Piperidine was purified by standing over potassium hydroxide pellets for 1 week. The pellets were removed by filtration and the filtrate was distilled through a 30-cm. Dufton column, b.p. 105–106°, n^{20}_{D} 1.4527.

Commercial anhydrous ether and benzene were allowed to stand over sodium for 1 week and redistilled.

Reaction of Piperidine and Chloroform.—Piperidine (8.5 g., 0.1 mole) was mixed separately with (1) chloroform I (11.9 g., 0.1 mole), (2) chloroform II (11.9 g., 0.1 mole), and (3) chloroform III (11.9 g., 0.1 mole). After 24 hr., excess anhydrous ether was added to each solution. A white solid (0.11 g.) precipitated immediately from reactions 1 and 2, whereas reaction 3 yielded only a slight precipitate (0.003 g.), m.p. 245°, corresponding to piperidine hydrochloride, after standing for a short time. The product of reactions 1 and 2 had a melting point of 236° and a mixture of both produced no depression in the melting point. (Pierce and Joullie[1] record 244° as the melting point of this product.)

The same product was produced next by interaction of piperidine (0.1 mole) with "purified" chloroform III (0.1 mole) containing authentic chlorobromomethane (0.5% v./v.), and by mixing piperidine (0.1 mole) with authentic chlorobromomethane (0.1 mole), when a vigorous exothermic reaction occurred and a white solid separated almost immediately. In Table I the melting points and mixture melting points of the products prepared by the various methods A, B, and C are listed.

Table I

Sample[a]	M.p., °C.
A	235
B	234
C	234
A + B	235
A + C	234
B + C	235

[a] A = piperidine + chloroform B.P. (I), B = piperidine + chlorobromomethane, C = piperidine + chlorobromomethane in "purified" chloroform (III).

The following considerations contribute towards the elucidation of the structure of this product. The substance gives qualitative reactions for bromide.[7] After controlled oxidation with nitric acid,[8] the aqueous solution gave a precipitate with silver nitrate. The volumes of 0.1 N silver nitrate required before and after treating the solid with sodium and alcohol (Stepanov method) were identical. Hence, both the chlorine and bromine are ionized and the product appears to be an equimolecular mixture of piperidine hydrochloride and piperidine hydrobromide.

Anal. Calcd. for $C_5H_{11}N\cdot HCl\cdot C_5H_{11}N\cdot HBr$: C, 41.74; H, 8.35; N, 9.74; ionic Br, 27.83, ionic Cl. 12.34. Found, for the products formed from reaction of piperidine with (a) chlorobromomethane (b) chloroform B.P. (I), (c) chloroform II, and (d) "purified" chloroform (III) containing chlorobromomethane: (a) C, 41.46; H, 8.59; N, 9.56; ionic Br, 28.06; ionic Cl, 12.51. (b) ionic Br, 25.33; ionic Cl, 15.08; (c) ionic Br, 24.42; ionic Cl, 14.50; and (d) ionic Br, 27.65; ionic Cl, 13.06.

A higher proportion of chloride in (b) and (c) may be due to reaction of the base with the methylene chloride impurity.[3] Finally, the products formed by methods A, B, and C (see Table I) did not depress the melting point of a mixture of authentic piperidine hydrochloride and hydrobromide (234°).

Reaction of Piperidine with Chlorobromomethane.—Piperidine (25.5 g., 0.3 mole) was added to chlorobromomethane (64.8 g., 0.5 mole) in dry benzene (100 ml.) contained in a flask fitted to a condenser carrying a tube containing calcium chloride and soda lime. The reaction was markedly exothermic and a turbidity formed within 3–5 min. After 24 hr., the white crystalline solid was removed by filtration, washed with dry benzene, and dried, yielding 20.96 g., m.p. 236°. It did not depress the melting point of a mixture of authentic piperidine hydrochloride and hydrobromide.

Anal. Calcd. for $C_5H_{11}N\cdot HBr\cdot C_5H_{11}N\cdot HCl$: Br, 27.83; Cl, 12.34. Found: Br, 28.53; Cl, 11.98.

The filtrate was concentrated and then fractionated under reduced pressure to give a colorless liquid (X) in 12.30-g. yield, b.p. 55–58° (0.8 mm.), 238° (760 mm.), n^{20}_{D} 1.4825.

Reaction of Piperidine with Methylene Bromide.—Piperidine (51 g., 0.6 mole) was added to methylene bromide (17.4 g., 0.1 mole) in dry benzene (50 ml.) in a flask fitted as before. The reaction was again exothermic and a white solid commenced separating within 0.25 hr. After 48 hr., the white crystalline solid was recovered and dried, yielding 29.73 g., m.p. 235°. It did not depress the melting point of authentic piperidine hydrobromide.

Anal. Calcd. for $C_5H_{11}N\cdot HBr$: Br, 48.19. Found: Br, 48.00.

The filtrate on fractionation under reduced pressure gave a colorless liquid (Y) in 15.03 g. yield, b.p. 58° (0.7 mm.), 238° (760 mm.), n^{20}_{D} 1.4820.

