of the areas in the part where there is not overlapping. Fig. 1. A_2/A_1 would give the ratio in which both isomers are present.

This kind of analysis was made in α-bromocyclohexanone; the curve was carefully measured at each cm.$^{-1}$ and its area calculated using Simpson's rule. The ratios A_2/A_1 obtained in two experiments were 1.372 and 1.278; that is a proportion of 57.85% and 56.10% for the axial isomer in the mixture. Further experiments on quantitative analysis of overlapped areas will be reported later.

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MEXICO 20, D. F.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON, AND THE NOBEL INSTITUTE OF CHEMISTRY]

Isolation and Proof of Structure of 1,1,4,4-Tetramethyl-6-*t*-butyl-1,2,3,4-tetrahydronaphthalene[1]

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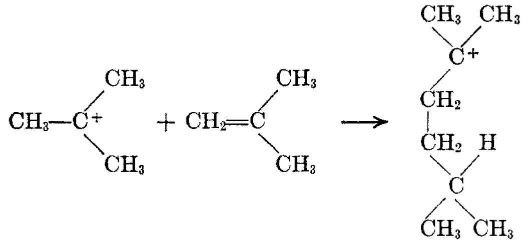
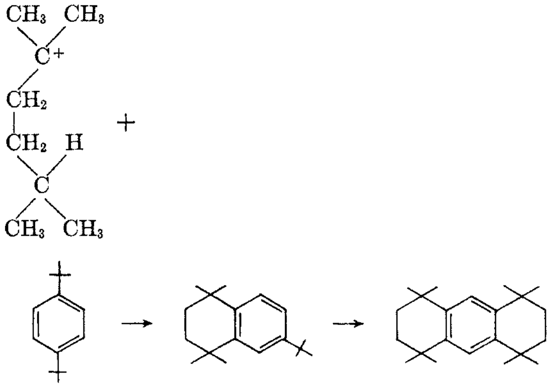
A new hydrocarbon has been isolated as a by-product of the preparation of 1,3,5-tri-*t*-butylbenzene by the reaction of 1,4-di-*t*-butylbenzene and *t*-butyl chloride in the presence of aluminum chloride. This hydrocarbon has been identified as 1,1,4,4-tetramethyl-6-*t*-butyl-1,2,3,4-tetrahydronaphthalene (II). Its properties indicate that it is not Senkowski's hydrocarbon, as previously proposed.

The Friedel-Crafts alkylation of 1,4-di-*t*-butylbenzene with *t*-butyl chloride gives a complex mixture.[3,4] The products previously identified are 1,3-di-*t*-butylbenzene,[3] 1,3,5-tri-*t*-butylbenzene (I)[3] and 1,1,4,4,5,5,8,8-octamethyl-1,2,3,4,5,6,7,8-octahydroanthracene (III).[4] It has been suggested that formation of compound III proceeds *via* the alkylation of 1,4-di-*t*-butylbenzene by the 2,5-dimethyl-2-hexyl cation with the attendant or prior loss of *t*-butyl cations from the aromatic nucleus, and that the unknown compound II is an intermediate (equations 2, 3, and 4).[5,6] The 2,5-dimethyl-2-hexyl cation is thought to arise by dimerization of isobutylene followed by several rearrangement steps (equation 1).[6] Evidence for the suggested mode of formation of III are the observations that (1) *t*-butyl chloride yielded about 1% of 2,5-dichloro-2,5-dimethylhexane when contacted briefly with aluminum chloride near 0°;[6] and (2) Friedel-Crafts alkylations of 1,4-di-*t*-butylbenzene and of benzene with 2-chloro-2,5-dimethylhexane produced III.[5]



(1)



II III

(2)

In these laboratories, application of the procedure of Bartlett, Roha, and Stiles[3] to the preparation of large quantities of 1,3,5-tri-*t*-butylbenzene led to the isolation of a small yield of a new colorless crystalline compound, m.p. 63–64°, which has been found to have the structure of the proposed intermediate II. This compound was obtained from a complex mixture of high boiling products by fractional distillation and recrystallization. Evidence for the structural assignment is presented below.

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(1) Taken in part from the Ph.D. thesis of Philip C. Myhre, University of Washington, 1958.

(2) National Science Foundation postdoctoral fellow at the Nobel Institute, 1958–59.

