

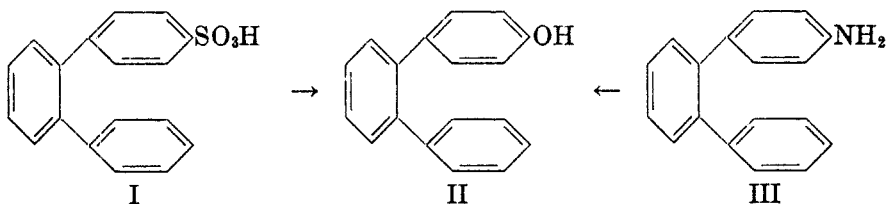
THE CHEMISTRY OF *o*-TERPHENYL. III. SULFONIC ACIDS

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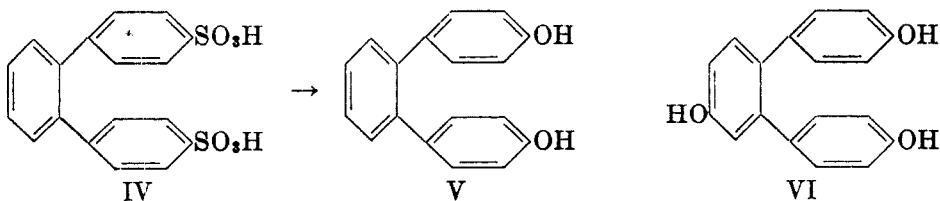
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In previous papers (1, 2, 3) the chemical behavior of *o*-terphenyl with all the common reagents except sulfuric acid has been described. In this communication an account is given of several sulfonic acids which contain the *o*-terphenyl nucleus.

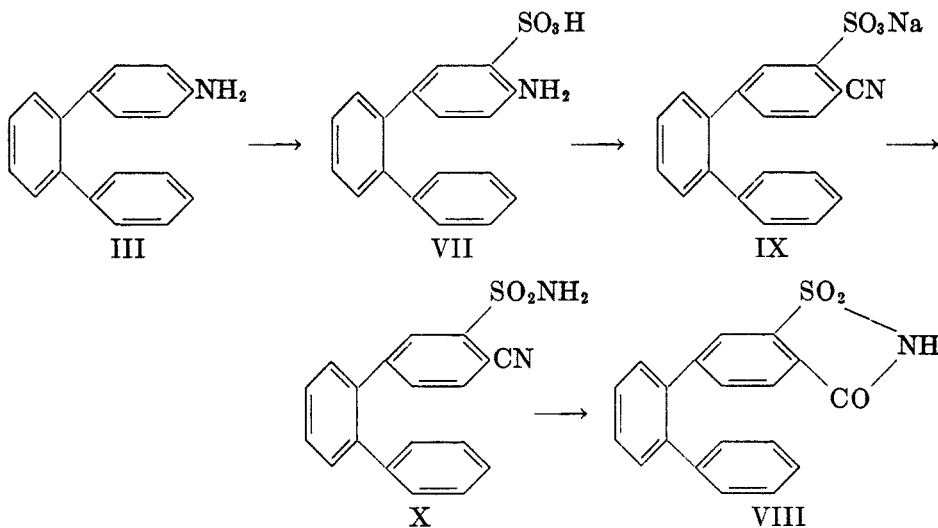
Mono-, di-, and tri-sulfonic acids have been obtained by direct sulfonation of the hydrocarbon; however, the mono-derivative was formed in very low yield. A more satisfactory method for the preparation of *o*-terphenyl-4-sulfonic acid (I) was by treatment of the hydrocarbon with one equivalent of chlorosulfonic acid. The position of the sulfonic acid group was shown by converting it into 4-hydroxy-*o*-terphenyl (II), which was synthesized from 4-amino-*o*-terphenyl (III) by the Sandmeyer reaction. The sulfonic acid was converted to a triphenylguanidine salt and to the sulfonamide.



