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FLUORINATED BIPHENYL DERIVATIVES

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3 Claims. (Cl. 260—649)

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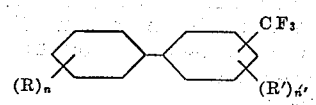
My invention relates to new fluorinated biphenyl derivatives and more particularly refers to biphenyls having substituted thereon at least one trifluoromethyl group. The present application is a continuation-in-part of my copending U. S. patent application Serial No. 785,533, filed November 12, 1947, now abandoned.

It is an object of this invention to produce chemically stable biphenyl derivatives which have substituted thereon fluorine atoms. In a more restricted sense, the invention is concerned with trifluoromethyl substituted biphenyls possessing unusual chemical and electrical stability.

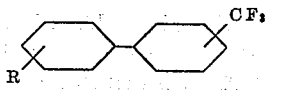
These objects are attained in accordance with the present invention which is directed to biphenyl derivatives having at least one trifluoromethyl group substituted on at least one phenyl nucleus. In one of its limited embodiments the invention is concerned with biphenyl derivatives having a trifluoromethyl group substituted on each of the phenyl nuclei. In one of its preferred embodiments the invention is concerned with a biphenyl derivative having a trifluoromethyl group substituted on one phenyl nucleus and an alkyl group substituted on the other phenyl nucleus.

The compounds of my invention conform to the following general formula:



wherein R and R' represent substituents selected from the group consisting of halogens, alkyl, aryl and aralkyl groups and halogenated derivatives thereof, n represents an integer from 0 to 5, and n' represents an integer from 0 to 4.

The preferred compounds of my invention conform to the formula:



wherein R represents a substituent selected from the group consisting of alkyl groups and fluorinated derivatives thereof.

Among the compounds which conform to the first general formula are the following:

Compound	R	n	R'	n'
x-ethyl-3'-trifluoromethyl-4'-methyl biphenyl and isomers	C_2H_5	1	CH_3	1
3,3'-bis-trifluoromethyl-4,4'-diethyl biphenyl and isomers	CF_3 / C_2H_5	2	C_2H_5	1
2,4,6-trichloro-3'-trifluoromethyl biphenyl and isomers	Cl	3	----	0
3-trifluoromethyl biphenyl	----	0	----	0

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Among the preferred compounds of the invention, conforming to the second general formula are the following:

3,3'-bis-trifluoromethyl biphenyl
2,2'-bis-trifluoromethyl biphenyl
4,4'-bis-trifluoromethyl biphenyl
2,3'-bis-trifluoromethyl biphenyl
2,4'-bis-trifluoromethyl biphenyl
3,4'-bis-trifluoromethyl biphenyl
3-trifluoromethyl-x'-methyl biphenyl
3-trifluoromethyl-x'-octyl biphenyl
3-trifluoromethyl-x'-hexyl biphenyl
3-trifluoromethyl-x'-ethyl biphenyl
3-trifluoromethyl-x'-butyl biphenyl
3-trifluoromethyl-x'-amyl biphenyl
3-trifluoromethyl-x'-propyl biphenyl

and the various isomers of these alkyl substituted compounds.

The compounds of my invention, as shown above, have saturated substituents and are very stable to chemical and electrical action, such as oxidation, hydrolysis and electrolysis. For this reason, they are particularly valuable for use as dielectric materials, as lubricating materials, as heat transfer materials, etc. While the boiling points of some of these compounds are not especially high, all of them are stable and possess desirable viscosity characteristics. Because of the structure of these polar molecules, it is feasible to employ them as intermediates in the synthesis of fine chemicals, pharmaceuticals, dyestuffs and the like. In such applications, atoms other than carbon, hydrogen and halogens can be incorporated in the molecule. For certain applications, the presence of a nitro group is beneficial. For example, 3-trifluoromethyl-2-nitro biphenyl and 3-trifluoromethyl-4'-nitro biphenyl are desirable dielectric additives and, furthermore, are readily prepared.

The following examples will serve to illustrate how the herein described compounds may be prepared.

EXAMPLE I

Preparation of 3,3'-bis-trifluoromethyl biphenyl

To 75 cc. of dry ether in a 2 liter 3 necked flask set up for a Grignard reaction were added 24.5 gms. of magnesium turnings and 140 gms. of anhydrous cupric chloride. Agitation was started, and 10 cc. of m-bromo benzotrifluoride were run in. When the reaction started, the rest (225 gms. total) was run in at such a rate that reflux continued. The mixture was then refluxed for 2 hours, cooled, poured on ice, and treated with excess HCl to redissolve cupric chloride. The ether extracts were shaken with water, dried and filtered, and the ether distilled off. The residue was distilled at reduced pressure through a Wid-

mer column. There was obtained approximately 65 gms. of liquid boiling at 30°–35° C. at 2 mm. (the m-bromo compound) and 75 gms. of the desired product boiling at 80–85° C. at 2 mm. The low boiling material was refractionated to yield 44 gms. of m-bromobenzotrifluoride. The biphenyl derivative was redistilled at 1 mm., and 62 gms. were collected at 78–81° C. to give a yield of 53% based on unrecovered meta-bromo compound.

