dichloro-3,3′,5,5′-tetranitrobiphenyl and not 2,2′-dichloro-4,4′,6,6′-tetranitrobiphenyl as he assumed.

3. The latter compound has been synthesized.

PHILADELPHIA, PA. RECEIVED JULY 24, 1943

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Studies on Some *t*-Butyl Homologs of Naphthalene[1]

BY FRANK C. WHITMORE AND WILLIAM HOLDEN JAMES

In view of the recent report by Bromby, Peters and Rowe,[2] we wish to present, from an investigation terminated by circumstances beyond our control, results obtained in preliminary experiments on the mono-*t*-butylnaphthalenes.

The Friedel–Crafts reaction between naphthalene and *t*-butyl chloride in carbon disulfide solution at 0–5° gave a 45% yield of monoalkylated product. The data, when collated with those recorded in the literature, indicate that the reaction leading to the di-*t*-butylnaphthalenes is much more accelerated by an increase in temperature so that dialkylation outstrips monoalkylation at higher temperatures.

The mono-*t*-butylnaphthalene obtained, b. p. 145° (15 mm.), 115° (6 mm.); $n^{20}_{\rm D}$ 1.5795; m. p. −4°, like the 2-*t*-butylnaphthalene synthesized by Bromby, Peters and Rowe, gave a picrate, m. p. 100–101°, and a quinone, m. p. 76–77°. The observation of these authors that no naphthoic acid could be obtained by oxidative degradation was substantiated. Treatment with bromine or phosphorus pentachloride gave halogenated products of unknown structure.

The preparation of *t*-butylnaphthalene by the dehydrogenation of *t*-butyltetralin, or by the reaction between isobutylene and naphthalene, gave lower yields and lacked the simplicity of the direct Friedel–Crafts reaction employing *t*-butyl chloride and naphthalene.

The preparation of 1-*t*-butylnaphthalene by the reaction between 1-naphthylmagnesium bromide and *t*-butyl chloride, or by the Wurtz–Fittig reaction between 1-naphthyl bromide and *t*-butyl chloride, was unsatisfactory because of the very poor yield of product.

Experimental

1. The Reaction between *t*-Butyl Chloride and Naphthalene.—The apparatus consisted of a five-liter, three-necked, round-bottomed flask equipped with a thermometer, a 50-cc. container for the aluminum chloride consisting of a small flask attached to one of the side-necks by a piece of large rubber tubing, and a trident adapter bearing a one-liter dropping funnel, a mercury-sealed mechanical stirrer and an ice-cooled spiral condenser connected through a trap containing distilled water for collecting the evolved hydrogen chloride, to a second trap containing a solution of bromine in carbon tetrachloride for detecting any gaseous olefins. In the reaction flask was placed about 50 cc. of a solution prepared by dissolving 896 g. (7 moles) of naphthalene in a mixture of 647.5 g. (7 moles) of *t*-butyl chloride, b. p. 50° (732 mm.), $n^{20}_{\rm D}$ 1.3848, and 1875 g. (1.5 liters) of carbon disulfide. The reaction was initiated at room temperature by adding about 1 g. of anhydrous aluminum chloride from a quantity previously weighed in the container. The reaction flask was then cooled in an ice–salt bath which maintained the temperature of the reaction mixture at 0°. With stirring, the 3 liters of carbon disulfide solution was added dropwise from the funnel over a period of five and one-half hours. During this time a steady evolution of hydrogen chloride was maintained by adding aluminum chloride in 1-g. portions from time to time; a total of 25.9 g. (0.194 mole) of aluminum chloride was used. After all the carbon disulfide solution had been added, the reaction mixture was stirred for forty minutes; then 750 cc. of water at 0° was added. The red-brown reaction mixture became colorless. It was allowed to stand for one hour. The carbon disulfide layer was separated. It was washed with 800 cc. of a 12% sodium carbonate solution and was dried, first for thirty hours over 100 g. of anhydrous calcium chloride, then for twenty-four hours over 30 g. of anhydrous potassium carbonate. The liquid was decanted and filtered from the drying agent. The carbon disulfide was removed by distillation at atmospheric pressure on the steam-bath. The residue was then distilled under reduced pressure through a 3.3 × 88 cm. packed, electrically heated, total condensation, adjustable take-off column.[3] Three fractions were collected: (1) 225 g., b. p. 99° (18 mm.); (2) 583 g., b. p. 115° (6 mm.), $n^{20}_{\rm D}$ 1.5795, m. p. −4°; (3) residue, 351 g. Fraction (1) solidified immediately when cooled to room temperature and presumably was unchanged naphthalene; the amount, 225 g., (1.75 moles), represented a recovery of 25% of the starting hydrocarbon. Fraction (2) was a colorless liquid; calculated as mono-*t*-butylnaphthalene, it corresponded to a yield of 45% based on the *t*-butyl chloride used. The residue was a white crystalline solid; calculated as di-*t*-butylnaphthalene, it corresponded to a yield of 41% based on the *t*-butyl chloride used.

