4',5'-tetrahydrophenyl)-naphthalene with a chromia–alumina or palladium-on-charcoal catalyst at 450–525° gives fluoranthene. Similar treatment of 1,2'-dinaphthyl gives a mixture of two hydrocarbons to which the structures of 7,8- and 8,9-benzfluoranthenes have been tentatively assigned.

PITTSBURGH, PENNSYLVANIA RECEIVED JULY 2, 1946

[CONTRIBUTION FROM THE VENABLE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

The Synthesis of Some Fluorohydroxybiphenyls

BY ARTHUR ROE AND H. L. FLEISHMAN[1]

The preparation and bactericidal properties of several alkyl fluorophenols were reported by Suter, Lawson and Smith[2]; one other related compound, 1-(2-hydroxy-5-fluorophenyl)-2-pentene, was reported by Deischel[3] to have bactericidal properties. No fluorohydroxybiphenyls are reported in the literature; the present synthesis of some of them was undertaken in view of the bactericidal properties shown by the alkyl fluorophenols and by certain 4-halo-4'-hydroxybiphenyls.[4a,b] This investigation is part of a study of the preparation and properties of aromatic and heterocyclic fluorine compounds under way in this Laboratory.

The new fluorohydroxybiphenyls are shown in the following table; all are white crystalline solids.

TABLE I

	Compound	M. p., °C.
I	4-Fluoro-4'-hydroxybiphenyl	167–168
II	2-Fluoro-2'-hydroxybiphenyl	103.5–104.5
III	2-Fluoro-4'-hydroxybiphenyl	131.5–133
IV	4,4'-Difluoro-2-hydroxybiphenyl	93.5–94.5

Fluorine was introduced using the method developed by Balz and Schiemann[5]; the phenolic groups were then introduced by standard methods starting from the corresponding nitro compounds.

A fifth compound was prepared but was not included in the above table because its structure is not known with certainty; available evidence indicates that it is 4,4'-difluoro-2,3'-dihydroxybiphenyl (V). The dinitro-4,4'-difluorobiphenyl from which V was prepared is, according to Shaw and Turner,[6] probably the 2,3'-dinitro derivative, although it may be 2,2'-dinitro-4,4'-difluorobiphenyl. Further work is being done to clarify the structure of this compound.

The bactericidal properties of these compounds will be reported elsewhere.

Experimental

4-Fluoro-4'-hydroxybiphenyl (I).—The preparation of 4-fluorobiphenyl in 82% yield was carried out essentially as outlined by Schiemann and Roselius,[7] except that $NaBF_4$ was used as a source of the fluoborate ion instead of HBF_4. The diazonium sulfate obtained by diazotization of 7 g. of 4-fluoro-4'-biphenylamine[8] was added slowly to a boiling mixture of 24 cc. of concentrated sulfuric acid and 18 cc. of water. The solution was boiled for five minutes after addition was complete, cooled and the insoluble material filtered off and dissolved in sodium hydroxide. Upon acidification 4 g. of crude (I) was obtained. Repeated crystallization from alcohol and petroleum ether would not remove the yellow color, so the material was refluxed with a small amount of tin and hydrochloric acid, then recrystallized from alcohol; colorless needles, m. p. 167–168°.

Anal.[9] Calcd. for $C_{12}H_9OF$: F, 10.09. Found: F, 10.36, 10.36.

2-Fluoro-2'-nitrobiphenyl (VI).—Diazotization of 30 g. of 2'-nitro-2-biphenylamine[10] followed by the addition of 30 g. of $NaBF_4$ dissolved in 40 cc. of water, produced a copious precipitate of 2'-nitro-2-biphenyldiazonium fluoborate (VII). The precipitate was washed with 10 cc. of cold saturated $NaBF_4$ followed by four 20-cc. portions of ether, the precipitate being sucked as dry as possible after each washing. The orange solid was then spread on a porous paper and allowed to dry overnight; yield 42 g.; m. p. 87° (dec.). In another run 35 g. of the amine hydrochloride was converted to 41 g. of VII.

