and ring size factors in cyclization reactions, the latter course appeared to be inherently more probable. Although analytical and spectral (ultraviolet, infrared) data did not allow a differentiation between structures IV and V for the olefin, it was unequivocally identified as V by catalytic reduction to 1,4-diphenylcyclohexane. When sodium ethoxide in ethanol was employed for the generation of the phosphorane (III), only unchanged II, triphenylphosphine were detected; no olefinic materials were isolated or detected. These findings differ from those of Bieber and Eisman[3] who obtained a significantly higher yield of 1-phenylcyclopentene from I with lithium ethoxide than with phenyllithium.

The formation of 1,4-diphenylcyclohexadiene-1,4 (V) and not the conjugated isomer, 1,4-diphenylcyclohexadiene-1,3 (VI), provides a further example of the specific double bond placement and lack of isomerization generally observed in the Wittig reaction. The assignment of the nonconjugated structure to the product follows from the similarity of its spectrum (λ_{max} 246 mμ) to those of model styryl systems: styrene (244 mμ)[6a]; *cis*-2-phenylbutene-2 (243 mμ)[7]; 1-phenylcyclohexene (246, 247 mμ).[8] Additionally the molar absorptivity (23,800) is, as expected for two isolated styryl systems, double that observed (11,700–12,000) in the model systems. The conjugated isomer (VI) would be expected to show a spectrum similar to that of 1,4-diphenylbutadiene (λ_{max} 328, 350 mμ; ϵ 25,000, 41,000)[6b] and markedly different from the observed styrene absorption.

While cyclopropenes might be formed by this procedure in a structurally more favorable case, this study does indicate an effective limitation to the synthesis of simple cyclic olefins by intramolecular Wittig processes.

Experimental[9]

Triphenyl(2-benzoylethyl)phosphonium Bromide (II).—A mixture of 40.0 g. (0.188 mole) of β-bromopropiophenone,[10] 49.6 g. (0.188 mole) of triphenylphosphine and 200 ml. of anhydrous benzene was refluxed with constant stirring for 3 hr., allowed to cool to room temperature and filtered to remove the precipitated phosphonium salt, 61.3 g. (69%). Recrystallization from chloroform gave a material melting at 180–181°.

Anal. Calcd. for $C_{27}H_{24}BrOP$: C, 68.22; H, 5.09; P, 6.52. Found: C, 66.64, 66.35; H, 5.31, 5.20; P, 6.54.

1,4-Diphenylcyclohexadiene-1,4 (V).—A solution of 0.11 mole of phenyllithium in anhydrous ether was added to a suspension of 31.7 g. (0.067 mole) of the phosphonium salt (II) in anhydrous benzene (total volume 200 ml.). An initial vigorous exothermic reaction occurred to give a dark red reaction mixture, which turned to orange after being refluxed for 1 hr. After a total reflux period of 30 hr., the reaction mixture was allowed to cool to room temperature, filtered, and concentrated under reduced pressure. Distillation of the residue gave a fraction, b.p. 90° (1 mm.), which solidified in the condenser and receiver to give 950 mg. (12%) of a waxy, colorless solid, m.p. 63.5–67.0°. This solid decolorized bromine in carbon tetrachloride and potassium permanganate in acetone. After two sublimations at 30 mm. and drying under vacuum over phosphorus pentoxide, the solid (V) melted at 67.5–68.5°.

Anal. Calcd. for C_6H_5 or $C_{12}H_{10}$: C, 93.06; H, 6.94. Found: C, 92.89; H, 6.78.

Examination of the infrared spectrum of the distillation residue showed the presence of unchanged II, triphenylphosphine, and triphenylphosphine oxide.

