2. This method which allows both for the variation of the alkyl and the aryl groups gives mixtures of isomers in all cases tried thus far.

IOWA CITY, IOWA RECEIVED DECEMBER 12, 1945

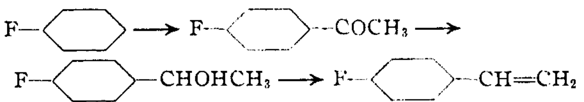
[CONTRIBUTION FROM THE CENTRAL RESEARCH DEPARTMENT, MONSANTO CHEMICAL COMPANY]

Vinyl Aromatic Compounds. III. Fluorinated Derivatives[1]

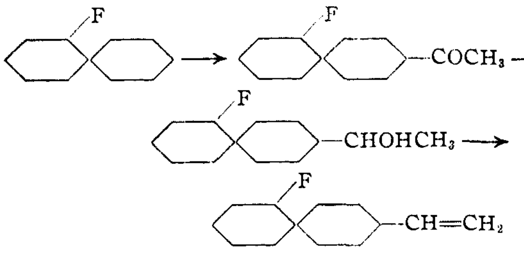
BY MARY W. RENOLL[1a]

As part of a study on substituted styrenes, vinyl derivatives of fluorinated benzene, toluene and biphenyl have been prepared, with the fluorine located in the benzene ring or in a methyl side chain. In all cases a fluorinated hydrocarbon was the starting point of the syntheses and the problem was thus one of introducing the vinyl substituent.

When the fluorine atom is in the ring the fluorinated hydrocarbon can be subjected to acetylation with acetic anhydride in presence of aluminum chloride, without loss of fluorine. This yields a methyl aryl ketone which can be reduced to a secondary carbinol; dehydration of the latter yields the desired vinyl compound. *p*-Fluorostyrene and 2-fluoro-4'-vinylbiphenyl were prepared in this way according to the following series of reactions:

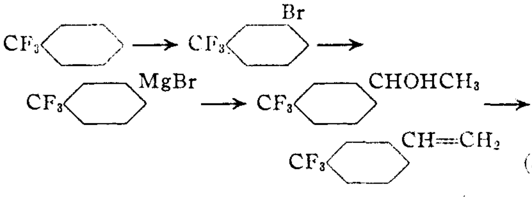


(1)



(2)

When the fluorine is present in a methyl side chain, as in benzotrifluoride, the above procedure cannot be used because of the halogen exchange which occurs between the organic fluoride and aluminum chloride.[2] It is, however, possible to introduce a bromine atom in a position meta to the trifluoromethyl group, transform the bromide into a Grignard reagent[3] and condense the latter with acetaldehyde. This series of reactions gives a methyl aryl carbinol which by dehydration yields the desired vinyl compound, *m*-trifluoromethylstyrene.



(3)

Only in series (2) is there a problem of structure determination. In 2-fluorobiphenyl, acetylation could affect the fluorinated ring but this was conconsidered improbable since the ortho–para-directing influence of the fluorine atom would be hindered by the phenyl group and reaction would be slower than in an unsubstituted ring. Also, it is known that nitration of 2-fluorobiphenyl[4] gives only traces of 2-fluoro-4-nitrobiphenyl, the main products being 2-fluoro-4'-nitrobiphenyl and 2-fluoro-2'-nitrobiphenyl. Oxidation of 2-fluorobiphenyl methyl ketone gave a fluorobiphenyl carboxylic acid. To establish the structure definitely the ketone was hydrogenated under conditions which would simultaneously eliminate fluorine as hydrogen fluoride, and saturate the aromatic ring.[5] The *p*-cyclohexylethylbenzene formed was found to be identical with a sample obtained by the reduction of *p*-phenylacetophenone. That hydrogenation had affected the benzene nucleus which was non-acetylated was confirmed by oxidation to terephthalic acid. It was thus proved that the introduction of the acetyl group in 2-fluorobiphenyl has taken place in the para position of the non-fluorinated ring.