(3) P. D. Bartlett, M. Roha, and R. M. Stiles, *J. Am. Chem. Soc.*, **76**, 2349 (1954).

(4) L. R. C. Barclay and E. E. Betts, *J. Am. Chem. Soc.*, **77**, 5735 (1955).

(5) L. R. C. Barclay and J. W. Hilchie, *J. Org. Chem.*, **22**, 633 (1957).

(6) F. E. Condon, *J. Org. Chem.*, **21**, 761 (1956).

The molecular formula of the compound as determined by carbon-hydrogen analysis and molecular weight measurements was found to be $C_{18}H_{28}$. The compound was inert to treatment with basic permanganate. Dehydrogenation of a sample of the hydrocarbon yielded a material which had an ultraviolet spectrum characteristics of a naphthalene, indicating that the compound is bicyclic. The ultraviolet spectrum of the hydrocarbon had the characteristic 260 mμ absorption band of a benzene derivative. There were no indications in the ultraviolet spectrum that strongly conjugating groups are attached to the benzene ring. The infrared spectrum indicated that the compound is an unsymmetrically trisubstituted benzene. This is, in the 900 to 675 cm.$^{-1}$ region assigned to out of plane bending vibrations of aromatic hydrogens, strong absorption bands were found at 892 cm.$^{-1}$ and 825 cm.$^{-1}$. The 825 cm.$^{-1}$ absorption is in the region (820 cm.$^{-1}$) assigned to out of plane bending vibrations of two adjacent hydrogens.[7] The band at 892 cm.$^{-1}$ although higher than the normally observed frequency (860 cm.$^{-1}$) might be considered to be an out of plane bending vibration of an isolated aromatic hydrogen.

Two independent syntheses of the hydrocarbon were achieved. The first synthesis involved the alkylation of *t*-butylbenzene with 2,5-dichloro-2,5-dimethylhexane (see Fig. 1). A product identical in all respects with the unknown hydrocarbon was isolated in 14% yield. In addition, the hydrocarbon identified by Barclay, III, was isolated in 20% yield. Moreover, a large amount of 1,4-di-*t*-butylbenzene also was obtained presumably through disproportionation of *t*-butylbenzene. Its occurrence makes the reaction of doubtful value as an unambiguous proof of structure. Consequently an alternative synthesis of the hydrocarbon was undertaken, starting with the previously reported 1,1,-4,4,6-pentamethyl-1,2,3,4-tetrahydronaphthalene, IV.[8] The 6-methyl group of IV was converted to a 6-*t*-butyl group by standard methods as shown in Fig. 1. None of these steps appears to be of a type which would lead to a rearrangement of the carbon skeleton. All conversions in this sequence were effected in yields of 80% or better with the exception of the last coupling step. The final product had a melting point identical with that of the hydrocarbon obtained in the alkylation of 1,4-di-*t*-butylbenzene with *t*-butyl chloride and the mixed melting point was not depressed. The infrared and ultraviolet spectra of the two materials were identical.

The structure of the acid V, obtained by oxidation of the known compound IV, also was related to the structure of the known phenol X. The acid V was converted to an aromatic primary amine by use of the Schmidt reaction and the resulting amine was converted *via* the diazonium salt to a phenol identical with compound X. The structure of X had previously been established by degradation as well as by its synthesis through the alkylation of phenol with 2,5-dichloro-2,5-dimethylhexane.[8]

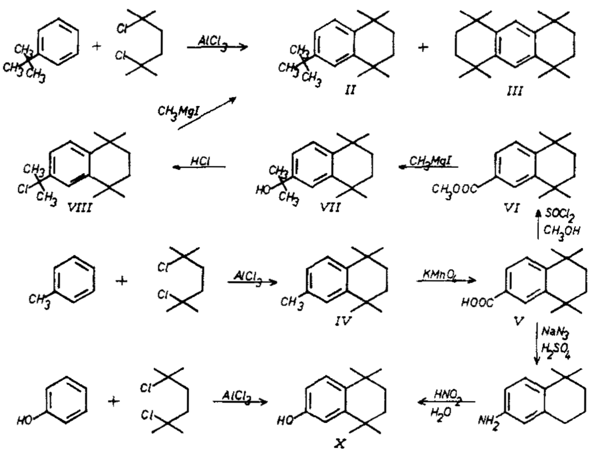

Figure 1

Barring unexpected rearrangements in the independent syntheses of the hydrocarbon, it appears definitely to have the structure II, *i.e.*, 1,1,4,4-tetramethyl-6-*t*-butyl-1,2,3,4-tetrahydronaphthalene.