A small portion of fraction (2) was treated with a solution of picric acid in 95% ethyl alcohol. A yellow, wax-like solid, m. p. 100–101°, was obtained.[4]

Oxidation of fraction (2) by boiling 50% nitric acid for forty-eight hours or 10% nitric acid for 240 hours or by 20% nitric acid at 180–200° for eight hours yielded no naphthoic acid.

A portion of the crystalline residue was distilled at atmospheric pressure. A fraction, b. p. 310–312° (730 mm.), 181° (15 mm.), when treated with a solution of picric acid in 95% ethyl alcohol gave golden yellow leaflets, m. p. 155–156°.[5]

---

[1] The experimental data in this paper are taken from a thesis submitted by William Holden James in partial fulfillment of the requirements for the Ph.D. degree at the Pennsylvania State College.

[2] Bromby, Peters and Rowe, *J. Chem. Soc.*, 144 (1943)

[3] Whitmore and Lux, THIS JOURNAL, **54**, 3451 (1932).

[4] For other values of the m. p. of the picrate, see: Wegscheider, *Monatsh.*, **5**, 236 (1884); Baur, *Ber.*, **27**, 1623 (1894); Barbot, *Bull. soc. chim.*, (4) **47**, 1314 (1930); Fieser and Price, THIS JOURNAL, **58**, 1838 (1936); Price and Ciskowski, *ibid.*, **60**, 2499 (1938); Tsukervanik and Terentieva, *J. Gen. Chem.* (U. S. S. R.), **7**, 637 (1937); and Pavelkina, *J. Applied Chem.* (U. S. S. R.), **12**, 1422 (1939).

[5] The composition of this picrate has been elucidated by Price, Shafer, Huber and Bernstein, *J. Org. Chem.*, **7**, 517 (1942), who re-

The material, b. p. 310–312°, was easily soluble in hot benzene from which it crystallized on cooling in the form of white needles which sintered at 80° and became entirely liquid at 110°. It was easily soluble in acetone, petroleum ether, diethyl ether, carbon disulfide, and ethyl alcohol. When recrystallized from 95% ethyl alcohol, it formed fine, white needles, m. p. 80–81°.[6] When the solid was recrystallized from petroleum ether, b. p. 69–90°, a small amount of large prismatic crystals, m. p. 146–147°, was obtained.[7]

The total amount, 1159 g., of recovered material corresponded to 89.9% of 1288 g., the amount of starting organic material calculated as naphthyl and butyl equivalents.

The solution of hydrogen chloride in the trap was diluted with distilled water to a volume of 4 liters. Of this solution, 5.0 cc. neutralized 39.18 cc. of 0.1859 *N* sodium hydroxide solution. These data indicated the presence of 5.82 moles of hydrogen chloride, or 83% of the calculated amount.

Fractions (2) and (3), calculated as mono- and di-*t*-butylnaphthalenes, respectively, corresponded to 86% of the starting *t*-butyl chloride. If the aluminum chloride (0.194 mole) in the reaction mixture bound the hydrogen chloride in a complex in a proportion of 1:1, the amount of hydrogen chloride thus required would represent an amount of *t*-butyl chloride corresponding to 2.77% of the starting halide, and the discrepancy between 86 and 83% would be changed to that between 86 and 85.7%.

The solution of bromine (0.05 mole) in carbon tetrachloride was not decolorized. This indicated the absence of evolved olefins. Presumably the *t*-butyl chloride which was not accounted for (14% of the starting amount) was removed with the carbon disulfide.