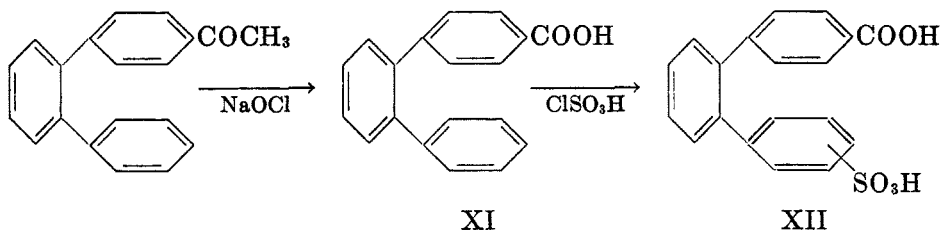
The di- and tri-sulfonic acids were readily obtained by direct sulfonation of the hydrocarbon, with slight changes in acid concentration, time, and temperature. These sulfonic acids were converted in good yield to the corresponding phenols by alkaline fusion. The disulfonic acid (IV) gave the known (4) 4,4'-dihydroxy-*o*-terphenyl (V), thus locating the positions of the sulfonic acid groups. The position of the third acidic radical in the trisulfonic acid has not been determined conclusively. The trihydroxy-*o*-terphenyl formed from it by alkaline fusion is a very weak coupler by photographic tests (5), which observation probably indicates coupling in an *ortho* position; if there were an unoccupied *para* position, the substance would be expected to be a strong coupler. In view of the behavior of *o*-terphenyl on polybromination (2), the third sulfonic acid group in all probability entered the central ring; its replacement by hydroxyl then would have given the triphenol, as shown in (VI).



4-Amino-*o*-terphenyl was monosulfonated by the "bake process," which gave 4-amino-*o*-terphenyl-3-sulfonic acid (VII). For proof of structure, the acid was converted to an analog of saccharin (VIII), thus showing that the groups were *ortho* to each other. The amine (VII) gave a nitrile (IX) by the Sandmeyer reaction; this nitrile then was transformed into the cyanosulfonamide (X) by the usual reactions. Treatment of the amide with sodium hydroxide (6) gave the cyclic derivative (VIII), which, like saccharin, has a sweet taste after the initial bitterness has disappeared.



4-*o*-Terphenoic acid (XI) was monosulfonated, using chlorosulfonic acid in tetrachloroethane. The resulting sulfocarboxylic acid (XII) gave *x*-sulfo-4-*o*-terphenyl dichloride, when treated with phosphorus pentachloride, and the corresponding diamide by the action of ammonia on the dichloride. The 4-*o*-terphenoic acid (XI) was prepared in quantity from 4-acetyl-*o*-terphenyl and sodium hypochlorite.



EXPERIMENTAL

Sodium o-terphenyl-4-sulfonate (I). A solution of 200 g. (0.87 mole) of Santowax O¹ in 600 ml. of dry chloroform was cooled to 10°, and a solution of 110 g. (0.94 mole) of freshly distilled chlorosulfonic acid was added dropwise, with stirring. The solution then was allowed to warm up to room temperature, and finally heated at 50° for four hours. Water (ca. 800 ml.) was added to the cold reaction mixture, and the chloroform removed at re-

duced pressure. The aqueous solution was filtered, neutralized with 750 ml. of a 5% solution of sodium hydroxide, and cooled in an ice-bath. The precipitated sodium salt was filtered and washed with a half-saturated brine solution. The crude salt was recrystallized from 1600 ml. of boiling water to give 234 g. (81%) of white platelets. A sample was recrystallized again from water for analysis.

Anal. Calc'd for $C_{18}H_{13}NaO_3S$: C, 65.0; H, 3.9.

Found: C, 64.5; H, 4.2.

The *1,2,3-triphenylguanidine salt* was prepared from an aqueous solution of the free acid. After two recrystallizations from aqueous methanol (1:3), the salt melted at 239.5–241°.

Anal. Calc'd for $C_{27}H_{21}N_5O_2S$: C, 74.4; H, 5.2.

Found: C, 74.4; H, 5.3.