The fact that compound II is obtained along with compound III in both the Friedel-Crafts alkylation of 1,4-di-*t*-butylbenzene with *t*-butyl chloride and the alkylation of *t*-butylbenzene with 2,5-dichloro-2,5-dimethylhexane lends support to Barclay's suggestion that compound II is an intermediate in the formation of III.[5] Barclay also has proposed that compound II is identical with hydrocarbon obtained by Senkowski in 1890.[9] Senkowski had obtained a "flaky white solid" (m.p. 128°, b.p. 291–292°/736.6 mm.) along with *t*-butylbenzene and 1,4-di-*t*-butylbenzene from the reaction of benzene, isobutyl chloride, and aluminum chloride and had erroneously thought it to be a tri-*t*-butylbenzene.[5] However, Senkowski's hydrocarbon is probably not compound II either, in view of the wide discrepancy in melting points.[10]

EXPERIMENTAL

Alkylation of p-di-t-butylbenzene with t-butyl chloride.[3] Cold *t*-butyl chloride (445 g., 4.8 moles) was added over a period of 2 hr. to a mixture of 785 g. (4.1 moles) of 1,4-di-*t*-butylbenzene, 661 g. (4.9 moles) of aluminum chloride, and 2 l. of ethylene dichloride which was cooled to below 5°. The reaction mixture was stirred vigorously for 4 hr. at a

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(7) N. B. Colthup, *J. Optical Soc. Am.*, **40**, 397 (1950).

(8) H. A. Bruson and J. W. Kroeger, *J. Am. Chem. Soc.*, **62**, 36 (1940).

(9) M. Senkowski, *Ber.*, **23**, 2412 (1890).

(10) The infrared spectrum of II differs considerably from that of a compound (m.p. 129°) isolated from the residues of a commercial preparation of 1,4-di-*t*-butylbenzene and believed to be Senkowski's hydrocarbon (ref. 3). We are indebted to Professor P. D. Bartlett for kindly furnishing us an infrared spectrum of the latter compound.

temperature between −5° and 5° and then was hydrolyzed by cautiously pouring onto ice and water. The organic layer was separated and washed several times with water and then was dried over sodium carbonate. The solvent was removed by distillation and the remaining oil was distilled through a modified Claisen distilling head under reduced pressure. The following fractions were obtained:

Fraction	B.P.	Pressure, Mm.	Wt., G.
1	105–110	12	115
2	113–118	12	116
3	119–124	12	282
4	>125	12–5	51
Residue	...	...	125

(a) *1,3,5-Tri-t-butylbenzene.* Fraction 3, which was partially solid, was suction filtered. The solid, which was washed with two 50-ml. portions of cold ethanol and air dried, weighed 107 g., m.p. 66–69°. Two recrystallizations from ethanol yielded 78 g., 8% yield, of 1,3,5-tri-*t*-butylbenzene, m.p. 70.5–72°.[11,12]

Further recrystallization and sublimation gave a sample melting at 72.2–72.8°, reported[8] m.p. 72.5–73.0°.

Anal. Calcd. for $C_{18}H_{30}$: C, 87.74; H, 12.26. Found: C, 87.66; H, 12.21.

(b) *1,1,4,4,5,5,8,8-Octamethyl-1,2,3,4,5,6,7,8-octahydroanthracene* (III). The solid collected by suction filtration from the partially crystallized fraction 4 was combined with the crystalline product obtained from the residue by crystallization from *n*-heptane. The combined solids after several recrystallizations from *n*-heptane and chloroform-methanol weighed 35 g. and melted at 205–210°, reported[8] m.p. 209–210°. The infrared and ultraviolet spectra of this material were identical with those reported by Barclay for compound III.[12]

