bromo-3-thianaphthenyl)-ethane, also indicated the presence of a Grignard reagent.

2-Iodothianaphthene was prepared by the action of iodine on 2-thianaphthenyllithium[2]; thianaphthene was converted directly to 3-iodothianaphthene by iodine and mercuric oxide. The structures of both isomers were confirmed by carbonation of the Grignard reagents. Attempts to chloromethylate the iodo compounds failed.

Decomposition of N-nitrosoacetanilide in excess thianaphthene gave as the only isolable product 2-phenylthianaphthene, which was desulfurized by Raney nickel to bibenzyl. Although this appears to be the first report of free-radical substitution in the thianaphthene series, the low yield and the fact that other isomers may have been present in the intractable mixture preclude any complete conclusion concerning orientation at this time.

Acknowledgment.—This work was supported by a grant-in-aid from the Graduate School and made possible by gifts of thianaphthene by Jefferson Chemical Company, New York, N. Y.

Experimental[3]

2-Bromo-3-(bromomethyl)-thianaphthene.—A solution of 12.4 g. of 2-bromo-3-methylthianaphthene,[4] 9.7 g. of N-bromosuccinimide and 0.4 g. of benzoyl peroxide in 130 ml. of carbon tetrachloride was heated under reflux for 90 minutes, cooled, filtered, and the solvent replaced by ligroin (b.p. 70–90°) by distillation. A total of 14.4 g. (86%) of needles separated; m.p. 97–99.5°, b.p. 148–151° (0.5 mm.) (dec.). After recrystallization and sublimation at 100° (0.1 mm.), 2-bromo-3-(bromomethyl)-thianaphthene melted at 97.6–98.6°.

Anal. Calcd. for $C_9H_6Br_2S$: C, 35.32; H, 1.98. Found: C, 35.55; H, 2.23.

When 19.3 g. of the halide was converted in the cyclic reactor,[5] titration of an aliquot after hydrolysis indicated a 67% yield of reagent, which gave a green Gilman test. The reagent was allowed to react with ethyl chlorocarbonate and formaldehyde. In the first case, the acidic fraction obtained by alkaline hydrolysis was polymeric and had a wide melting range (about 200–240° with decomposition). From the neutral material, by recrystallization from benzene–hexane, was isolated 1.2 g. of crude 1,2-bis-(2-bromo-3-thianaphthenyl)-ethane. By recrystallization from ethanol–benzene, colorless crystals were obtained, m.p. 195–196°.

Anal. Calcd. for $C_{18}H_{12}Br_2S$: C, 47.80; H, 2.68. Found: C, 48.04; H, 2.64.

By conversion of 21.3 g. of the bromide, and reaction with formaldehyde, only a taffy-like polymer was obtained.

3-Iodothianaphthene.—To a solution of 44.4 g. of thianaphthene in 70 ml. of benzene, heated at 55–65°, were added during an hour in small alternate portions with stirring 54 g. of yellow mercuric oxide and 76 g. of iodine. Filtration and aspiration of the benzene, followed by distillation of the residue, gave, in addition to 15.7 g. of recovered starting material, 39.6 g. (71%, based on recovery) of a dark brown liquid which was decolorized by passing a solution in benzene through a column of charcoal and alumina. When redistilled, 3-iodothianaphthene (d^{20}_4 1.898, $n^{20}_D > 1.7$) was a very light yellow mobile liquid boiling mainly at 120–121° (1.6 mm.), which darkened rapidly in the light.

Anal. Calcd. for C_8H_5IS: C, 36.94; H, 1.94. Found: C, 37.11; H, 2.18.

It was recovered unchanged from an attempted chloromethylation at 90° in the presence of zinc chloride, only a trace of higher-boiling material being formed. The iodo compound (19.5 g.) reacted normally with magnesium, forming a nearly immiscible layer under ether. Carbonation yielded 7.4 g. (55%) of 3-thianaphthoic acid, m.p. 176–177.5°. Additional crude material (1.4 g., m.p. 150–165°) from the mother liquors may have contained isomeric acids.

2-Iodothianaphthene.—Thianaphthene (67 g.) was converted to the lithium derivative[2] and this solution was added dropwise with stirring to a mixture of 252 g. of iodine and 100 ml. of ether with cooling in a salt–ice-bath. The mixture was stirred and allowed to warm to room temperature and water was added. The excess iodine was removed from the solvent layer by shaking with sodium thiosulfate solution. The recovered crude thianaphthene weighed 48.2 g. and probably contained butyl iodide. The dark product (37.4 g., 29% based on total starting material), distilled in a sausage flask, boiled principally at 119–120° (1.6 mm.), m.p. 59–62°. Recrystallization from hexane (charcoal) and sublimation at 70° (0.3 mm.) gave nearly colorless crystals, m.p. 63.4–65°.

Anal. Calcd. for C_8H_5IS: C, 36.94; H, 1.94. Found: C, 36.89; H, 2.13.

An attempted chloromethylation failed. Conversion of 13 g. to the Grignard reagent, also ether-immiscible, and carbonation gave an unexpectedly low yield (1.02 g., 12%) of pure 2-thianaphthoic acid, m.p. 242–243°.