The thermal decomposition of VII proceeds with great vigor; this rapid and unruly decomposition is characteristic of diazonium fluoborates containing a nitro group. Part of the salt was decomposed by adding it a little at a time to a flask (fitted with a reflux condenser) held at 100°; steam distillation of the black residue gave only a 10% yield of VI. In an attempt to improve the yield, 40 g. of VII was mixed with 80 g. of sodium fluoride in the hope that the boron trifluoride evolved would be absorbed forming $NaBF_4$, perhaps lessening the violence of the reaction. The mixture was placed in a 2-liter flask fitted with a reflux condenser with a tube leading to a trap containing sodium hydroxide; the reaction was carried out in a hood. Decomposition took place rapidly but with less vigor than before when heat was applied; 4 g. (13%) of pure VI was obtained, m. p. 71–72° (recorded m. p. of VI produced by nitration of 2-fluorobiphenyl,[8] 71.5°).

2-Fluoro-2'-hydroxybiphenyl (II).—Compound VI was reduced to 2-fluoro-2'-biphenylamine as described by Van Hove.[8] Conversion of 4.3 g. of this amine to 1.1 g. of pure II was carried out as described for compound I; colorless needles from alcohol, m. p. 103.5–104.5°.

Anal. Calcd. for $C_{12}H_9OF$: F, 10.09. Found: F, 9.87.

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[1] The work reported in this paper is taken from the Master's thesis submitted by H. L. Fleishman to the Graduate School of the University of North Carolina.

[2] Suter, Lawson and Smith, THIS JOURNAL, **61**, 161–165 (1939).

[3] I. G. Farbenind, A.-G., German Patent 667,063 (November 7, 1938).

[4] (a) Schmidt, Savoy and Abernethy, THIS JOURNAL, **66**, 491 (1944); (b) Savoy and Abernethy, *ibid.*, **64**, 2219 (1942).

[5] Balz and Schiemann, *Ber.*, **60B**, 1186 (1927).

[6] Shaw and Turner, *J. Chem. Soc.*, 509 (1932).

[7] Schiemann and Roselius, *Ber.*, **62B**, 1805 (1929).

[8] Van Hove, *Bull. soc. chim. Belg.*, **32**, 52 (1923).

[9] Fluorine analyses were made by a slight modification of the method of Vaughn and Nieuwland, *Ind. Eng. Chem.*, *Anal. Ed.*, **3**, 274 (1931).

[10] Purdie, THIS JOURNAL, **63**, 2276 (1941).

2-Fluoro-4'-hydroxybiphenyl (III).—The preparation of 2-fluorobiphenyl in 71% yield was carried out essentially as described by Schiemann and Roselius,[7] except that $NaBF_4$ was used as a source of the fluoborate ion instead of HBF_4. Conversion of 7 g. of 2-fluoro-4'-biphenylamine[8] to 1 g. of pure III was carried out as described for compound I; colorless needles from ethanol, m. p. 131.5–133°.

Anal. Calcd. for $C_{12}H_9OF$: F, 10.09. Found: F, 9.98, 10.19.

4,4'-Difluoro-2-hydroxybiphenyl (IV).—The diazonium sulfate prepared from 37 g. of 4,4'-difluoro-2-biphenylamine[6] was added slowly to a boiling mixture of 120 cc. of concentrated H_2SO_4 and 90 cc. of water. Steam distillation produced 29 g. of faintly yellow IV. A second steam distillation gave 20 g. of pure IV; colorless needles from 70% ethanol, m. p. 93.5–94.5°.

Anal. Calcd. for $C_{12}H_8OF_2$: F, 18.43. Found: F, 18.41, 18.58.

$C_{12}H_8O_2F_2$, Probably 4,4'-Difluoro-2,3'-dihydroxybiphenyl (V).—The dinitro-4,4'-difluorobiphenyl (m. p. 106–114°) was prepared following the directions of Shaw and Turner.[5] Recrystallization from various solvents and a second distillation did not change the melting point of the product, which Shaw and Turner found to consist of at least 75% 2,3'-dinitro-4,4'-difluorobiphenyl (m. p. 109–110°), the remainder being 2,2'-dinitro-4,4'-difluorobiphenyl (m. p. 163–165°).