Reaction of Piperidine with Methylene Chloride.—Piperidine (17 g., 0.2 mole) was added to methylene chloride (25.5 g., 0.3 mole) in dry benzene (50 ml.) in a flask fitted as before. The reaction was exothermic, but no solid separated on standing for 2 hr. After boiling under reflux for 24 hr., the white crystalline solid which had formed was removed by filtration, washed with dry benzene, and dried, yielding 14.71 g., m.p. 243°. It did not depress the melting point of authentic piperidine hydrochloride.

Anal. Calcd. for $C_5H_{11}N\cdot HCl$: Cl, 29.16. Found: Cl, 28.71.

The filtrate on fractionation under reduced pressure gave a colorless liquid (Z) in 3.61-g. yield, b.p. 60° (1.0 mm.), 236° (760 mm.), n^{30}_{D} 1.4825.

Authentic 1,1′-dipiperidylmethane was prepared from piperidine and aqueous formaldehyde.[9] It was a colorless liquid, b.p. 58–60° (1.0 mm.), 238° (760 mm.), n^{20}_{D} 1.4825; lit. b.p. 235°, n^{25}_{D} 1.4810.[10]

Anal. Calcd. for $C_{11}H_{22}N_2$: C, 72.52; H, 12.09. Found: C, 72.95; H, 12.01.

Identification of Liquids X, Y, and Z.—The identity of liquids X, Y, and Z was established by the following considerations. Their boiling points and refractive indices were identical with those ofa uthentic 1,1′-dipiperidylmethane; the infrared spectra of X, Y, Z, and authentic 1,1′-dipiperidylmethane were identical.

Anal. Calcd. for $C_{11}H_{22}N_2$: C, 72.52; H, 12.09; N, 15.38. Found for X: C, 72.98; H, 12.02; N, 15.99. Found for Y: C, 71.75; H, 12.06. Found for Z: C, 71.81; H, 12.13.

In the preparation according to the directions of Erhenberg[11] of derivatives with carbon disulfide, X, Y, and Z gave products, which after recrystallization from petroleum ether (b.p. 60–80°) had identical melting points (60°). Mixtures of these derivatives, in turn, with an authentic sample of the carbon disulfide derivative of 1,1′-dipiperidylmethane showed no depression in melting point (lit.[11] m.p. 58°).

Reaction of Piperidine with "Purified" Chloroform III.—Piperidine (17 g., 0.2 mole) was added to "purified" chloroform (35.7 g., 0.3 mole) in dry benzene (50 ml.) in a flask fitted as before. After boiling under reflux for 120 hr., a small quantity of white crystals had separated. These were removed by filtration, washed with "purified" chloroform, and dried, yielding 1.53 g., m.p. 245°. It did not depress the melting point of authentic piperidine hydrochloride.

Anal. Calcd. for $C_5H_{11}N\cdot HCl$: Cl, 29.16. Found: Cl, 29.22.

The filtrate on fractionation under reduced pressure gave a colorless liquid in 0.13-g. yield, b.p. 48–50° (1.0 mm.), whose properties (infrared spectrum, mercuric chloride derivative) were identical with those of authentic N-formylpiperidine.[1]

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[7] F. Fiegel, "Spot Tests," Vol. 1, 4th Ed., Elsevier Publishing Co., London, 1954, p. 246.

[8] "British Pharmacopoeia," Pharmaceutical Press, London, 1958, p. 509.

[9] Knoevenagel, *Ber.*, **31**, 2585 (1898).

[10] T. C. Simmons and F. W. Hoffmann, *et al.*, *J. Am. Chem. Soc.*, **79**, 3429 (1957).

[11] Erhenberg, *J. prakt. Chem.*, [2]**36**, 117 (1877).

1,12-Dioxa[5.5]paracyclophane

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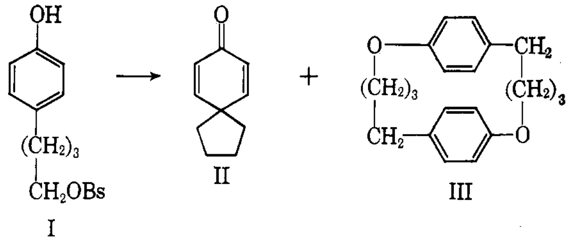
We wish to report the isolation and characterization of 1,12-dioxa[5.5]paracyclophane[2] (III), a by-product of the solvolysis of 4-(p-hydroxyphenyl)butyl brosylate

(I). The solvolysis of I and the isolation and characterization of the principal product (II) has been previously described.[3]

The neutral products from the solvolysis of I were chromatographed on a column of grade I basic alumina rather than distilled as previously described. Elution with benzene–pentane (1:9) gave a solid (III). Continued elution with benzene–pentane (2:3) gave II. The minor product (III) is clearly a dimer (osmometric molecular weight 294, calculated for III 296.4).[4] The infrared spectrum of III shows no hydroxyl absorption. The ultraviolet spectrum (λ_{max} 223, 277, and 285 mμ) is comparable with that of 4-methylanisole (223, 279, and 286 mμ).[5] The nuclear magnetic resonance spectrum of III shows eight aromatic protons as a pair of superimposed A_2B_2 patterns centered at τ 3.48, four protons as an unsymmetric triplet at 6.08 (–CH_2–O–), four protons as a similar triplet at 7.58 (benzylic methylene protons), and eight protons as a broad multiplet at 8.52 (remaining methylene protons).