N-Nitrosoacetanilide and Thianaphthene.—A solution of 25 g. of the nitrosoamide[6] was dissolved in 200 g. of molten thianaphthene at 32°. The dark red solution (in a 500-ml. flask) began slowly to evolve a gas; when left unattended for 30 minutes, it apparently reacted violently, foaming and spattering almost exactly half of the total reaction mixture onto the desk and floor. Unchanged thianaphthene in the residue was removed by distillation *in vacuo*, followed by 10.5 g. of an amber liquid, b.p. 150–155° (0.3 mm.); it solidified to a slushy mixture. No other distillate could be obtained up to a temperature in the bath of 220°. Recrystallization of the mixture from benzene–methanol and benzene–hexane gave 1.63 g. of white plates, m.p. 171–173°. Further recrystallization and sublimation at 100° (0.1 mm.) gave 2-phenylthianaphthene,[7] m.p. 174.2–175.2°.

Anal. Calcd. for $C_{14}H_{10}S$: C, 79.96; H, 4.79. Found: C, 80.00; H, 5.05.

Further confirmation of the structure was obtained by heating 1.00 g. with about 12 g. of Raney nickel catalyst in 70 ml. of ethanol for 3 hours to give 0.81 g. of colorless crystals, m.p. 49–51° (alone and mixed with authentic bibenzyl).

Only thianaphthene (as 2.5 g. of the picrate) could be isolated from the mother liquors in the original recrystallization. Benzene, hexane, ether, ethanol and methanol were tried unsuccessfully as solvents to obtain another picrate. An attempt to prepare a 1,1-dioxide[8] produced a gummy polymer.

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[2] D. A. Shirley and M. D. Cameron, THIS JOURNAL, **74**, 664 (1952), prepared this reagent and described a number of its reactions, including that with bromine.

[3] Melting points, but not boiling points, are corrected. Microanalyses were by Micro-Tech Laboratories, Skokie, Illinois.

[4] R. Gaertner, THIS JOURNAL, **74**, 2185 (1952).

[5] See, for typical procedures, R. Gaertner, *ibid.*, **73**, 3934 (1951).

[6] W. S. M. Grieve and D. H. Hey, *J. Chem. Soc.*, 1797 (1934).

[7] A. W. Horton, *J. Org. Chem.*, **14**, 761 (1949), prepared this compound from 2-phenylthiophene.

[8] F. G. Bordwell, B. B. Lampert and W. H. McKellin, THIS JOURNAL, **71**, 1702 (1949).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF OREGON
EUGENE, OREGON

3-Nitrodurene

BY GABRIELLO ILLUMINATI

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3-Nitrodurene was first reported by Willstätter and Kubli[1] in 1909 to result from the reaction of 3-iododurene with silver nitrite. The compound was not isolated, but its formation was demonstrated by identifying as 3-aminodurene the

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[1] R. Willstätter and H. Kubli, *Ber.*, **42**, 4159 (1909).

product obtained from its reduction with zinc and acetic acid. In the same year Cain[2] claimed the preparation of 3-nitrodurene, in the course of an earlier work in 1895, by reduction of the diazo-salt of 3-nitro-6-aminodurene in alcoholic solution. Cain's 3-nitrodurene melted at 70°; however, it was neither analyzed nor otherwise identified except by reduction to an uncharacterized amine. As reported by Ingham and Hampson,[3] the deamination of the nitroaminodurene by using ethanol as a reducing agent leads to the formation of a steam-volatile mixture containing much 3-nitro-6-ethoxy-durene. Obviously, reduction of the latter compound with tin and hydrochloric acid can still yield an amino derivative.

In the course of work in this Laboratory related to the chemistry of polymethylbenzenes, we have succeeded in reducing the diazo-salt of the nitroaminodurene with hypophosphorus acid to give a compound, m.p. 113–114°, which proved identical (mixed m.p.) with 3-nitrodurene as described by Smith and Taylor[4] and obtained either by the action of nitric acid (sp. gr. 1.26) on 3-acetoxymercuridurene or by oxidizing 3-nitrosodurene to the corresponding nitro compound.

The molecule of 3-nitrodurene offers an important case for testing the effect of steric hindrance of resonance, as was first recognized several years ago by Birtles and Hampson[5] in a dipole moment investigation. Unfortunately, the sample used in that work for the measurement of the dipole moment of this substance was prepared according to the misleading early report of Cain.[6]

Experimental

Reduction of the Nitroduryldiazonium Ion by Hypophosphorous Acid. (a) **Materials.**—3-Nitro-6-aminodurene, m.p. 160–161.5°, was prepared by reduction of dinitrodurene with sodium disulfide according to Ingham and Hampson's improved procedure.[3] In all runs commercial 50% hypophosphorous acid (E. Merck, Darmstadt) was used as such.[7] As far as our results are concerned, the efficiency of this reagent did not seem to decrease over a period of six months.