The molecular refractions, MR_D, were calculated by means of the Lorentz–Lorenz formula. The atomic refraction for fluorine, AR_F, was obtained by subtracting from the molecular refraction the increments for C(2.418), H(1.100), Br(8.865), benzene ring (5.199), and O(carbonyl 2.211 or hydroxyl 1.525). The exaltation, EM for MR_D +1.17, for styrene was applied as a correction in calculating AR_F for *p*-fluorostyrene and *m*-trifluoromethylstyrene. A similar correction, EM for MR_D +0.78, for acetophenone was applied in the case of *p*-fluoroacetophenone. The theoretical values used are those reported by Eisenlohr.[6] All the compounds studied show values for AR_F in line with those found in aliphatic compounds.

---

(1) The preceding paper of this series, Huber, Renoll, Rossow and Mowry, THIS JOURNAL, **68**, 1109 (1946).

(1a) Present address: Chemistry Department, The Ohio State University, Columbus, Ohio.

(2) Henne and Newman, THIS JOURNAL, **60**, 1697 (1938).

(3) Simons and Ramler, *ibid.*, **65**, 389 (1943).

(4) van Hove, *Bull. classe sci., Acad. roy. Belg.*, [5] **8**, 505 (1922).

(5) Swarts, *ibid.*, **6**, 399 (1920).

(6) Eisenlohr, *Z. physik. Chem.*, **A75**, 585 (1910); Auwers and Eisenlohr, *J. prakt. Chem.*, **84**, 1 (1911).

Experimental[7]

_p_-Fluoroacetophenone.[8]—This compound was prepared from fluorobenzene in 74% yield by the Friedel–Crafts reaction following the usual procedure.[9] It boiled at 79.0° (10 mm.), f. p. −2.7°, d^{25}_{4} 1.1382, n^{25}_{D} 1.5081, MR_D 36.19, AR_F 1.09.

_p_-Fluorophenylmethylcarbinol.[10]—By hydrogenation of 502 g. of ketone at 132° and 1660 lb. pressure over copper chromite catalyst there was obtained 496 g. (98.4%) of carbinol, a colorless liquid boiling at 90.5° (10 mm.), f. p. 9.3°, d^{25}_{4} 1.1108, n^{25}_{D} 1.4980, MR_D 36.99, AR_F 1.02. *Anal.* Calcd. for C_8H_9OF: F, 13.56. Found: F, 13.71.[11] In one run in which part of the catalyst had been re-used several times, a higher temperature was required to complete the reduction and there was obtained a 10% yield of *p*-fluoroethylbenzene, boiling at 139–141° (748 mm.), d^{25}_{4} 0.9743, n^{25}_{D} 1.4707, MR_D 35.59, AR_F 1.15.

The carbinol obtained by reduction of the ketone with aluminum isopropoxide as described for *p*-chloroacetophenone,[12] was identical with that from catalytic hydrogenation.

_p_-Fluorostyrene.[10,13]—The carbinol (350 g.) was dehydrated by passage at 285–300° and 65–70 mm. pressure through a 20 mm. i. d. silica tube filled to a length of about 60 cm. with 4–8 mesh activated alumina, and mounted in a vertical position. The rate of addition of the carbinol was approximately 2 drops per sec. The product was collected in a receiver cooled in "Dry Ice." When all the carbinol had been added the tube was washed with a little benzene and the washings added to the main product. After separation of water, the benzene was removed under reduced pressure and *p*-fluorostyrene was fractionally distilled at 50 mm. in the presence of hydroquinone as a polymerization inhibitor. The yield was 271. g. (89%). The product was a colorless liquid boiling at 67.4° (50 mm.), f. p. −34.5°, d^{25}_{4} 1.0178, n^{25}_{D} 1.5130, MR_D 36.07, AR_F 0.92.

Anal. Calcd. for C_8H_7F: F, 15.56. Found: F, 15.46.