Fractionated at 1 mm., B. P. 78.5–79.5° C.
Refractive Index 20° C.=1.4899.
Density 20/4=1.3675

EXAMPLE II

Preparation of 3 - trifluoromethyl - x' - methyl biphenyl

200 gms. of m-aminobenzotrifluoride (prepared as described in J. A. C. S. 68 (1946), p. 1603) were dissolved in 300 cc. of concentrated hydrochloric acid to which were added 200 cc. of water. The suspension of amine hydrochloride was cooled to 0–5° C. and diazotized by adding a solution of 94 gms. of sodium nitrite in 186 cc. of water. 760 cc. of toluene were then added to the clear diazo solution. With vigorous agitation 500 cc. of 5 N sodium hydroxide solution were added, the mixture being held at 0–5° C. Agitation was continued for 2 hours at 0–5° C. and for about 16 hours at room temperature. The aqueous layer was removed, and the residue steam distilled. The toluene was removed by distillation at atmospheric pressure and the residue distilled at reduced pressure to give a broad fraction boiling between 71° C. and 80° C. at a pressure of about 0.3 mm. This broad fraction was shaken with concentrated sulfuric acid, washed with caustic and with water, dried and redistilled to give 26 gms. of a colorless liquid boiling between 65° and 68° C. at 0.25–0.3 mm. The product thus obtained had a refractive index at 20° C. of 1.5226 and a density of 1.192.

EXAMPLE III

Preparation of 4,4' - bis - (trifluoromethyl) - biphenyl

2,2'-diamino - 4,4' - bis - (trifluoromethyl)-biphenyl (5 g.) was dissolved in 50% hypophosphorous acid (123,6 g.; 0.94 mole). Water (50 cc.) was added, and the solution was cooled to 5°. A solution of 97% sodium nitrite (2.3 g.) in water (10 cc.) was added, with stirring, over fifteen minutes while the temperature of the reaction mixture was maintained at 0–5°. During the addition of the nitrite solution a tan-colored solid deposited. After addition of the nitrite solution, the reaction slurry was stirred at 0° for one hour, allowed to come to room temperature and finally permitted to stand four hours. The crude product was filtered and steam distilled to yield 1.25 g. (27.6%) of 4,4'-bis - (trifluoromethyl)-biphenyl; colorless crystals; M. P. 82–87°. Crystallization from methanol-water gave colorless plates; M. P. 93–94.5°.

EXAMPLE IV

Preparation of 4,4' - bis-trifluoromethyl-biphenyl

6.2 g. of parabromo benzotrifluoride, .67 g. of magnesium turnings and 50 cc. of dry ether were employed in the usual manner to make a Grignard complex to which was added 6.2 g. of anhydrous silver bromide. The mixture was stirred over night and filtered. The filtrate was washed with dilute hydrochloric acid, then with water, then with dilute sodium hydroxide and finally with water. The organic layer was separated and the ether evaporated therefrom. The residue was 3 g. of crude product with the melting point 75–85° C. Recrystallization was accomplished from water and methanol to give a final pure product melting at 91–92° C. A mixed melting point with this compound and the one produced by Example III gave no melting point depression.

While the examples given above illustrate methods for preparation of the compounds of the invention, other procedures may be employed. For example, it is contemplated that compounds possessing a trifluoromethyl group on each of the phenyl nuclei may be produced by reacting diazotized 3-amino benzotrifluoride with benzotrifluoride, instead of with toluene as in Example II, or by the Ullman synthesis with halogen substituted benzotrifluoride.

As mentioned heretofore, the compounds disclosed herein are useful in a number of fields where great stability to chemical and electrical action is desired. They are especially useful as dielectric materials, for which purpose they must be stable in the electrical field, as well as to oxidation, hydrolysis and the like. For example, the 3,3'-bis-trifluoromethyl biphenyl has a dielectric constant at 1000 cycles and at 28° C. of 8.1 and a power factor under these conditions of 0.06%. Thus the high dielectric constant obtained with such a polar molecule does not suffer from a coincident high loss factor, such as is found with many of the random chlorinated aryl compounds.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope hereof, it is to be understood that the invention is not limited to the specific embodiments hereof except as defined in the appended claims.

What I claim is:

1. A symmetrical bis-trifluoromethyl biphenyl.
2. 3,3'-bis-trifluoromethyl biphenyl.
3. 4,4'-bis-trifluoromethyl biphenyl.

References Cited in the file of this patent

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