(b) **3-Nitrodurene.**—In a 300-ml. erlenmeyer flask, 7.77 g. of the nitroaminodurene (0.040 mole) was dissolved in a hot solution of 95% sulfuric acid (8.5 ml.) in water (25 ml.). On cooling to room temperature, a light yellow crystalline mass was formed; the flask was then immersed in an ice-water bath. Then 10.36 ml. of an aqueous solution containing 2.90 g. of sodium nitrite (0.042 mole) was added dropwise from a buret over a period of 22 minutes, while the flask was being shaken effectively. After ten minutes, the light yellow suspension thus obtained was treated dropwise over about 15 minutes with 60 ml. of 50% hypophosphorous acid; during the addition a mild evolution of nitrogen became evident very soon. The reaction flask was then kept loosely stoppered and immersed in ice-water for four days. After this time, the reaction mixture was filtered; the filtrate was allowed to stand, under the same conditions, for another four days and then filtered again.

The yellow products collected from both filtrations were worked up separately in the following manner. Their chloroform solutions were extracted with a 10% sodium hydroxide solution until the deep red color in the alkaline extracts disappeared, then washed with water and dried. After removing the solvent, residues of 5.81 and 0.10 g., respectively, of crude 3-nitrodurene, m.p. 102–107°, were obtained, which is a combined 82.7% yield. After two crystallizations from ethanol, light yellow crystals, m.p. 113–114°, were obtained. A mixed m.p. with an authentic specimen prepared by the method of Smith and Taylor[4] was not depressed.

For further identification, 1.0 g. of the crude compound was reduced with tin and hydrochloric acid in boiling acetic acid for four hours and the reaction mixture was worked up in the conventional manner to yield 0.8 g. of 3-aminodurene, m.p. 70–72°.

In other experiments, the crude nitrodurene could also be obtained by steam distillation of the original reaction product in alkaline solution and crystallized once from ethanol. Such a procedure led to lighter-colored crystals, m.p. 112–114°.

(c) **3-Nitro-6-hydroxydurene.**—The combined deep red alkaline liquor from the extractions referred to in (b) was heated to boiling to remove any trace of chloroform, made acid with concd. hydrochloric acid, boiled until a clear solution resulted and finally filtered. On cooling, greenish yellow plates of 3-nitro-6-hydroxydurene[3] crystallized from the solution. The yield was 0.38 g. (4.8%), m.p. 119–123°.

(d) **Comparative Results from Other Runs.**—From similar experiments using the same amount of the nitroaminodurene there is some indication that both the concentration of the hypophosphorous acid and the temperature affect the relative yields of the two compounds formed. In one run in which only 20 ml. of 50% hypophosphorous acid was used and the reaction mixture was let stand at 5° to room temperature, the extent of hydrolysis of the diazonium salt was markedly increased (a 24% yield of the nitrohydroxydurene was obtained) while the yield of the crude nitrodurene was as low as 56%. In three other runs, each using 40 ml. of 50% hypophosphorous acid and conducted in ice-water, the yields were 76.2, 72.0 and 74.6%, for the nitrodurene, and 6.4, 7.2 and 8.9, respectively, for the nitrohydroxy compound.

DEPARTMENT OF GENERAL CHEMISTRY
UNIVERSITY OF ROME
ROME, ITALY

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(2) J. C. Cain, *Proc. Chem. Soc.*, 260 (1909).

(3) C. E. Ingham and G. C. Hampson, *J. Chem. Soc.*, 981 (1939).

(4) L. I. Smith and F. L. Taylor, THIS JOURNAL, **57**, 2460 (1935).

(5) R. H. Birtles and G. C. Hampson, *J. Chem. Soc.*, 10 (1937). See, also, L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, p. 221; G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, p. 149; M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford at the Clarendon Press, London, 1949, p. 200; Melvin Fields, C. Valle and M. Kane, THIS JOURNAL, **71**, 421 (1949).

(6) NOTE ADDED IN PROOF.—After this note was submitted for publication, a paper has appeared (H. Kofod, L. E. Sutton, W. A. DeJong, P. E. Verkade and B. M. Wepster, *Rec. trav. chim.*, **71**, 521 (1952)), including results which confirm those herein contained.

(7) For the purification and stability of this reagent, see W. A. Jenkins and R. T. Jones, *ibid.*, **74**, 1353 (1952).

A Synthesis of the Diethylacetal of Glutamic-γ-semialdehyde[1]

BY NORMAN GOOD[2] AND HERSCHEL K. MITCHELL

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A number of investigations[3-5] have provided evidence that enzymatic interconversions of glutamic acid, proline and ornithine may proceed through a common intermediate, glutamic-γ-semialdehyde. Vogel and Davis[5] have demonstrated that a proline requiring mutant of *E. coli* accumulates a substance that is probably Δ'-pyrroline-5-carboxylic acid and that this substance supports the growth of a mutant that can utilize either glutamic acid or proline for growth.

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(2) Department of Botany, University of Minnesota, Minneapolis, Minnesota.

(3) J. V. Taggart and R. B. Krakaur, *J. Biol. Chem.*, **177**, 641 (1949).

(4) M. R. Stetten, *ibid.*, **189**, 503 (1951).

(5) H. J. Vogel and B. D. Davis, THIS JOURNAL, **74**, 109 (1952).