Early in the distillation solid iodine tended to plug the distillation column or condenser. This difficulty is avoided in the procedure described, in which the yield (72%) compares favorably with Bigot's (58%).

Iodine monochloride (650 g., 4.00 moles) was added dropwise during 1.5 hours to a vigorously stirred mixture of allyl alcohol (240 g., 4.13 moles) and crushed ice (200 g.). Each addition of iodine monochloride produced a vigorous release of acidic, white fumes. The initial addition turned the solution yellow and further amounts caused the product to become red and finally black. Stirring was maintained for an additional 1.25 hours while the reaction flask was kept surrounded by ice. Then the dense black oil was separated and the aqueous layer extracted with ether (250 cc.) and the extracted oil combined with the original oily layer. The oily layer was placed in a simple distilling flask attached to a condenser connected in succession to receivers A and B. The distilling flask was warmed in an oil-bath and its contents vacuum distilled. A forerun containing water was followed by copious evolution of iodine. Steam was passed through the condenser and receiver A was heated in a water-bath until iodine was no longer evolved. Receiver B was cooled in an ice-bath at all times so that the aqueous forerun and iodine collected in it. Then cold water was passed through the condenser and receiver A was cooled in an ice-bath. The red, oily allyl alcohol chloroiodides (638 g., 2.89 moles, 72%) were collected in A at 69–95° (1.5 mm.). The total distillation time was 5.5 hours. There was a residue of 151 g.

**Action of Sodium Hydroxide on Allyl Alcohol Chloroiodides.**—Bigot's procedure[2] was followed as closely as his description permitted. He reported stopping the addition of powdered sodium hydroxide to the allyl alcohol chloroiodides when the ethereal solution became colorless. The amount of sodium hydroxide was not stated. In the present work the molar ratio of sodium hydroxide was varied from 1.15 (A) to 3.19 (B). In neither case did the yellow color of the solution completely disappear, and increasing the amount of alkali reduced the yield of distillable products.

**A.**—Allyl alcohol chloroiodides (1014 g., 4.60 moles) in anhydrous ether (1500 cc.) were warmed in a water-bath (45°) under reflux until the deep red ether solution began to boil. The water-bath was then removed and powdered (20 mesh) sodium hydroxide (212 g., 5.30 moles) was added in 1–2 g. portions, with vigorous stirring, during 4.75 hours. The vigorous exothermic reaction following each addition was allowed to subside before more sodium hydroxide was added. The mixture was allowed to remain at room temperature overnight without stirring, and then was stirred for an additional 5.5 hours. The inorganic solids were filtered off and dissolved in water (400 cc.). The ethereal filtrate was washed with water (200 cc.) and the aqueous solutions were combined and washed twice with ether (210 cc. each). The combined ether solutions were dried over anhydrous potassium carbonate. The ether was removed under reduced pressure and the resulting yellow oil vacuum-distilled through a 2 × 30 cm. column containing Cannon protruded packing to give 301 g. of distillable products. Further distillation gave epichlorohydrin (49.9 g., 0.54 mole, 12%) and 2-chloroallyl alcohol (67.2 g., 0.73 mole, 16%). Redistillation gave epichlorohydrin b.p. 116° (742 mm.), $n^{25.5}\text{D}$ 1.4350, $\nu_{\overset{\diagup \text{O} \diagdown}{\text{C—C}}}$ 1271, 855, $\nu_{\text{C—Cl}}$ 724 cm.$^{-1}$, identical in infrared spectrum with that of redistilled Eastman Kodak material, and 2-chloroallyl alcohol, b.p. 133.5–133.6° (735 mm.), $n^{25}\text{D}$ 1.4565, $\nu_{\text{OH}}$ 3330, $\nu_{\text{C=C}}$ 1648, $\nu_{\text{C—Cl}}$ 716 cm.$^{-1}$, identical in infrared spectrum with that of redistilled Shell Development Co. material. None of the distillable products had infrared spectra containing all of the bands of redistilled Shell Development Co. 3-chloroallyl alcohol, b.p. 52–52.5° (12 mm.), $n^{25.5}\text{D}$ 1.4640, $\nu_{\text{OH}}$ 3350, $\nu_{\text{C=C}}$ 1631, $\nu_{\text{C—Cl}}$ 743 cm. $^{-1}$.

