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THE CHEMISTRY OF *o*-TERPHENYL. V. 4-VINYL-*o*-TERPHENYL

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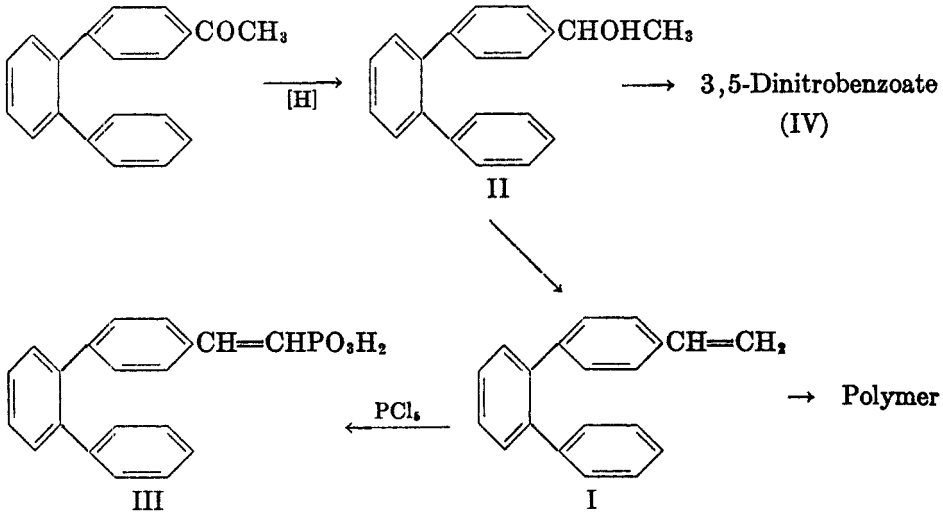
Since *o*-terphenyl can be acylated, in good yield, to form the 4-acetyl derivative (1,1a) it seemed desirable to investigate the feasibility of converting this ketone to the substituted styrene, 4-vinyl-*o*-terphenyl (I). This hydrocarbon should be capable of undergoing polymerization to give a xenylated polystyrene.

4-Vinyl-*o*-terphenyl is readily obtained by the catalytic dehydration of methyl-4-*o*-terphenylylcarbinol (II) over aluminum oxide. As a styrene derivative, the new hydrocarbon decolorizes bromine instantly, and, when treated with phosphorus pentachloride in the usual way (2, 3, 4, 5), gives the phosphonic acid (III). It is readily polymerized by the action of peroxides and by heat, some of the hydrocarbon being lost during the preparation, for this reason.



The methyl-4-*o*-terphenylylcarbinol (II) was obtained by reduction of 4-acetyl-*o*-terphenyl in the presence of copper chromite. Since the carbinol is a liquid at room temperature, it was characterized by the formation of a solid 3,5-dinitrobenzoate (IV).

EXPERIMENTAL

Methyl-4-o-terphenylyl carbinol (II). A solution of 109 g. (0.4 mole) of 4-acetyl-*o*-terphenyl (1a) in 300 ml. of absolute alcohol and 1 g. of copper chromite catalyst were placed in a hydrogenation bomb of 1300-ml. capacity. Hydrogen was introduced to an initial pressure of 1100 p.s.i. (75 atm.), and the bomb heated, with shaking, to 150–160°. After one hour at this temperature, it was cooled, the contents were filtered, and the filtrate was evaporated under reduced pressure to a colorless syrup. Distillation *in vacuo* yielded 95

g. (86.5%) of the carbinol; b.p. 174°/1.5 mm. (187°/3.0 mm.); $n_D^{29.3}$ 1.6178. A portion was recrystallized from methanol by cooling in Dry Ice, but the crystals melted upon warming the sample to room temperature.

Anal. Calc'd for $C_{20}H_{18}O$: C, 87.6; H, 6.6.
Found: C, 87.6; H, 6.8.

The *3,5-dinitrobenzoate* (IV) was prepared by treating a solution of 0.9 g. of the carbinol in 3 ml. of pyridine with 0.88 g. of 3,5-dinitrobenzoyl chloride. The solution was warmed and poured into water. The insoluble residue was taken up in ether, and washed with dilute carbonate solution and water. The ether solution was evaporated, and the residue recrystallized twice from absolute ethanol, yielding pale yellow crystals, m.p. 147–147.5°.

Anal. Calc'd for $C_{27}H_{20}N_2O_6$: N, 6.0. Found: N, 5.8.

4-Vinyl-o-terphenyl (I). A solution of 70 g. of methyl-4-*o*-terphenylyl carbinol (II) and 80 ml. of xylene was dehydrated by Mowry's procedure (6) over aluminum oxide at 310–320°, under a pressure of 25 mm. Some polymeric material was noticed in the column and, later, in the distilling apparatus.

The styrene, b.p. 193–195°/4 mm., was obtained as a water-white liquid in a yield of 34 g. (52%). It is soluble in benzene, but insoluble in methanol. It decolorizes instantly a solution of bromine in carbon tetrachloride.

Anal. Calc'd for $C_{20}H_{16}$: C, 93.7; H, 6.3; mol. wt., 232.
Found: C, 93.5; H, 6.5; mol. wt., 216 (in boiling C_6H_6).

4-Vinyl-*o*-terphenyl slowly polymerizes on standing, in the absence of an inhibitor. With one-half per cent of benzoyl peroxide, it gives a tacky material which becomes brittle on cooling to 25°. This product is soluble in benzene but insoluble in acetone; its refractive index is 1.652.

(4-o-Xenyl)styrene-β-phosphonic acid (III). To a solution of 10.4 g. of phosphorus pentachloride in 25 ml. of dry benzene there was added 6.4 g. of 4-vinyl-*o*-terphenyl in 50 ml. of the same solvent. After standing overnight, the mixture was decomposed by pouring it into water, the benzene layer was separated, and the solvent removed. The residue was treated with a dilute alkaline solution prepared by mixing 10 ml. of 40% sodium hydroxide and 300 ml. of water, and decanted from considerable polymeric material. Upon acidification, an oily acid separated; the aqueous solution was decanted, and the acid recrystallized from boiling methanol, water being added to turbidity. The acid separated in shining plates, m.p. 209°, in a yield of 0.5 g. (4%).

Anal. Calc'd for $C_{20}H_{17}O_3P$: C, 71.4; H, 5.1.
Found: C, 70.9; H, 5.2.

SUMMARY

4-Vinyl-*o*-terphenyl and related substances have been prepared and described.

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