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THE CHEMISTRY OF *o*-TERPHENYL. IV. AMINE DERIVATIVES

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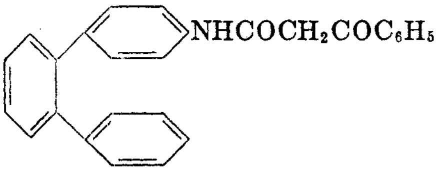
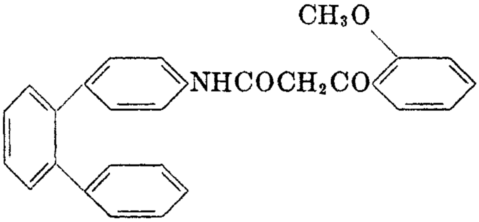
The current accessibility of *o*-terphenyl and many of its derivatives (1, 2, 3, 4, 5) has made it possible to prepare representatives of many classes of compounds containing this ring system. For instance, 4-amino-*o*-terphenyl can readily be converted to 4-benzoylacetamido- (I), 4-(2′-methoxybenzoylacetamido)- (II), and 4-(1′-hydroxy-2′-naphthoylamido)- (III) *o*-terphenyls, while 4,4″-disalicylamido-*o*-terphenyl is readily prepared from the corresponding diamine.



I



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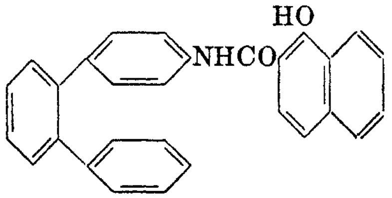
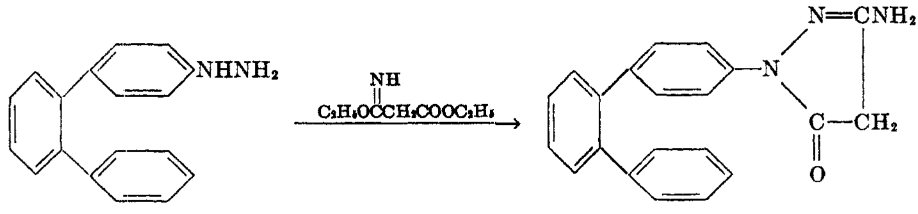


III

An *n*-butyl homolog of (I) was prepared from 4-*n*-butyryl-*o*-terphenyl, obtained by the Friedel-Crafts reaction; a Clemmensen reduction of the ketone gave 4-*n*-butyl-*o*-terphenyl, which was then nitrated and reduced, and the amine condensed with ethyl benzoylacetate. The position of the nitro group was not determined.

The 4-amino-*o*-terphenyl was converted into 4-hydrazino-*o*-terphenyl (IV) by the usual procedure, reduction of the diazotized amine. The hydrazine was used to prepare 1-(4-*o*-terphenylyl)-3-amino-5-pyrazolone (V) by interaction with ethyl *β*-ethoxy-*β*-iminopropionate.



IV V

EXPERIMENTAL

4-n-Butyryl-o-terphenyl. A solution of 138 g. of *o*-terphenyl, 67 g. of *n*-butyryl chloride, and 150 g. of ethylene dichloride was cooled to −10°, and 87 g. of resublimed aluminum chloride added in portions, with stirring, during one hour. The mixture was stirred for four hours at −5 to 0° and decomposed with iced hydrochloric acid. The organic layer was removed, washed with dilute acid, mixed with water, and made almost neutral with sodium carbonate solution. The solvent was removed by steam-distillation, and the residual oil extracted with 700 ml. of ether. After removal of the solvent, distillation of the crude, fluorescent oil yielded 120 g. of the ketone; b.p. 187–190° (1 mm.). It crystallized from methanol in hard, transparent prisms; m.p. 78°.

Anal. Calc'd for $C_{22}H_{20}O$: C, 87.9; H, 6.7.
Found: C, 87.6; H, 6.7.