(c) *Compound* II. *1,1,4,4-Tetramethyl-6-t-butyl-1,2,3,4-tetrahydronaphthalene.* The filtrate from fraction 4 was distilled through a 20-in. spinning band column under reduced pressure. The first fraction collected was mainly 1,3,5-tri-*t*-butylbenzene. The second fraction (10 g. of viscous oil, b.p. 130–131°/5 mm., n_D^{25} 1.5066) crystallized after standing for several days. The solid was collected on a suction funnel, washed with cold ethanol (about 20 ml.) and recrystallized twice from absolute ethanol yielding 2.5 g. of colorless, square platelets (m.p. 62.5–64°). Repeated crystallization and sublimation yielded a sample which melted at 63–64°. The infrared spectrum in the aromatic C—H bending region[7] had strong bands at 825 and 892 cm.$^{-1}$. The ultraviolet spectrum in ethanol had the following λ_{max} and ϵ_{max} values: 266 mμ (515): 274 mμ (418); shoulder at 260 mμ (375).

Anal. Calcd. for $C_{18}H_{28}$: C, 88.45; H, 11.55. Found: C, 88.66; H, 11.33. Calcd. mol. wt.: 244. Found: 242 (Rast method).

(d) *Other products.* 1,3-Di-*t*-butylbenzene and 1,4-di-*t*-butylbenzene were the principal constituents of fractions 1 and 2. These compounds were not isolated in a pure state. There were also considerable amounts of high boiling materials and residue which were not identified. Solutions of these materials were fluorescent in normal artificial light indicating the presence of polycyclic aromatic hydrocarbons.

Dehydrogenation of compound II. Compound II (0.10 g.) was dehydrogenated over 5% palladium on charcoal (2 g.) in an evacuated sealed tube heated to 450° for 12 hr. After releasing the internal pressure, the contents of the tube were placed in a gravity filter and washed thoroughly with purified pentane. The filtrate was evaporated to dryness and the residue was dissolved in ethanol. The ultraviolet spectrum of the ethanol solution possessed the characteristic absorption bands of a naphthalene in the 300–320 mμ and 280–290 mμ region. Absorption bands at 266 and 276 mμ characteristic of the starting hydrocarbon also were present, indicating that the dehydrogenation had not gone to completion.

Alkylation of t-butyl benzene with 2,5-dichloro-2,5-dimethylhexane. Alternative preparation of compound II. Anhydrous aluminum chloride (0.18 g.) was added to a solution of *t*-butylbenzene (10.6 g., 0.79 mole) and 2,5-dichloro-2,5-dimethylhexane[4] (3.3 g., 0.18 mole) in a flask fitted with a magnetic stirrer. The reaction mixture was stirred vigorously at room temperature for 40 min. and then was hydrolyzed with ice and dilute hydrochloric acid. Pentane was added, and the organic phase was separated, washed with water, and dried over anhydrous sodium sulfate. The pentane and *t*-butylbenzene were removed by distillation, and the semisolid residue was distilled through a spinning band column under reduced pressure. 1,4-Di-*t*-butylbenzene (1.9 g., b.p. 120°/12 mm.) was isolated from the distillate. This compound was characterized by its melting point, infrared spectrum, and elementary analysis. The residue remaining in the distillation flask was dissolved in chloroform-methanol and allowed to crystallize. The crystalline material collected (0.55 g., m.p. 195–211°) was shown to be III by comparison of the infrared spectra. The filtrate was concentrated and the residue was collected. Fractional crystallization from ethanol and sublimation yielded 0.65 g. of colorless square platelets, m.p. 62.5–64°, no depression in melting point when mixed with the hydrocarbon, m.p. 62.5–64°, obtained in the alkylation of 1,4-di-*t*-butylbenzene with *t*-butyl chloride (described above).

1,1,4,4,6-Pentamethyl-1,2,3,4-tetrahydronaphthalene (IV).[8] Two grams of aluminum chloride was added cautiously to a stirred solution of 2,5-dichloro-2,5-dimethylhexane (47 g.) and toluene (100 ml.) and cooled to 0°. The mixture was warmed slowly to room temperature (24–26°) and was stirred overnight. The mixture was hydrolyzed with dilute hydrochloric acid and washed with water until neutral. The organic phase gave a negative test when treated with methanolic silver nitrate. After the solution was dried over magnesium sulfate, the excess toluene was removed by distillation under 20 mm. pressure, leaving 50.5 g. (88%) of a colorless solid, m.p. 32–34°. Recrystallization from methanol-acetone yielded platlets, m.p. 34°.