2-Fluoro-4′-acetylbiphenyl.—2-Fluorobiphenyl was prepared in 60% yield from 2-amino-biphenyl by the method of Schiemann and Roselius.[14] A solution of 400 g. of 2-fluorobiphenyl in one liter of carbon bisulfide was acetylated by the Friedel–Crafts reaction following the usual procedure.[9] Recrystallization from benzene–hexane (equal volumes) gave 386 g. (77.7%) of ketone, colorless prisms, m. p. 84–85.5°.

Anal. Calcd. for $C_{14}H_{11}OF$: F, 8.87. Found: F, 8.72.

2-Fluoro-4′-biphenylylmethylcarbinol.—Reduction of 324 g. of ketone by aluminum isopropoxide[12] gave 266 g. (81.6%) of carbinol after recrystallization from benzene-hexane (equal volumes). The fine colorless needles melted at 87–88.5°; mixed m. p. with ketone 59–61.5°. Catalytic hydrogenation of 350 g. of ketone in 350 ml. of ethanol over copper chromite gave a quantitative yield of carbinol.

Anal. Calcd. for $C_{14}H_{13}OF$: F, 8.79. Found: F, 8.72.

2-Fluoro-4′-vinylbiphenyl.—A solution of 363 g. of carbinol in 700 ml. of dioxane was dehydrated at 300 ± 5° and 40–50 mm. pressure over alumina as previously described. After removal of dioxane under reduced pressure the residue was distilled using sulfur as a polymerization inhibitor. The yield of vinyl compound boiling at 105–107° (1 mm.), m. p. 34–35.5°, was 255 g. (76.6%). After two recrystallizations from 95% ethanol the melting point remained unchanged at 37.2–37.8°; yield 244 g. (73.3%).

Anal. Calcd. for $C_{14}H_{11}F$: F, 9.58. Found: F, 9.53.

Proof of Structure.—Oxidation of the ketone with chromic anhydride in glacial acetic acid[15] gave fine needles melting at 230–231°, slightly soluble in benzene, insoluble in hexane. The analytical figures indicate that it is a biphenylcarboxylic acid containing fluorine. That the acetyl group was originally present in the para position on the benzene ring is indicated by comparison of the melting point with values for the unsubstituted biphenylcarboxylic acids (*o*- 110°, *m*- 159°, *p*- 221°).

Anal. Calcd. for $C_{13}H_9FO_2$: F, 8.79; neut. equiv., 216. Found: F, 8.45; neut. equiv., 214.

Hydrogenation of the ketone in methylcyclohexane over nickel supported on kieselguhr at 125–150° and 2000 lb. of hydrogen pressure gave a liquid product. After fractional distillation the main portion boiled at 136–138° (13 mm.) n^{25}_{D} 1.5167, d^{25}_{4} 0.9291 and was identified as *p*-cyclohexylethylbenzene by oxidation to terephthalic acid[16] and by analysis.

Anal. Calcd. for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 88.88; H, 10.80.

A qualitative test for fluorine was negative. *p*-Phenylacetophenone was reduced under similar conditions and gave a liquid product which on fractionation yielded a main portion, b. p. 137.2–137.8° (13 mm.), n^{25}_{D} 1.5154, d^{25}_{4} 0.9246. It was identified as *p*-cyclohexylethylbenzene by oxidation to terephthalic acid[16] and by analysis.

Anal. Calcd. for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.41; H, 10.85.

_m_-Trifluoromethylphenylmethylcarbinol.—*m*-Bromobenzotrifluoride was prepared from benzotrifluoride in 50% yield as described by Simons and Ramler.[3] It boiled at 155.3°, d^{25}_{4} 1.6206, n^{25}_{D} 1.4705, MR_D 38.77, AR_F 1.13. To the Grignard reagent from 397 g. of *m*-bromobenzotrifluoride, 45 g. of magnesium and 425 ml. of ether there was added during two hours a solution of 82 g. of acetaldehyde in 100 ml. of ether at 2–3° with vigorous stirring. The reaction product was poured over 1 kg. of cracked ice and 500 ml. of 15% sulfuric acid added with stirring. The ether layer was separated and the water layer extracted three times with ether. After removal of ether under reduced pressure there was obtained 249 g. (79.5%) of the carbinol which boiled at 99–99.5° (15 mm.), froze to a glass in "Dry Ice," d^{25}_{4} 1.2369, n^{25}_{D} 1.4560, MR_D 41.79, AR_F 1.14.