Structure III is confirmed by the following chemical evidence. Refluxing constant boiling hydriodic acid converts III to 4-(4-iodobutyl)phenol (IV). Immediate reduction of IV using 5% palladium on sodium carbonate as catalyst gives 4-*n*-butylphenol (V) identified by its spectral properties[6] and the crystalline phenylcarbamate, m.p. 114–115°.



The preparation of III by dimerization of I points to a useful synthetic method for heteroatom substituted paracyclophanes. Although the solvolysis reaction was run in this study at twice the original[3] concentration, the results imply that solvolysis of I in still more concentrated solutions should favor higher yields of 1,12-dioxa[5.5]paracyclophane.

Experimental

General Procedure.—A solution containing 14.5 g. of 4-(*p*-hydroxyphenyl)butyl brosylate (I) in 950 ml. of 0.025 *N* potassium *t*-butoxide in *t*-butyl alcohol was heated in a constant temperature bath at 54.8 ± 0.1° for 7 hr. The work-up of the reaction mixture was identical with that of Baird and Winstein[3] except the crude residue (usually 4–4.5 g.) was not distilled, but carefullly chromatographed on Woelm grade I basic alumina using increasing concentrations of benzene in pentane.

Elution with benzene in pentane (1:9) gave III (5–7% yield, m.p. 123–126°). One recrystallization from cyclohexane gave pure III, m.p. 132–132.5°. The infrared spectrum (KBr) of III showed bands at 3.30, 3.42, 3.51, 6.22, 6.33, 6.65, 6.92, 7.72, 8.15, 12.05, 12.20, 12.50, and 12.91 μ. In the ultraviolet, III showed $\lambda_{max}^{95\%\ EtOH}$ 223 mμ (ϵ 14,000), 277 (2320), and 285 (1710).

Anal. Calcd. for $C_{20}H_{24}O_2$: C, 80.97; H, 8.16; mol. wt., 296.4. Found: C, 80.90; H, 7.93; mol. wt., 294 (osmometric).

Elution (2:3 benzene–pentane) provided nearly pure II as determined by ultraviolet analysis, $\lambda_{max}^{95\%\ EtOH}$ 242 mμ (ϵ 14,500).[3] For complete purity, the liquid was distilled[7] giving a product that was solid at room temperature.

Degradation of 1,12-Dioxa[5.5]paracyclophane (III) to 4-*n*-Butylphenol (V).—A solution containing 400 mg. of III in 7 ml. of constant boiling hydriodic acid was heated under reflux for 5 hr., at which time all but a very small amount of III had gone into solution. The cooled reaction mixture was diluted with 25 ml. of water and extracted with three 15-ml. portions of ether. The combined ether fractions were dried over anhydrous sodium sulfate. After removal of the ether under reduced pressure, a semisolid, reddish residue was obtained that showed hydroxyl absorption in the infrared. The residue was immediately dissolved in 10 ml. of 5% ethanolic potassium hydroxide. A small quantity of solid would not dissolve and was filtered off. After the addition of 5% palladium on sodium carbonate (400 mg.), the ethanolic solution was hydrogenated at atmospheric pressure. The solution absorbed 23.5 ml. (60.5 ml. theory) of hydrogen. After removal of the catalyst by filtration, the solution was diluted with 50 ml. of water and extracted with four 15-ml. portions of ether. The ether extracts were combined and dried over anhydrous sodium sulfate. Removal of the ether under reduced pressure left 310 mg. of a yellow oil. The oil was chromatographed on a silicic acid column (15 × 300 mm.) providing 153 mg. of 4-*n*-butylphenol (V). The infrared spectrum (CCl_4) of V showed bands at 3.00, 3.32, 3.43, 3.50, 6.21, 6.62, 8.08, 12.12, and 12.42 μ. A concentrated solution of V in CCl_4 showed absorption at 5.33 and 5.70 μ.[6]

The reaction of V with phenyl isocyanate gave 4-*n*-butylphenyl phenylcarbamate, m.p. 114–115°, lit.[8] m.p. 115°.

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Cyclopropanes from an Easily Prepared, Highly Active Zinc–Copper Couple, Dibromomethane, and Olefins

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The general reaction developed by Simmons and Smith for the preparation of cyclopropanes[1] from olefins, diiodomethane, and zinc–copper couple has proven to be exceedingly useful. The single drawback of their procedure, the inconvenience of preparing an active zinc–copper couple, was alleviated somewhat by the findings of Shank and Shechter[2] that a more conveniently prepared zinc–copper couple described by Hennion and Sheehan[3] will take part in the Simmons–Smith reaction. The couples described by these various groups may require several hours of tedious manipulations to prepare, may vary in activity from batch to batch, frequently requiring activation by iodine, and will react only with the expensive diiodomethane and chloroiodomethane. Reported here is a vastly simplified preparation of a *highly active* zinc–copper couple which, in the presence of olefins and without the use of

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