2. **(A) The Reaction between *t*-Butyl Chloride and Tetralin.**—The apparatus consisted of a two-liter, three-necked, round-bottomed flask equipped with a thermometer, a container for the aluminum chloride, and a trident adapter bearing a dropping funnel, a mercury-sealed mechanical stirrer, and a reflux condenser attached to a hydrogen chloride exit-tube. In the reaction flask, cooled to 0–5° in an ice-salt bath, were placed 75 cc. of carbon disulfide, and about 25 cc. of a solution prepared by mixing 264 g. (2 moles) of tetralin, b. p. 205–206° (735 mm.), $n^{20}_{\rm D}$ 1.5409, 185 g. (2 moles) of *t*-butyl chloride, b. p. 50.5–51° (744 mm.), $n^{20}_{\rm D}$ 1.3848, and 250 cc. of carbon disulfide. The reaction was initiated and carried out in a manner similar to that described for naphthalene and *t*-butyl chloride. A period of ninety minutes was required for the addition of the carbon disulfide solution. A total of 20 g. (0.15 mole) of aluminum chloride was used. After all the reactants had been added, the mixture was stirred for one hour and then was treated with 500 cc. of ice water. The yellow colored carbon disulfide layer was separated. It was washed with 200 cc. of water, then with 300 cc. of 8% sodium carbonate solution. It was dried over 30 g. of anhydrous calcium chloride. The mixture was worked up in a manner similar to that described for the product from naphthalene and *t*-butyl chloride. Distillation through a column under reduced pressure gave three fractions: (1) 30 g., b. p. 50–100° (6 mm.); (2) 200 g., b. p. 100–102° (6 mm.), $n^{20}_{\rm D}$ 1.5260; (3) residue, 50 g. Fraction (1), if considered as tetralin (b. p. 64–65° (5 mm.)), represented 11.3% of the starting hydrocarbon. Fraction (2), calculated as *t*-butyltetralin, represented a yield of 53% based on the *t*-butyl chloride used.[8] The residue was a resin.

A similar run made at 30–40° gave a yield of only 16% of *t*-butyltetralin.

2. **(B) The Reaction between *t*-Butyltetralin and Sulfur.**—In a 500-cc., round-bottomed flask equipped with a reflux condenser connected to a hydrogen sulfide exit-tube were placed 113 g. (0.6 mole) of *t*-butyltetralin, b. p. 100–102° (6 mm.), $n^{20}_{\rm D}$ 1.5260, and 39 g. (1.2 atoms) of powdered sulfur. The flask was heated in an oil-bath at 230–240° for about five hours until the evolution of hydrogen sulfide ceased. The reaction mixture was cooled to room temperature and washed with 300 cc. of a 10% sodium hydroxide solution. The oily layer was separated and dried over 10 g. of anhydrous calcium chloride. The liquid was decanted and filtered from the desiccant. It was fractionated through a distilling column under reduced pressure. Two fractions of distillate were collected: (1) 20 g., b. p. 100–106° (5 mm.), $n^{20}_{\rm D}$ 1.5661; (2) 55 g., b. p. 106–107° (5 mm.), $n^{20}_{\rm D}$ 1.5714. Fraction (1) evidently was chiefly *t*-butylnaphthalene containing a small amount of *t*-butyltetralin. Fraction (2), calculated as *t*-butylnaphthalene, represented a yield of 50% based on the *t*-butyltetralin used. This material, $n^{20}_{\rm D}$ 1.5714, did not solidify at −10°.

3. **The Reaction between Isobutylene and Naphthalene.**—The isobutylene was generated by refluxing gently in a one-liter, round-bottomed flask a mixture of 200 g. (1.58 moles) of oxalic acid, $((CO_2H)_2\cdot 2H_2O)$, and 390 g. (5.27 moles) of *t*-butyl alcohol. The evolved olefin was led through two suitably trapped calcium chloride drying towers before entering the Friedel–Crafts reaction flask which consisted of a two-liter, three-necked, round-bottomed flask equipped with a tube for introducing isobutylene, a container for the aluminum chloride, and a trident adapter bearing a mercury-sealed mechanical stirrer, a 500-cc. dropping funnel, and a reflux condenser connected to a gas exit-tube. In the reaction flask, cooled to 0° in an ice-salt bath, was placed about 100 cc. of carbon disulfide which was then saturated with isobutylene. From the dropping funnel, over a period of about four hours, was gradually added a solution of 384 g. (3 moles) of naphthalene and 500 cc. of carbon disulfide. During this time, 35 g. of aluminum chloride was added from time to time in 1-g. portions; a steady stream of isobutylene into the reaction mixture was maintained. The reaction mixture became blue in color but gave no other sign of reaction. The reactivity was tested by the addition of 15 cc. (12.9 g., 0.139 mole), of *t*-butyl chloride; no evolution of hydrogen chloride occurred. The stirring was continued for one hour and then about 10 g. of aluminum chloride was added at one time. A vigorous evolution of hydrogen chloride immediately occurred. The stirrer was stopped for about five minutes to prevent loss of material. When the reaction had subsided the stirring was resumed and was continued for about one hour. A total of 47 g. (0.35 mole) of aluminum chloride was used. The reaction mixture was treated with 500 cc. of ice water. The yellow colored carbon disulfide layer was separated, washed with two 150-cc. portions of 13% sodium carbonate solution, and dried over 40 g. of anhydrous calcium chloride. After standing overnight, about 10 g. of anhydrous potassium carbonate was added to the solution. The mixture was worked up in a manner similar to that described for the product from naphthalene and *t*-butyl chloride. The unreacted naphthalene was removed by distillation through a column at atmospheric pressure; the amount, 37 g., b. p. 217° (735 mm.), represented 9.6% of the starting naphthalene. A fraction, b. p. 278° (735 mm.), 144–146° (15 mm.), $n^{20}_{\rm D}$ 1.5781, amounting to 174 g., was obtained; calculated as *t*-butylnaphthalene, this corresponded to a yield of 34% based on the unrecovered naphthalene. The residue, 270 g., was a viscous liquid and had an appearance similar to that of lubricating oil.