The *sulfonamide* was prepared from the sodium salt, and recrystallized from benzene; m.p. 182–183°.

Anal. Calc'd for $C_{18}H_{15}NO_2S$: N, 4.5. Found: N, 4.5.

Potassium o-terphenyl-4,4''-disulfonate (IV). A solution of 23 g. (0.1 mole) of Santowax O and 60 g. of concentrated sulfuric acid was heated on the steam-bath for four hours, then cooled and poured upon ice. Sufficient potassium chloride was added to form a 20% solution, and the mixture was stirred for two hours. The precipitated sulfonate salt was removed, washed with a little potassium chloride solution, and recrystallized from 150 ml. of hot water. After a second recrystallization from 100 ml. of water, 23.6 g. (51%) of white glistening plates were obtained. A sample was again recrystallized for analysis.

Anal. Calc'd for $C_{18}H_{12}K_2O_6S_2$: C, 46.3; H, 2.6.

Found: C, 46.2; H, 3.1.

Potassium o-terphenyl-4,4',4''-trisulfonate. A mixture of 115 g. (0.5 mole) of Santowax O and 750 g. of 100% sulfuric acid was heated at 110° (oil-bath temperature) for one and one-half hours. The solution was cooled, and poured upon 2 kg. of ice. After the addition of 480 g. of potassium chloride, the sulfonate salt precipitated. The mixture was cooled in ice, filtered, and washed with cold 20% potassium chloride solution. The crude salt was recrystallized once from 550 ml. of hot water, and twice more using the minimum amount of water. The filter cake was washed with methanol to remove any remaining free acid. The yield of thrice-recrystallized potassium salt dihydrate was 173 g. (54%). A sample was recrystallized once more for analysis.

Anal. Calc'd for $C_{18}H_{11}K_3O_9S_3+2H_2O$: C, 34.8; H, 2.4.

Found: C, 34.5; H, 2.1.

4-Hydroxy-o-terphenyl (II). (a) *From sodium o-terphenyl-4-sulfonate*. A mixture of 240 g. of potassium hydroxide and 10 ml. of water was heated to 250° in a nickel crucible, and 120 g. of powdered sodium *o-terphenyl-4-sulfonate* was added gradually. The melt was heated at 250–280° for one-half hour, and then at 310° for five minutes. The reaction mixture was allowed to cool somewhat, and the tarry solid was transferred to 1200 ml. of ice-water, in which it gradually dissolved. The solution was acidified with hydrochloric acid, precipitating the hydroxy compound as a tar which gradually became crystalline. After filtration, the crude product was dissolved in 750 ml. of 2% aqueous sodium hydroxide, filtered, and reprecipitated with acetic acid to give 78 g. (88%) of material melting at 119–126°. Recrystallization from 600 ml. of carbon tetrachloride gave 60 g. (67.6%) of 4-hydroxy-*o-terphenyl*, m.p. 127.5–128.5°. A sample, recrystallized twice more for analysis, melted at 129–130°.

Anal. Calc'd for $C_{18}H_{14}O$: C, 87.8; H, 5.7.

Found: C, 87.4; H, 6.0.

(b) *From 4-amino-o-terphenyl*. A mixture of 2.45 g. (0.01 mole) of 4-amino-*o-terphenyl*, 100 ml. of water, and 8.5 ml. of 6 *N* hydrochloric acid was heated on the steam-bath until solution was complete. Cooling caused fine needles of the hydrochloride to separate. The mixture was cooled to 0°, and then a solution of 0.70 g. of sodium nitrite in 5 ml. of water was added dropwise, with stirring. Stirring was continued for fifteen minutes after

the addition; then, the cold solution was dropped through a steam-filled tube into boiling water. The orange-red tar which formed was dissolved in benzene, boiled with Darco, filtered, and evaporated to dryness. The residue was recrystallized twice from 10-ml. portions of carbon tetrachloride to give 0.95 g. (39%) of pale orange needles; m.p. 128-129.5°. A melting point of the mixture with a sample of 4-hydroxy-*o*-terphenyl prepared from the sulfonic acid was not depressed.