Anal. Calcd. for $C_{15}H_{22}$: C, 89.04; H, 10.96. Found: C, 89.06; H, 10.92.

1,1,4,4-Tetramethyl-6-carboxy-1,2,3,4-tetrahydronaphthalene (V). The procedure used was essentially that of Schlatter[13] as adapted by Wepster *et al.*[14] A 500-ml. flask equipped with a stirrer and reflux condenser was charged with 35 g. of IV, 10 g. of sodium hydroxide, 120 ml. of pyridine, and 60 ml. of water. The flask was heated in an oil bath maintained at 95° and 67 g. of potassium permanganate was added in portions over a period of 3 hr. The reaction mixture was heated and stirred for an additional 2 hr. Then 10 ml. of ethanol was added slowly to reduce any remaining permanganate. After being cooled, the reaction mixture was suction filtered (Hyflo), and the collected manganese dioxide was washed with 350 ml. of 2*N* sodium hydroxide. The combined filtrate was concentrated to about 250 ml. and acidified with 10% sulfuric acid. The flocculent precipitate was collected by suction filtration, redissolved in ether, and extracted with 10% sodium hydroxide. The basic solution was acidified and the precipitate collected by suction filtration. Recrystallization from glacial acetic acid gave 32 g. (80%) of fine white crystals, m.p. 197–199°. Repeated recrystallization from benzene–petroleum ether (80–90°) gave a sample, melting at 198–199.5°.

Anal. Calcd. for $C_{15}H_{20}O_2$: C, 77.61; H, 8.68. Found: C, 77.67; H, 8.92. Neut. equiv.: Calcd. 232.3. Found: 232.

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(11) Undoubtedly the best method of preparation of this compound is described by Barclay and Betts.[12]

(12) L. R. C. Barclay and E. F. Betts, *Can. J. Chem.*, **33**, 672 (1955).

(13) M. J. Schlatter, U. S. Patent **2,635,114**; *Chem. Abstr.*, **48**, 7059 (1954).

(14) W. van Hartinsveldt, P. E. Verkade, and B. M. Wepster, *Rec. trav. chim.*, **75**, 349 (1956).

1,1,4,4-Tetramethyl-6-carbomethoxy-1,2,3,4-tetrahydronaphthalene (VI). A mixture of 13.0 g. of the acid V and 15.0 ml. of thionyl chloride was heated gently to reflux for 1 hr. and allowed to stand for 3 hr. Excess thionyl chloride was removed by distillation under reduced pressure. Fifteen milliliters of absolute methanol was added to the residual acid chloride and the mixture was heated at reflux temperature overnight. The reaction mixture was dissolved in 30 ml. of ether and washed successively with water, 5% sodium bicarbonate, and water. After being dried over anhydrous magnesium sulfate the ether was removed by distillation under reduced pressure, leaving a viscous straw-colored liquid which was distilled to yield 12.9 g. (93%), b.p. 161–164°/7–8 mm., n_D^{25} 1.5258.

Anal. Calcd. for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 78.25; H, 9.47.

1,1,4,4-Tetramethyl-6-(α-hydroxy-α,α-dimethyl)methyl-1,2,3,4-tetrahydronaphthalene (VII). A solution of methyl magnesium iodide was prepared in the usual manner starting with 12.7 g. of methyl iodide, 2.16 g. of magnesium turnings and 35 ml. of absolute ether. A solution of 10.0 g. of the ester VI and 25 ml. of absolute ether was added dropwise to the Grignard reagent (20 min.). The resulting mixture was heated at reflux for 1 hr. and allowed to stand overnight. After hydrolysis with 2*N* hydrochloric acid, the ether layer was washed with water, 5% sodium bicarbonate, 5% sodium thiosulfate, and water. After being dried over magnesium sulfate, the ether was removed by distillation, and the residue was recrystallized from petroleum ether (80–90°) to yield 12.5 g. (98%) of flocculent white crystals, m.p. 91–93°. Repeated crystallization from petroleum ether and sublimation afforded a sample melting at 95.5–96.3°.

Anal. Calcd. for $C_{17}H_{26}O$: C, 82.87; H, 10.64. Found: C, 83.02; H, 10.75.

