

1-Phenylcyclobutanol (III) was synthesized from cyclobutanone and phenyl lithium. The solid alcohol could be dehydrated to phenylcyclobutene (IV) which was converted to the solid 1-phenylcyclobutene nitrosochloride, presumably 1-chloro-1-phenyl-2-nitrosocyclobutane (V). The hydrogenation of this compound using Raney nickel or Adams' platinum catalysts led largely to dark resinous materials with varying amounts of 4-phenylbutylamine. Reduction of (V) with lithium aluminium hydride under a variety of conditions always gave 4-phenylbutylamine (VI) identified by comparison with an authentic sample.⁵

Experimental*

3-Phenylcyclobutanone oxime. A solution of 3-phenylcyclobutanone^{4†} (9.6 g, 66 mmoles) and hydroxylamine hydrochloride (36 g, 530 mmoles) in dry pyridine (100 ml) was heated on a steam bath at 90° for 8 h. After cooling, the solution was poured into 800 ml of water and carefully neutralized with dilute sulphuric acid. The mixture was extracted with four 125-ml portions of ether, and the combined extracts were washed with water and then exhaustively with 5 per cent potassium hydroxide solution. The combined basic extracts were neutralized carefully with dilute hydrochloric acid, and the precipitated oil was extracted into ether. The ether extract was washed with water, dried over sodium sulphate, the solvent was distilled off, and the residue extracted with several portions of low boiling (40–45°) petroleum ether. When the petroleum ether solutions were cooled to 0°, 3.5 g (33 per cent) of colourless 3-phenylcyclobutanone oxime crystallized out which after recrystallization from petroleum ether melted at 58.5–59.5°.

Anal. Calcd. for C₁₀H₁₁NO: C, 74.50; H, 6.89. Found: C, 74.29; H, 6.86.

3-Phenylcyclobutylamine. A solution of 3-phenylcyclobutanone oxime (5.3 g, 33 mmoles) in ether (100 ml) was added dropwise to a solution of lithium aluminium hydride (5.6 g, 0.15 mole) in ether

* All melting points are corrected. Microanalyses by Mrs. Margaret Logan.

† This ketone could be purified via its sodium bisulphite addition compound followed by distillation, but this procedure entailed considerable loss of material. The crude ketone from the catalytic hydrogenation of 2,2-dichloro-3-phenylcyclobutanone⁴ was used in this experiment.

(100 ml), and the mixture was refluxed for 8 h. After decomposing the excess hydride with water, the precipitated alumina was filtered off, the ether layer was separated, the aqueous layer was extracted with 50 ml of ether, and the combined ether solutions were dried over potassium hydroxide. Dry hydrogen chloride was passed into the filtered solution, and the colourless salt (4.9 g, 81 per cent) was recrystallized from ethanol-ethyl acetate to give 3.7 g (61 per cent) of *hydrochloride*, m.p. 198–190°.

Anal. Calcd. for $C_{10}H_{14}ClN$: C, 65.38; H, 7.66. Found: C, 65.44; H, 7.52.

Treatment of the oily base with acetic anhydride in ether gave a colourless *N-acetyl derivative* which after recrystallization from dilute ethanol melted at 125–126.5°.

Anal. Calcd. for $C_{12}H_{15}NO$: C, 76.12; H, 7.99. Found: C, 75.83; H, 7.87.

1-Phenylcyclobutanol. To a solution of phenyl lithium, prepared by adding a solution of bromobenzene (102 g, 0.650 mole) in ether (160 ml) to lithium wire (9.3 g, 1.3 g-atom) under 450 ml of ether, was added slowly with stirring a solution of cyclobutanone (20.0 g, 0.286 mole) in ether (45 ml). The mixture was stirred for 4 h after addition was completed, and was then decomposed carefully with water. The aqueous layer was extracted with 150 ml of ether, and the combined ether solutions were washed and dried over sodium sulphate. After removal of the ether the residue was distilled, b.p. 92–98°/1 mm. The semi-solid distillate was recrystallized from pentane at –15°, m.p. 41–42°.

Anal. Calcd. for $C_{10}H_{12}O$: C, 81.04; H, 8.18. Found: C, 80.89; H, 8.07.

1-Phenylcyclobutene. A mixture of 1-phenylcyclobutanol (25.4 g) and *p*-toluenesulphonic acid monohydrate (*ca.* 20 mg) was heated under reduced pressure in an oil bath at 100°, and the product was allowed to distil from the reaction flask through a short column. When most of the material had distilled, the residue suddenly turned dark and distillation ceased. The yield of colourless oil was 19.4 g (87 per cent), b.p. 74–75°/3.5 mm, n_D^{25} 1.5639.

Anal. Calcd. for $C_{10}H_{10}$: C, 92.24; H, 7.77. Found: C, 91.10; H, 7.63.

Azeotropic distillation of the tertiary alcohol with toluene in the presence of oxalic acid,⁶ or heating at 120° with trace amounts of iodine, gave erratic results, and led to considerable decomposition.

1-Phenylcyclobutene nitrosochloride. A solution of 1-phenylcyclobutene (2.5 g) in Diglyme (20 ml) was cooled to -20° and nitrosyl chloride was passed in slowly. The solution turned green, and a white precipitate formed gradually. After about 45 min the green colour turned yellowish-brown, signifying the end of the reaction. The precipitate was filtered off and washed with cold methanol. The colourless product (2.6 g, 68 per cent) melted at 96° (d.); the melting point did not change on recrystallization from chloroform-methanol.

Anal. Calcd. for C₁₀H₁₀ClNO: C, 61.37; H, 5.15. Found: C, 60.91; H, 4.97.

Reduction of 2 g of 1-phenylcyclobutene nitrosochloride with 1.5 g of lithium aluminium hydride in ether at 0° with slow warming and ultimate refluxing for 16 h, followed by standard working-up procedures, gave an ether solution of amines which was chromatographed over alumina, using ether and later ether-acetone eluants. After a fraction of 0.1 g which gave an oily fumarate salt, 0.02 g of a fraction furnishing a solid fumarate of m.p. 105-107° was obtained. This melting point was not raised by recrystallization from ethanol-ethyl acetate.

Anal. Calcd. for C₁₄H₁₇NO₄: C, 63.84; H, 6.50. Found: C, 63.75; H, 6.60.

Continued elution gave 0.25 g of material yielding a *fumarate*, m.p. 175.5-177°, after recrystallization from ethanol-ethyl acetate.

Anal. Calcd. for C₁₄H₁₉NO₄: C, 63.36; H, 7.24. Found: C, 63.36; H, 7.11.

A *hydrochloride* of the base from this fumarate was prepared in dry ether and recrystallized from ethanol-ether, m.p. 163-165°. It was identical (mixture melting point) with 4-phenylbutylamine hydrochloride of m.p. 164.5-165.5° (reported⁵ m.p. 161°). The 4-phenylbutylamine required for this identification was prepared by lithium aluminium hydride reduction of 4-phenylbutyramide.

Catalytic hydrogenation of 1-phenylcyclobutene nitrosochloride in ethanol or dioxane using Raney nickel or platinum oxide catalysts and sodium carbonate, potassium hydroxide or pyridine as

hydrogen chloride acceptors permitted an uptake of 50–70 per cent of the calculated amount of hydrogen. From the dark oily products, only 4-phenylbutylamine could be isolated in small amounts.

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