The *acetyl derivative* was prepared by refluxing a mixture of 0.5 g. of the compound, 10 ml. of acetic anhydride, and 2 g. of sodium acetate for two hours. The yield of crude product was 0.57 g.; m.p. 99-101°. Recrystallization from methanol produced fine white needles; m.p. 102-103°.

Anal. Calc'd for $C_{20}H_{16}O_2$: C, 83.3; H, 5.6.

Found: C, 83.4; H, 5.9.

4,4''-Dihydroxy-o-terphenyl (V). To a molten mixture of 24 g. of potassium hydroxide and 1 ml. of water at 250°, there was added 6 g. of potassium *o*-terphenyl-4,4''-disulfonate. The mixture was stirred at 280° for fifteen minutes, and then at 340° for five minutes. The melt was cooled, dissolved in water, and the resulting solution acidified. The gray-white product (m.p. 228-230°) was recrystallized from 75 ml. of *p*-cymene, with Darco; yield, 2 g. (59%); m.p. 230-231°. A melting point of the mixture with an authentic sample of 4,4''-dihydroxy-*o*-terphenyl, prepared from the 4,4''-diamino compound (4), was not depressed.

The *diacetyl derivative* was prepared as described for the monohydroxy compound. After a single recrystallization from methanol, the product melted at 184.5-186.5°; this compares favorably with the value reported, by Price and Mueller (186.0-186.4°) for 4,4''-diacetoxy-*o*-terphenyl.

4,4',4''-Trihydroxy-o-terphenyl (VI). To 30 g. of molten potassium hydroxide in a nickel crucible at 250°, there was added, with stirring, 10 g. of potassium *o*-terphenyl-4,4',4''-trisulfonate. The temperature was then increased gradually, and at 270-280° the mixture became clear. It was stirred for fifteen minutes at 290-300°, cooled somewhat, and dissolved in ice-water. The clear solution was acidified to yield 3.9 g. (89%) of crude trihydroxy compound; m.p. 233-236°. After two recrystallizations from methanol, the fine white needles melted at 237-237.5°.

Anal. Calc'd for $C_{18}H_{14}O_3$: C, 77.7; H, 5.1.

Found: C, 77.4; H, 5.2.

The *triacetyl derivative* was prepared as described for the monohydroxy compound, and recrystallized from methanol; m.p. 179-180°.

Anal. Calc'd for $C_{24}H_{20}O_6$: C, 71.2; H, 5.0.

Found: C, 70.7; H, 5.2.

Sodium 4-amino-o-terphenyl-3-sulfonate (VII). A mixture of 49 g. (0.2 mole) of 4-amino-*o*-terphenyl, 20.5 g. (0.2 mole) of 95% sulfuric acid, and 250 ml. of water was stirred for one-half hour on the steam-bath, and then evaporated to dryness. The dry salt was heated under reduced pressure (15 mm.) in an oil-bath at 190-210° for forty-eight hours. The reaction mixture was cooled, and dissolved in 500 ml. of water containing 11 g. of sodium carbonate. After treatment with Darco, the solution was evaporated to dryness, yielding 64.5 g. of the crude salt. Recrystallization from 150 ml. of hot water produced clusters of transparent needles which were washed on the filter with cold water and acetone; yield, 54.2 g. (78.2%). A sample was recrystallized twice more from water.

Anal. Calc'd for $C_{18}H_{14}NNaO_3S$: C, 62.2; H, 4.1; N, 4.0.

Found: C, 61.2; H, 4.3; N, 3.9.