1,1,4,4-Tetramethyl-6-(α-Chloro-α,α-dimethyl)methyl-1,2,3,4,4-tetrahydronaphthalene (VIII). An ether solution (30 ml.) of the alcohol VII (7.0 g.) was cooled to 0°. Anhydrous hydrogen chloride was passed through the solution for 2 hr. During this time square platelets deposited from the ether solution. Ice and water were added and the ether layer was washed rapidly with water, 5% sodium bicarbonate, and water. The ether layer was dried over magnesium sulfate and the ether removed by distillation to leave 7.1 g. (93%) of the white crystalline chloride which was used without purification in the next step.

1,1,4,4-Tetramethyl-6-t-butyl-1,2,3,4-tetrahydronaphthalene (II). A solution of the crude chloride VIII (7.0 g.) in ether (30 ml.) was added dropwise to a Grignard solution prepared from 7.0 g. of methyl iodide, 1.0 g. of magnesium turnings, and 20 ml. of absolute ether. The reaction mixture was stirred and heated at reflux temperature for 3 days. The mixture was hydrolyzed with 20 ml. of 3*N* hydrochloric acid and washed in the usual manner, followed by drying of the ether solution over magnesium sulfate. A viscous, colorless oil (5.5 g.) was obtained upon evaporation of the ether. When the oil was dissolved in 30 ml. of absolute ethanol, 0.60 g. of white crystalline material precipitated upon cooling. After recrystallization from petroleum ether (90–100°), the material melted at 213–216°. This is possibly a diphenylethylene derivative arising from the coupling of two molecules of VIII.

The filtrate was distilled to remove the ethanol and the residual oil was sublimed (80°/6–7 mm.) to yield 2.5 g. (39%) of crystalline product, m.p. 52–58°. After repeated crystallization from methanol-acetone (3 to 1), 1.2 g. of flaky colorless crystals (m.p. 62.5–64°) were obtained. The infrared spectrum of this material was identical with that of compound II. A mixed melting point showed no depression.

1,1,4,4-Tetramethyl-6-hydroxy-1,2,3,4-tetrahydronaphthalene (X).[8] Three grams of phenol and 5 g. of 2,5-dichloro-2,5-dimethylhexane were suspended in 6 ml. of petroleum ether (90–100°). Aluminum chloride (0.3 g.) was added and the mixture was stirred at room temperature for 24 hr. The reaction mixture was hydrolyzed with dilute hydrochloric acid, and the partially crystallized organic layer was dissolved in warm benzene, washed with water until neutral, and dried over magnesium sulfate. Concentration of the solvent to about 10 ml. and cooling give 3.2 g. of crystalline product, m.p. 140°. Two recrystallizations from petroleum ether (90–100°) raised the melting point to 145°, reported[8] m.p. 145°.

1,1,4,4-Tetramethyl-6-amino-1,2,3,4-tetrahydronaphthalene (IX). Sodium azide (1.70 g.) was added in small portions to a well stirred mixture of V (5.0 g.), chloroform (20 ml.), and 96% sulfuric acid (6.0 ml.) over a 30-min. period. The temperature was maintained at 45° with an oil bath during the addition and for 1 hr. following. The mixture was then heated at 65° for 3 hr. Evolution of nitrogen was rapid during the first hour. The product was isolated by the addition of water, neutralization with sodium hydroxide, and extraction with ether. Evaporation of the solvent left 3.5 g. (80%) of brownish crystals, m.p. 73°.

Anal. Calcd. for $C_{14}H_{21}N$: C, 82.69; H, 10.41; N, 6.89. Found: C, 82.89; H, 10.21; N, 7.05.

X *from* IX. A solution of sodium nitrite (0.33 g. in 6 ml. of water) was added dropwise to an iced suspension of the amine hydrochloride IX (1.0 g.) in 20 ml. of 0.1*N* hydrochloric acid. After the addition of sodium nitrite, 50 ml. of cold water was added and the resulting suspension was stirred vigorously for 4 hr. The fine yellow precipitate which formed during this period was collected and dried (0.51 g.). Recrystallization from petroleum ether (Norit) yielded 0.4 g. colorless needles, m.p. 145°. A mixed melting point with X prepared from phenol and 2,5-dichloro-2,5-dimethylhexane showed no depression.

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