4-n-Butyl-o-terphenyl. Amalgamated zinc was prepared by treating 250 g. of mossy zinc with 300 ml. of water, 25 g. of mercuric chloride, and 12 g. of concentrated hydrochloric acid. To the zinc amalgam thus obtained there were added 35 ml. of concentrated hydrochloric acid, 10 ml. of acetic acid, and a solution of 50 g. of 4-*n*-butyryl-*o*-terphenyl in 100 ml. of toluene. The mixture was heated under reflux for twenty-four hours; hydrogen chloride was passed in slowly during the first six hours. The toluene solution was removed, washed, and distilled. The hydrocarbon (34 g.) was collected at 165–167° (1 mm.), and crystallized from methanol in large, transparent prisms; m.p. 44°.

Anal. Calc'd for $C_{22}H_{22}$: C, 92.3; H, 7.7.
Found: C, 92.3; H, 7.7.

4-n-Butyl-x-nitro-o-terphenyl. The nitration of 8.6 g. of 4-*n*-butyl-*o*-terphenyl was carried out in the manner described for 4-nitro-*o*-terphenyl (5). Distillation of the crude product yielded 6.7 g. of yellow oil; b.p. 196–206° (1 mm.).

Anal. Calc'd for $C_{22}H_{21}NO_2$: N, 4.2. Found: N, 4.3.

x-Amino-4-n-butyl-o-terphenyl. The reduction of 4-*n*-butyl-*x*-nitro-*o*-terphenyl was carried out in the manner described for 4-amino-*o*-terphenyl (5). The product was an intractable oil which was purified by preparation of the *p*-nitrobenzanilide derivative, followed by hydrolysis.

x-p-Nitrobenzamido-4-n-butyl-o-terphenyl was prepared by adding 15 ml. of 10% sodium hydroxide solution, in portions with shaking, to a solution of 3 g. of the amine and 3 g. of *p*-nitrobenzoyl chloride in dioxane. After fifteen minutes, the solution was poured into water. The product which separated was recrystallized twice from two 200-ml. portions of ethanol; yield, 2.8 g.; m.p. 155.5°.

Anal. Calc'd for $C_{29}H_{26}N_2O_3$: N, 6.2. Found: N, 6.3.

A pure sample of the *amine* was obtained by hydrolysis of the pure *p*-nitrobenzamido derivative. This was accomplished by boiling under reflux a solution of 1.3 g. of the amide in 90 ml. of alcohol with 18 ml. of 50% sulfuric acid for about 60 hrs.

The solution was cooled, neutralized with alkali, the alcohol evaporated, and the aqueous solution extracted with ether. Removal of the ether gave an oil which crystallized from 80% alcohol as fine, colorless needles; yield, 0.5 g.; m.p. 59.5–60°.

Anal. Calc'd for $C_{22}H_{23}N$: N, 4.6. Found: N, 4.9.

4-Hydrazino-o-terphenyl (IV). The diazonium chloride of 4-amino-*o*-terphenyl was prepared at 0° from 7.4 g. of the amine, 9 ml. of concentrated hydrochloric acid, 40 ml. of water, and 2.2 g. of sodium nitrite. The resulting solution was added gradually to a cold (−10°) solution of 18 g. of stannous chloride dihydrate in 30 ml. of concentrated hydrochloric acid. The insoluble complex was removed, and stirred for 15 minutes with 22 ml. of 40% sodium hydroxide solution and sufficient crushed ice to keep the temperature below 10°. The cream-colored solid was filtered, suspended in ether, and shaken with 30 ml. of 5% sodium hydroxide solution until completely dissolved. The ether solution was washed, dried, and evaporated to a small volume, and petroleum ether was added to precipitate 4.1 g. of the crude, cream-colored hydrazine (m.p. 118–124°). Recrystallization from alcohol raised the melting point to 123–125°. The hydrazine gradually becomes tacky and appears to decompose in a few weeks.

Anal. Calc'd for $C_{18}H_{16}N_2$: C, 83.1; N, 6.2.
Found: C, 82.7; H, 6.4.