Reduction of 10 g. of the dinitro compound was carried out in the usual way with tin and hydrochloric acid. The mixture was made basic with sodium hydroxide and extracted with ether. The ether solution was dried overnight with solid sodium hydroxide, the ether removed, and the residue distilled under reduced pressure. A fraction of 7 g. of apparently pure material, b. p. 160–162° (3 mm.), was obtained; there was a slight forerun, and a residue of about 2 cc. remained in the flask. Standing at 0° for a week caused solidification to a light yellow mass, m. p. 54–72°. A second distillation and fractional precipitation from acid solution did not change the melting point appreciably.

Conversion of the diamine to V was carried out by adding the diazonium sulfate obtained from 6 g. of the amine to a boiling mixture of 25 cc. concentrated sulfuric acid and 19 cc. of water. The solution was steam distilled; very little product distilled. The solution was extracted with ether and the ethereal solution dried overnight with sodium sulfate; evaporation left 0.5 g. of a white solid which was recrystallized from 70% ethanol; fluffy white needles, m. p. 112.5–113°. This compound is presumably 4,4'-difluoro-2,3'-dihydroxybiphenyl (V).

Anal. Calcd. for $C_{12}H_8O_2F_2$: F, 17.10. Found: F, 17.39.

Summary

Several new fluorohydroxybiphenyls have been prepared: 4-fluoro-4'-hydroxybiphenyl, 2-fluoro-2'-hydroxybiphenyl, 2-fluoro-4'-hydroxybiphenyl, 4,4'-difluoro-2-hydroxybiphenyl, and a compound whose probable structure is 4,4'-difluoro-2,3'-dihydroxybiphenyl.

CHAPEL HILL, NORTH CAROLINA

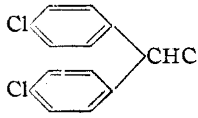
RECEIVED OCTOBER 4, 1946

[CONTRIBUTION FROM THE BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE, AGRICULTURAL RESEARCH ADMINISTRATION, U. S. DEPARTMENT OF AGRICULTURE]

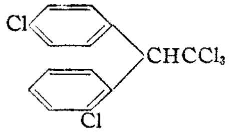
Isolation of the *o,o'*-DDT Isomer from Technical DDT[1,2]

BY STANLEY J. CRISTOL,[2a] S. B. SOLOWAY AND H. L. HALLER

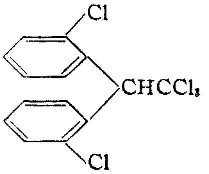
Previous fractionations[3] of various samples of technical DDT have shown that the two major products in the DDT condensation are *p,p'*-DDT (1-trichloro-2,2-bis-(*p*-chlorophenyl)-ethane, I) and *o,p'*-DDT (1-trichloro-2-*o*-chlorophenyl-2-*p*-chlorophenylethane, II). Small amounts of twelve other materials were found, but no other DDT isomer was isolated in that work, although substantial amounts of oily residues were isolated which were not well characterized and were suspected to contain other isomers of DDT. It is the purpose of this paper to describe the work resulting in the isolation of the *o,o'*-DDT isomer (1-trichloro-2,2-bis-(*o*-chlorophenyl)-ethane, III) from technical DDT and in its proof of structure. Isolation of this compound was of interest in the course of a study of the effect of halogen position upon toxicity of DDT isomers.



p,p'-DDT, I



o,p'-DDT, II



o,o'-DDT, III

The methods which had been used previously for separation included fractional crystallization and chromatographic adsorption techniques. In the previous work an oil (oil C, see Chart 1 of reference 3) had been isolated from technical DDT which represented 12.7% of the original technical DDT and from which over 90% of the *p,p'*-DDT and 70% of the *o,p'*-DDT known to be present in technical DDT had been removed. It had been

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[1] This work was conducted as part of a program supported by a transfer of funds, recommended by the Committee on Medical Research, from the Office of Scientific Research and Development and from the Office of the Quartermaster General to the Bureau of Entomology and Plant Quarantine. Not copyrighted.

[2] This paper was presented before the Division of Organic Chemistry at the Atlantic City meeting of the American Chemical Society, April 8–12, 1946.

[2a] Present address: Department of Chemistry, University of Colorado.

[3] Haller, Bartlett, Drake, Newman and co-workers, THIS JOURNAL, **67**, 1591 (1945).