---

ported that for it the analytical data indicated the formula $(C_{18}H_{24})_3$, $(C_6H_3O_7N_3)_2$. Moreover, they showed that this substance was comprised of one mol of a di-*t*-butylnaphthalene, m. p. 146°, two mols of an isomeric di-*t*-butylnaphthalene, m. p. 104°, and two mols of picric acid.

(6) This solid, m. p. 80–81°, which previously had been isolated by Wegscheider, *loc. cit.*; Gump, THIS JOURNAL, **53**, 380 (1931); Simons and Archer, *ibid.*, **60**, 2954 (1938); Fieser and Price, *loc. cit.*; and Price and Ciskowski, *loc. cit.*, was shown by Price, Shafer, Huber and Bernstein, *loc. cit.*, to be a mixture of one part of a di-*t*-butylnaphthalene, m. p. 145–146°, and two parts of a hitherto unreported di-*t*-butylnaphthalene, m. p. 103–104°.

(7) *Cf.* Wegscheider, *loc. cit.*; Meyer and Bernhauer, *Monatsh.*, **54**, 721 (1929); Gump, *loc. cit.*; Fieser and Price, *loc. cit.*; Simons and Archer, *loc. cit.*; Calcott, Tinker and Weinmayr, THIS JOURNAL, **61**, 1010 (1939); and Price, Shafer, Huber and Bernstein, *loc. cit.*

(8) *Cf.* Barbot, *loc. cit.*, and Lévy, *Ann. chim.*, (11) **9**, 5 (1938).

4. The Reaction between Bromine and *t*-Butylnaphthalene.—The apparatus consisted of a one-liter, three-necked, round-bottomed flask equipped with a mercury-sealed mechanical stirrer, a 250-cc. dropping funnel, and a reflux condenser provided with a gas exit-tube. In the reaction flask were placed 2 g. (0.035 atom) of iron in the form of filings, and 184 g. (1 mole) of *t*-butylnaphthalene, b. p. 150° (22 mm.), $n^{20}\mathrm{D}$ 1.5795, prepared by the reaction between naphthalene and *t*-butyl chloride in the presence of aluminum chloride. From the dropping funnel was added slowly with stirring, 160 g. (1 mole) of bromine over a period of about one hour. The mixture was heated gently to maintain a moderately rapid evolution of hydrogen bromide. When the evolution of hydrogen bromide ceased, the reaction mixture was cooled and diluted with 150 cc. of carbon disulfide. The resulting solution was washed with 200 cc. of water, then with 250 cc. of 10% sodium hydroxide solution, then again with 200 cc. of water. The mixture was dried over anhydrous calcium chloride and potassium carbonate for about ten hours. The liquid was decanted and filtered from the drying agents. The carbon disulfide was removed by distillation on the steam-bath. The residue was fractionated under reduced pressure through a distilling column. Four main fractions of distillate were collected: (1) 30 g., b. p. 85–135° (4 mm.); (2) 75 g., b. p. 135–136° (4 mm.), $n^{20}\mathrm{D}$ 1.6060; (3) 30 g., b. p. 136–162° (4 mm.), $n^{20}\mathrm{D}$ 1.6050–1.6041; (4) 35 g., b. p. 162–165° (4 mm.), $n^{20}\mathrm{D}$ 1.5990. The amounts and b. p.'s of fractions (2) and (4) suggest that these materials were chiefly individual compounds.

