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(1) Part II of this series; J. L. Speier, J. A. Webster, and G. H. Barnes, *J. Am. Chem. Soc.*, **79**, 974 (1957).

(2) H. Gilman and F. J. Marshal, *J. Am. Chem. Soc.*, **71**, 2066 (1949).

(3) All NMR spectra and their interpretation were obtained by P. C. Lauterbur, Mellon Institute, Pittsburgh, Pa.