1-(4-o-Terphenylyl)-3-amino-5-pyrazolone (V) was obtained by the following procedure: A mixture of 1.5 g. of 4-hydrazino-*o*-terphenyl, 1.5 g. of ethyl β-ethoxy-β-iminopropionate, and 15 ml. of ethanol was heated to boiling, 0.5 ml. of acetic acid added, and the solution refluxed for two minutes; it became orange-red. It was cooled to room temperature, and freshly prepared sodium ethoxide solution (0.3 g. sodium in 10 ml. of absolute ethanol) added, after which the mixture was refluxed for one-half hour. It was then acidified (4 ml. of acetic acid), seeded with a previously prepared sample, and allowed to crystallize. After two hours, the pyrazolone was collected and recrystallized from 40 ml. of alcohol, with Darco. The recrystallized material, obtained in a yield of 24%, forms tan flakes, m.p. 223–225°.

Anal. Calc'd for $C_{21}H_{17}N_3O$: C, 77.1; H, 5.2; N, 12.9.
Found: C, 76.7; H, 5.1; N, 13.1.

1-(4-o-Terphenylyl)-3-benzamido-5-pyrazolone was made by benzoylating the above amine in dry pyridine, warming it on the steam-bath for one-half hour, followed by appropriate manipulation; the yield was 76%. It forms tan-colored crystals, m.p. 234–235°, after recrystallization from acetic acid.

4-(1′-Hydroxy-2′-naphthoylamido)-o-terphenyl (III) was prepared by heating a mixture of 5 g. of 4-amino-*o*-terphenyl and 7.3 g. of phenyl 1-hydroxy-2-naphthoate in a small distilling flask *in vacuo* at 140–160° for ten minutes. The molten liquid was then taken up in 300 ml. of alcohol, treated with Darco, and allowed to crystallize; the yield was 5.7 g. The pure amide melts at 181°.

Anal. Calc'd for $C_{29}H_{21}NO_2$: C, 83.9; H, 5.1; N, 3.4.
Found: C, 83.6; H, 5.1; N, 3.4.

4-Benzoylacetamido-o-terphenyl was obtained by gently heating a mixture of 2.5 g. of ethyl benzoylacetate, 10 ml. of xylene, and 2.5 g. of 4-amino-*o*-terphenyl for one hour, and allowing the alcohol formed to escape; the solution was cooled to 70°, and 4 volumes of technical hexane added. The product crystallized on chilling the solution; the yield was 2.6 g. (65%); m.p. 163–164°.

Anal. Calc'd for $C_{27}H_{21}NO_2$: C, 82.5; H, 5.3.
Found: C, 82.4; H, 5.7.

4-o-Methoxybenzoylacetamido-o-terphenyl was obtained similarly. It melts at 149–150°.

Anal. Calc'd for $C_{28}H_{23}NO_3$: C, 79.9; H, 5.5.
Found: C, 79.9; H, 5.6.

x-Benzoylacetamido-4-n-butyl-o-terphenyl was made in the same way, but failed to crystallize. It gave a yellow azomethine dye with oxidized 2-amino-5-diethylaminotoluene, as expected.

4,4″-Disalicylamido-o-terphenyl. A mixture of 2.0 g. of 4,4″-diamino-*o*-terphenyl, 3.3 g. of phenyl salicylate, and 25 ml. of α-methylnaphthalene was heated at 230° (bath temperature) for two hours. The resulting solution was cooled, and allowed to stand until crystallization was complete. The crystalline product was washed with ligroin, and recrystallized from 350 ml. of *p*-cymene. The light tan crystals weighed 2.2 g. and melted at 264–267°.

Anal. Calc'd for $C_{32}H_{24}N_2O_4$: C, 76.8; H, 4.8.
Found: C, 77.4; H, 5.2.

SUMMARY

The preparation and properties of a variety of amides, derived from 4-amino-*o*-terphenyls, are described. 4-Hydrazino-*o*-terphenyl and a pyrazolone containing the *o*-terphenyl group are included.

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