Anal. Calcd. for $C_8H_9OF_3$: F, 29.97. Found: F, 29.91.

_m_-Trifluoromethylstyrene.—The carbinol (479 g.) was dehydrated at 290–310° and 70 mm. pressure over alumina as previously described. After removal of benzene under reduced pressure the styrene distilled in presence of hydroquinone as polymerization inhibitor at 78–79° (57 mm.). The yield was 342 g. (79%). When redistilled it boiled at 76.2° (55 mm.), froze to a glass below −100°, d^{25}_{4} 1.1588, n^{25}_{D} 1.4632, MR_D 40.93, AR_F 1.12.

Anal. Calcd. for $C_9H_7F_3$: F, 33.11. Found: F, 32.87.

---

(7) All melting points were determined with an Anschütz thermometer and were not corrected for stem immersion. The freezing points were determined with a calibrated thermocouple and are accurate to ±0.2°.

(8) Evans, Morgan and Watson, *J. Chem. Soc.*, 1167 (1935).

(9) Adams and Noller, "Organic Syntheses," Coll. Vol. I, 2nd ed., p. 109.

(10) Since the completion of this work, the preparation of this compound by a somewhat different method of synthesis has been reported by Brooks, THIS JOURNAL, **66**, 1295 (1944).

(11) All the fluorine analyses were carried out by decomposition of the sample with sodium peroxide (Parr bomb) in the usual manner and precipitation of the fluorine as lead chlorofluoride. The procedure was adapted from Furman, "Scott's Standard Methods of Chemical Analysis," D. Van Nostrand Co., New York, N. Y., 1939, Vol. I, p. 405.

(12) Marvel and Schertz, THIS JOURNAL, **65**, 2054 (1943).

(13) A product composed of a mixture of *o*- and *p*-fluorostyrenes has been reported by Dreisbach, U. S. Patent 2,226,809 (1940).

(14) Schiemann and Roselius, *Ber.*, **62B**, 1805 (1929).

(15) Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1935, p. 230.

(16) Identified through its dimethyl ester (see Norris, "Experimental Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., second edition, 1924, p. 173).

Acknowledgment.—The assistance of Dr. David T. Mowry and Dr. W. Frederick Huber in carrying out the dehydrations and some of the reductions is gratefully acknowledged.

Summary

p-Fluorostyrene and 2-fluoro-4′-vinylbiphenyl have been synthesized from the corresponding methyl aryl ketones by reduction to the secondary carbinol and dehydration of the latter to the vinyl derivative.

m-Trifluoromethylstyrene has been prepared by dehydration of the secondary carbinol which was obtained through the Grignard reaction from *m*-bromobenzotrifluoride.

DAYTON, OHIO RECEIVED MARCH 6, 1946

[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT AND THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY]

Methylbromosilanes

BY W. F. GILLIAM, R. N. MEALS[1] AND ROBERT O. SAUER

Mixtures of the methylbromosilanes were first prepared by Rochow[1a] by the vapor phase reaction of methyl bromide with copper–silicon masses. This alkyl halide reacts smoothly at about 300° to give a dense liquid condensate from which we have isolated methyltribromosilane, dimethyldibromosilane, and trimethylbromosilane. In addition, indications of small amounts of tribromosilane and silicon tetrabromide have been found in the crude product. It is interesting to note that the apparent anomaly in the boiling points of the methylchlorosilanes[2] is not repeated with the methylbromosilanes; the boiling points of the latter all lie within the range fixed by the boiling points of silicon tetramethyl (27°) and silicon tetrabromide (151°).