As the boiling point of the brominated material increased from 135° (4 mm.) to 165° (4 mm.), the index of refraction, $n^{20}\mathrm{D}$, decreased from 1.6060 to 1.5990.

In another experiment in which no iron was used, the time required to add the bromine was much longer. The composition of the resulting reaction product also appeared to be changed; while the b. p. increased from 145° (4 mm.) to 170° (4 mm.), the index of refraction, $n^{20}\mathrm{D}$, *increased* from 1.6062 to 1.6114.

5. The Reaction between Phosphorus Pentachloride and *t*-Butylnaphthalene.—In a two-liter, three-necked, round-bottomed flask equipped with a thermometer, a mercury-sealed mechanical stirrer, and a reflux condenser attached to a hydrogen chloride exit-tube, were placed 184 g. (1 mole) of *t*-butylnaphthalene, $n^{20}\mathrm{D}$ 1.5795, and 343 g. (1.64 moles) of phosphorus pentachloride. The mixture was heated for three hours in an oil-bath at 150–160°; the resulting phosphorus trichloride refluxed gently and maintained the temperature of the reaction mixture at 125–130°. The reaction mixture was allowed to stand overnight at room temperature. The phosphorus trichloride was removed by distillation at atmospheric pressure; the residue from the distillation was added to about 600 g. of crushed ice. After the ice had melted, the lower organic layer was separated and diluted with 250 cc. of carbon disulfide. The mixture was washed first with two 250-cc. portions of water, then with 300 cc. of 8% sodium carbonate solution. It was dried over anhydrous calcium chloride and potassium carbonate. The liquid was decanted and filtered from the drying agents. The carbon disulfide was removed by distillation on the steam-bath. The residue was fractionated through a distilling column under reduced pressure. Of six fractions of distillate totaling 128.5 g., b. p. 125–170° (4 mm.), $n^{20}\mathrm{D}$ 1.5898–1.6159, only one fraction, 35 g., b. p. 125–128° (4 mm.), $n^{20}\mathrm{D}$ 1.5929, might be regarded as being composed chiefly of material having a constant b. p. and a constant index of refraction.

Similar results were obtained in other experiments made under slightly different conditions. In one of these, the resulting phosphorus trichloride and hydrogen chloride were removed by a stream of nitrogen during the reaction, trapped and measured separately. The data indicated that 276 g. (1.5 moles) of *t*-butylnaphthalene and 208.3 g. (1 mole) of phosphorus pentachloride gave 105.8 g. (0.77 mole) of phosphorus trichloride and 62.4 g. (1.71 moles) of hydrogen chloride.

6. The Reaction between Chromium Trioxide and *t*-Butylnaphthalene in Acetic Acid Solution.—In a three-liter, round-bottomed flask equipped with a thermometer, a mechanical stirrer, and a reflux condenser, were placed 120 g. (1.2 moles) of chromium trioxide and 700 cc. of glacial acetic acid. To this was added slowly with stirring and cooling to maintain the temperature below 60°, a solution of 27.6 g. (0.15 mole) of *t*-butylnaphthalene, $n^{20}\mathrm{D}$ 1.5795, and 300 cc. of acetic acid. The heat of reaction maintained the temperature at 55–60° for about forty-five minutes after the addition was complete; the mixture was then gradually heated to 80° where it was held for ten hours. The resulting green solution was added to nine liters of distilled water. After standing forty-eight hours, a yellow precipitate had formed. It was collected on a filter and washed with 500 cc. of water. When dry, this crude product amounted to 6.3 g. and melted at 75–77°; calculated as *t*-butylnaphthoquinone, it corresponded to a yield of 19.6%. It was recrystallized from ethyl alcohol. The glistening yellow leaflets melted at 76–77°. This substance was shown to be 2-*t*-butyl-1,4-naphthoquinone by Bromby, Peters and Rowe,[3] who obtained it in a yield of 31% by using other concentrations of reactants and a shorter heating period.

Summary

The results obtained in preliminary experiments of an investigation, now interrupted, of the synthesis, halogenation, and oxidation of some *t*-butyl homologs of naphthalene are presented. Evidence for the presence in the monoalkylated product, b. p. 145° (15 mm.), 115° (6 mm.); $n^{20}\mathrm{D}$ 1.5795; m. p. −4°, of 2-*t*-butylnaphthalene is cited.

STATE COLLEGE, PENNSYLVANIA RECEIVED JULY 17, 1943