The ultraviolet spectrum of V in 95% ethanol showed a maximum at 246 mμ (ϵ 23,800). The infrared spectrum was recorded in chloroform (5000–840 cm.$^{-1}$) and in acetonitrile (840–650 cm.$^{-1}$) and showed bands at the following frequencies (cm.$^{-1}$): 3077 m-s, 3030 m-s, 1605 s, 1577 m, 1488 s, 1462 w, 1435 s, 1387 w 1340 w, 1323 w, 1271 w, 11.76 w, 11.57 w, 1075 s, 1045 m, 1011 s, 992 s, 969 s, 920 w, 907 m, 840 w, 786 m, 741 s, 702 s.

A 370-mg. (0.0016 mole) sample of V in 50 ml. of ethanol was hydrogenated over a platinum catalyst at room temperature and at a pressure of 3.1 atm. Hydrogen uptake (70.4 ml., 0.0031 mole) ceased after 3 hr. The catalyst was removed by filtration and the solvent was evaporated to give a colorless oil which crystallized from 95% ethanol to give colorless crystals, m.p. 167–169°. Recrystallization from 95% ethanol gave 280 mg. (75%) of 1,4-diphenylcyclohexane, m.p. 169–170° (lit.,[11] m.p. 170°).

The 1,4-diphenylcyclohexane was treated with 355 mg. (0.0045 mole) of selenium at 325° until the evolution of hydrogen selenide ceased (3 hr.). The reaction mixture was cooled and extracted with benzene; the benzene extracts were filtered and concentrated to dryness at 50°. The solid residue was recrystallized twice from benzene to give 208 mg. of *p*-terphenyl, m.p. 209–210°. This material was identical with an authentic sample of *p*-terphenyl in all respects (mixture melting point, infrared and ultraviolet spectra).

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New Synthesis of 3,5-Diiodothyroacetic Acid

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Known methods of preparation of 3,5-diiodothyroacetic acid are based on 3,4,5-triiodonitrobenzene (requiring eight steps),[1] 4-hydroxyphenyl-

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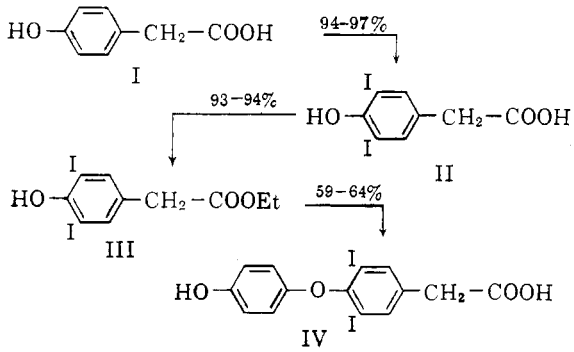
acetic acid (requiring six steps),[2] or 3-iodo-4-hydroxy-5-nitrobenzaldehyde (requiring eight steps).[3]

By means of a modified phenylation method using diaryliodonium salts,[4] we have recently prepared this compound from 4-hydroxyphenylacetic acid in three steps providing an over-all yield of 51–58%:



Experimental

4-Hydroxy-3,5-diiodophenylacetic Acid (II).—Within 1 hr., 21 ml. of 2 *N* iodine solution was added to a mixture of 15.2 g. (0.1 mole) of 4-hydroxyphenylacetic acid and 170 ml. of aqueous solution of ethylamine (15% w./v.) at 20°; after stirring for 30 min., ice was added to the solution which was then acidified with concentrated hydrochloric acid to pH 1–2 (addition of a little sodium bisulfite at pH 5–6). Cold filtration gave 38–39.2 g. (94–97% yield) of 4-hydroxy-3,5-diiodophenylacetic acid (II), m.p. 218°.

Ethyl 4-Hydroxy-3,5-diiodophenylacetate (III).—A mixture of 40.4 g. (0.1 mole) of II, 2 g. of *p*-toluenesulfonic acid, and 200 ml. of absolute ethanol was heated for 15 hr. The solution was poured onto ice and the ethyl 4-hydroxy-3,5-diiodophenylacetate (III) was filtered; yield 40.2–40.5 g. (93–94%); m.p. 121°.