Trimethylbromosilane has also been synthesized in good yield by the action of phosphorus tribromide on hexamethyldisiloxane. This reaction is analogous to the cleavage of alkoxysilanes by phosphorus trichloride, as reported by Friedel and Ladenburg.[3]

As further evidence of the identity of the di- and tribromo compounds we have also prepared the 2-bromoethyl ethers by the action of ethylene oxide.[4] In the case of trimethylbromosilane hydrolysis yielded the known hexamethyldisiloxane. The properties of the new compounds prepared are given in Table I.

TABLE I

THE NEW METHYLBROMOSILANES AND METHYL-2-BROMOETHOXYSILANES

Formula	B. p., °C.	Press., mm.	d^{20}_4 (vac.)	n^{20}_D
$(CH_3)_3SiBr$	79.9	754	1.189	....
$(CH_3)_2SiBr_2$	112.3	760	1.727	....
CH_3SiBr_3	133.5	764	2.253	....
$(CH_3)_2Si(OCH_2CH_2Br)_2$	95	3	1.5425	1.4780
$CH_3Si(OCH_2CH_2Br)_3$	130–131	1	1.7635	1.5001

Our experiments indicate that occasionally some of our samples of dimethyldibromosilane were contaminated by an impurity which was presumed to be tribromosilane because of the proximity of its boiling point (111.8°) to that of dimethyldibromosilane (112.3°) and the fact that trichlorosilane is a product of the reaction[1a] of methyl chloride with copper–silicon. We found that this impurity could be eliminated by treatment of the sample with bromine, removal of the excess bromine with mercury, and subsequent distillation to obtain the pure dimethyldibromosilane.

Since we were unable to find a literature reference to the reaction

$$HSiBr_3 + Br_2 \longrightarrow SiBr_4 + HBr$$

we treated tribromosilane[5] with bromine to provide assurance that bromination did occur. We found, as expected,[5a] that tribromosilane slowly decolorized bromine at room temperature, and that the reaction was decidedly photosensitive.

Experimental

Dimethyldibromosilane and Methyltribromosilane—Run 1.—A mixture of crude products[1a,6] prepared by passing methyl bromide over a pressed sintered mass of copper–silicon (20:80) at 275° was fractionally distilled in a 0.8 × 65 cm. column[6a] of approximately 50 theoretical plates packed with 1/16-in., single turn helices made from platinum–iridium wire. From a definite plateau in the boiling point curve a middle fraction, b. p. 112.3° at 760 mm., was separated. Analysis showed this substance to be **dimethyldibromosilane.**

Anal. Calcd. for $C_2H_6SiBr_2$: Br, 73.33. Found: Br, 73.4, 73.0.

A middle fraction, b. p. 133.5° at 764 mm., from a second plateau was identified as **methyltribromosilane.**

---

(1) Present address: Buckman Laboratories, Memphis, Tenn.

(1a) Rochow, THIS JOURNAL, **67**, 963 (1945).

(2) Gilliam, Liebhafsky and Winslow, *ibid.*, **63**, 801 (1941).

(3) Friedel and Ladenburg, *Ann.*, **145**, 179 (1868).

(4) Sauer and Patnode, THIS JOURNAL, **67**, 1548 (1945).

(5) The authors desire to thank Prof. Walter Schumb of the Massachusetts Institute of Technology who kindly supplied the sample of pure tribromosilane used in this experiment.

(5a) Ladenburg [*Ann.*, **164**, 329 (1872)] and Kraus and Nelson [THIS JOURNAL, **56**, 195 (1934)] brominated triethylsilane to give triethylbromosilane, and Friedel and Ladenburg [*Ann.*, **145**, 187 (1867)] isolated trichlorobromosilane as a bromination product of trichlorosilane.

(6) The authors wish to thank Dr. E. G. Rochow of the Research Laboratory who prepared and kindly provided this material.

(6a) Whitmore, *et al.*, THIS JOURNAL, **62**, 797 (1940).