Sodium 4-cyano-o-terphenyl-3-sulfonate (IX). A solution of 16.4 g. (0.047 mole) of sodium 4-amino-*o*-terphenyl-3-sulfonate and 3.8 g. (0.055 mole) of sodium nitrite in 830 ml. of water was cooled to 0°. The resulting suspension was added slowly to ice and 20 ml. of concentrated hydrochloric acid, the temperature being kept below 5°. The solution was allowed to stand for twenty minutes and the pale yellow solid was filtered and washed with ice-water. The moist diazonium salt was added in portions to a solution of cuprous

cyanide (prepared from 15 g. of sodium cyanide, 18 g. of cupric sulfate pentahydrate, and 110 ml. of water), while the temperature was maintained at 55–63°. The solution was heated at 60–80° for one hour; then 12 g. of salt was added. On cooling, the product separated as a dark brown semi-crystalline mass, which was removed, washed with cold brine, and dried. The crude product was extracted with methanol and the extract evaporated to dryness. The dark yellow solid weighed 15.3 g. (91%).

4-Cyano-o-terphenyl-3-sulfonamide (X). An intimate mixture of 7.1 g. (0.02 mole) of crude sodium 4-cyano-*o*-terphenyl-3-sulfonate and 9.3 g. (0.043 mole) of phosphorus pentachloride was heated at 140–150° for one-half hour, cooled, dissolved in warm benzene, and filtered. The benzene filtrate was washed with water, and then stirred overnight with 30 ml. of 28% ammonium hydroxide. The benzene layer was decanted and the residual yellow solid removed, washed, and dried; yield, 3.8 g.; m.p. 190–220° (dec.). After three recrystallizations from alcohol, the white crystalline product melted at 273–276°.

Anal. Calc'd for $C_{19}H_{14}N_2O_2S$: C, 68.3; H, 4.2; N, 8.4.

Found: C, 68.3; H, 4.3; N, 8.2.

4-o-Terphenoyl-3-sulfimide (VIII). To a suspension of 0.5 g. (0.0015 mole) of 4-cyano-*o*-terphenyl-3-sulfonamide in 10 ml. of water, there was added 1.5 ml. of 1 *N* sodium hydroxide, and the mixture was heated under reflux for four hours. By this time complete solution had taken place, and the odor of ammonia was no longer detectable. Upon acidification of the solution, the product separated oily, but soon crystallized, to give 0.5 g. of material of m.p. 241–247°. Recrystallization from dilute methanol brought the melting point to 244.5–247.5°, which was not altered by further recrystallization from dilute acetone.

Anal. Calc'd for $C_{19}H_{13}NO_2S$: C, 68.1; H, 3.9; N, 4.2.

Found: C, 68.2; H, 4.3; N, 4.3.

4-Acetyl-o-terphenyl. The following method, using acetyl chloride in ethylene chloride, was found to be more convenient and to give better yields than the one previously described (2). A solution of 138 g. (0.60 mole) of Santowax O¹ in 150 ml. of ethylene dichloride, and 50 g. (0.63 mole) of acetyl chloride was cooled in an ice-salt bath to below 0° and 87 g. (0.65 mole) of resublimed aluminum chloride was added in portions during one hour, while the temperature was kept below 0°.² Stirring was continued for two hours after the addition, and the mixture was poured into ice and concentrated hydrochloric acid. The organic layer was separated, an equal volume of water was added, and the mixture was made nearly neutral with sodium carbonate solution. The solvent was then removed by steam-distillation, the residual oil was dissolved in ether, washed with water, and filtered. The filtrate was evaporated to about 300 ml. and allowed to crystallize. The crystals were washed with ether; yield (first crop) 89 g.; m.p. 93.5–94.0°. Concentration of the filtrate to 150 ml. and cooling gave an additional 12.3 g. (m.p. 92.5–93.5°) for a total yield of 101.3 g. (62.2%).