Anal. Calcd. for $C_{10}H_{10}I_2O_3$: I, 58.75. Found: I, 58.8.

3,5-Diiodothyroacetic Acid (IV).—A mixture of 43.2 g. (0.1 mole) of III, 87 g. (0.2 mole) of dianisyliodonium bromide, 14 ml. of triethylamine, 15 g. of copper powder, and 90 ml. of absolute methanol was stirred at room temperature for 24 hr. After filtration of the copper, the solution was concentrated under reduced pressure; the residue was taken up by 50 ml. of benzene and washed successively with 1 *N* hydrochloric acid, water, 1 *N* sodium hydroxide, water, and 5% aqueous acetic acid; the dried, clarified benzene solution was evaporated under reduced pressure.

The residue was triturated with 150 ml. of petroleum ether (b.p. 40–60°), filtered, and heated for 3 hr. in a mixture of 160 ml. of acetic acid and 160 ml. of hydriodic acid (d = 1.7). The solution was cooled and poured into 1 l. of ice water to which a little sodium bisulfite had been added. Filtration gave 36–37.6 g. (yield 73–76%) of crude 3,5-diiodothyroacetic acid (IV), m.p. 214°. Recrystallization of IV in 53 ml. of acetic acid with 18 ml. of water and drying at 100°, under reduced pressure, gave 29.2–31.7 g. (yield 59–64%) of pure IV, m.p. 216–218°.

Anal. Calcd. for $C_{14}H_{10}I_2O_4$: I, 51.16. Found: I, 51.0.

Electrophoretic control: Whatman 3 MM, 500 volts, ethanolic solution pH 12. 5 hr.: 12.0–13.3 cm. from the cathode (ultraviolet 2543 Å.).

Dianisyliodonium Bromide.—A 12.8-g. sample (0.06 mole) of potassium iodate was introduced into 50 ml. of concentrated sulfuric acid (exothermic reaction). A 5.1-g. sample (0.02 mole) of iodine was added at 15–20°. After stirring for 15 hr., the iodyl sulfate[5] was filtered, washed with acetic acid until all the sulfuric acid was eliminated, and suspended in 25 ml. of acetic acid. A mixture of 33 g. (0.6 mole) of anisol and 20 ml. of acetic anhydride was added within 1 hr. at 15–20°. Stirring was maintained for 24 hr. at room temperature and the mixture was poured onto ice. After removal of the oil by decantation, the aqueous solution was clarified with Norit, and 20 g. of potassium bromide was added to the solution. After cooling, the dianisyliodonium bromide was filtered and washed successively with water, acetone, and ether; yield 16.8–19.3 g. (40–46%); m.p. 240°.

(5) Warning: Do not allow contact with ether.

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A New Preparation of 8-Nitro-2-naphthylamine

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The technique of preparing nitronaphthylamines by nitration of aminonaphthalenesulfonic acids, followed by desulfonation, has been used by several investigators. Nietzki and Zubelen[1] and also Bucherer and Uhlmann[2] nitrated acetylnaphthionic acid and subsequently hydrolyzed and desulfonated the product to 5-nitro-1-naphthylamine.

Ward and Pearson[3] nitrated acetylnaphthionic acid in the presence of boron trifluoride and obtained a 2-nitro derivative which was hydrolyzed and desulfonated to 2 - nitro - 1 - naphthylamine. Friedlander and Kielbasinski[4] have nitrated 1-aminonaphthalene-2-sulfonic acid but did not attempt to desulfonate the product.

In this work, the authors have nitrated Tobias acid (2-aminonaphthalene-1-sulfonic acid) at low temperatures in sulfuric acid medium and obtained a mixture of mononitro derivatives. This product was shown to consist of approximately 80–85% of the 8-nitro and 15–20% of the 5-nitro Tobias acids. It could be desulfonated to a mixture of the corresponding nitro-β-naphthylamines. 8-Nitro-2-naphthylamine can be conveniently prepared in

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