4-o-Terphenoic acid (XI). This compound was reported by Allen and Pingert (2), but no details were given. A sodium hypochlorite solution was prepared by passing 111 g. (3.13 g. atoms) of chlorine into a solution of 150 g. (3.75 moles) of sodium hydroxide in 225 ml. of water and containing 450 g. of crushed ice. The temperature was kept below 0° during the addition of chlorine by an ice-salt bath. The hypochlorite solution was added in a fine stream, with stirring, to a warm (50°) solution of 90 g. (0.33 mole) of 4-acetyl-*o*-terphenyl in 1200 ml. of methanol. Finally, the mixture was heated under reflux for five hours, cooled to about 5°, filtered, and washed with water. The solid cake was dissolved in 900 ml. of hot water, filtered, and the hot filtrate acidified with hydrochloric acid. The weight of crude acid was 75 g. By concentration of the methanolic filtrate, the yield of crude acid was increased to 90 g. Recrystallization from 1 liter of methanol,

¹ Santowax O, containing approximately 95% *o*-terphenyl, is available commercially from the Monsanto Chemical Company.

² A higher temperature and a longer reaction time favor isomerization to the *m*- and *p*-terphenyl analogs (1).

with Darco, gave 68.4 g. of pure acid, m.p. 202–203°; the yield was increased to 79.4 g. (87.7%) by concentration of the filtrate to 200 ml.

The *amide* was prepared by the action of thionyl chloride followed by ammonia, on the free acid, and recrystallized twice from absolute alcohol. The rectangular, transparent plates melted at 246.5–248.5°.

Anal. Calc'd for $C_{19}H_{15}NO$: N, 5.1. Found: N, 4.9.

The *methyl ester*³ was prepared in quantitative yield by the action of thionyl chloride followed by methanol, on the free acid. After recrystallization from methanol, the ester melted at 99.5–100.5°.

Anal. Calc'd for $C_{20}H_{16}O_2$: C, 83.3; H, 5.6.

Found: C, 83.2; H, 5.8.

x-Sulfo-4-o-terphenic acid (XII). A solution of 27.0 g. of 4-*o*-terphenic acid in 200 ml. of purified *s*-tetrachloroethane was cooled to about 10°, and 12 g. of redistilled chlorosulfonic acid in 25 ml. of tetrachloroethane was added dropwise. Finally, the mixture was stirred at 55–60° overnight, cooled in an ice-bath, filtered, and the product washed with cold chloroform, followed by ether. The crude yield was 23 g. (66%). Recrystallization from 500 ml. of nitroethane (or nitromethane) yielded 19.1 g. (55%) of nearly colorless plates; m.p. 243–248°.

x-Sulfo-4-o-terphenyl dichloride. An intimate mixture of 19 g. (0.054 mole) of *x*-sulfo-4-*o*-terphenic acid and 22.4 g. (0.108 mole) of phosphorus pentachloride was warmed on a steam-bath, with occasional shaking. When the reaction had subsided and the melt was homogeneous, the mixture was cooled. The solid was broken up, transferred to a beaker of ice-water, and extracted with ether. The ether solution was washed with cold water, dried over magnesium sulfate, and filtered. The solvent was removed at reduced pressure to give 13 g. (62%) of white solid (m.p. 141–149°) which could not be recrystallized from any common solvent.

Anal. Calc'd for $C_{19}H_{12}Cl_2O_3S$: C, 58.3; H, 3.1; Cl, 18.1.

Found: C, 58.6; H, 3.30; Cl, 16.1, 15.8.

The *diamide* was prepared from the dichloride by heating with ammonium carbonate and ammonia. After recrystallization from alcohol, the compound melted at 272–277°.

Anal. Calc'd for $C_{19}H_{14}N_2O_3S$: N, 8.0. Found: N, 7.7.

SUMMARY

The following sulfonated *o*-terphenyl derivatives have been prepared and described: *o*-terphenyl-4-sulfonic acid; *o*-terphenyl-4,4''-disulfonic acid; *o*-terphenyl-4,4',4''-trisulfonic acid; 4-amino-*o*-terphenyl-3-sulfonic acid; *x*-sulfo-4-*o*-terphenic acid. Related substances, also described for the first time, include 4-hydroxy-*o*-terphenyl, 4,4',4''-trihydroxy-*o*-terphenyl, and derivatives of all the foregoing. A homolog of saccharin also has been obtained.

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³ This substance was prepared by Roger J. Tull, formerly of these Laboratories.