**B.**—Allyl alcohol chloroiodides (578 g., 2.62 moles) in anhydrous ether (500 cc.) were treated with powdered sodium hydroxide (334.5 g., 8.36 moles) as in A. Distillation through a 1.5 × 6 cm. column containing Cannon protruded packing gave 121 g. of distillable products. The first fraction (2.0 g.) corresponded in boiling point, 87–89 (743 mm.), to that of an azeotrope of allyl alcohol (72.3%) and water (27.7%), b.p. 88.89°.[17] The 3,5-dinitrobenzoate from this fraction showed no depression in mixed melting point (49°) with a sample prepared[15] from allyl alcohol.

Further distillation of the main fractions yielded epichlorohydrin (43.1 g., 0.466 mole, 18%) and 2-chloroallyl alcohol (46.0 g., 0.498 mole, 19%). Redistillation gave samples whose infrared spectra were identical with those of the authentic samples. The *p*-nitrobenzoate and 3,5-dinitrobenzoate of the 2-chloroallyl alcohol also had infrared spectra identical with those of authentic samples and there was no depression in mixed melting points with the authentic samples.

The higher boiling fractions contained substantial amounts of a new component (19.7 g., 0.133 mole, 10%). Redistillation gave a sample, b.p. 80–82° (9 mm.), $n^{25}\text{D}$ 1.4605, having an infrared spectrum identical with that of 2-chloroallyl glycidyl ether.

**Synthesis of 2-Chloroallyl Glycidyl Ether** (with David O. Halvorson).—2-Chloroallyl alcohol (40 g., 0.43 mole) and epichlorohydrin (40 g., 0.43 mole) in anhydrous ether (500 cc.) were treated with powdered sodium hydroxide (30 g., 0.75 mole) as in Reaction A. The addition of sodium hydroxide produced an exothermic reaction. After the mixture was refluxed for 16 hours the organic layer was separated, washed with water, dried over anhydrous potassium carbonate, and distilled through a 2 × 30 cm. column containing Cannon protruded packing to give 23 g. of distillable products. In addition to unreacted starting materials, there was obtained 2-chloroallyl glycidyl ether (10 g., 0.68 mole, 16%). Redistillation gave a sample, b.p. 37.5–38.0° (3 mm.), $n^{25.5}\text{D}$ 1.4591, $d^{25.5}{}_4$ 1.1468, $M\text{D}$ calcd.[18] 36.11, found 35.43. The infrared spectrum was identical with that of the corresponding sample from reaction B, $\nu_{\text{C=C}}$ 1640, $\nu_{\overset{\diagup \text{O} \diagdown}{\text{C—C}}}$ 1250, 857, $\nu_{\text{C—O—C}}$ 1097, $\nu_{\text{C—Cl}}$ 716 cm.$^{-1}$.

*Anal.* Calcd. for $C_6H_9O_2Cl$ (148.59): C, 48.50; H, 6.11. Found: C, 48.61; H, 6.38.

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[17] Shell Chemical Corp., "Allyl Alcohol," Technical Publication SC:46-32, San Francisco, Calif., 1946, p. 2.

[18] See reference in note 7.

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# Dehydration of β-Phenylethylcyclohexanol-3

BY B. C. PAI

RECEIVED JUNE 14, 1954

Perlman and Bogert in their study of the dehydration of β-phenylethyl-3-methylcyclohexanol-1[1] and β-phenylethylcyclohexanol-1[2] (I) showed that under the acid conditions of the dehydration with sulfuric acid, the olefins formed immediately cyclized to 2-methyloctahydrophenanthrene and octahydrophenanthrene, respectively. These experiments led to the view that β-phenylethyl-$\Delta^1$-cyclohexene is the intermediate in the Bardhan–Sengupta synthesis[3,4] of octahydrophenanthrene through cyclodehydration of β-phenylethylcyclohexanol-2 (II). We believed that the intermediate formation of β-phenylethyl-$\Delta^2$-cyclohexene in the above synthesis might also be a possibility and with that idea in view, we decided to prepare β-phenylethylcyclohexanol-3 and study the course of its dehydration.

In the first instance, 1-styryl-cyclohexan-3,5-dione, prepared according to the method of Vorländer and Groebel, was converted through the unsaturated chloroketone to β-phenylethylcyclohexanone-3. Reduction of this substance by sodium and moist ether afforded β-phenylethylcyclohexanol-3 (III) which, on treatment with phospho-

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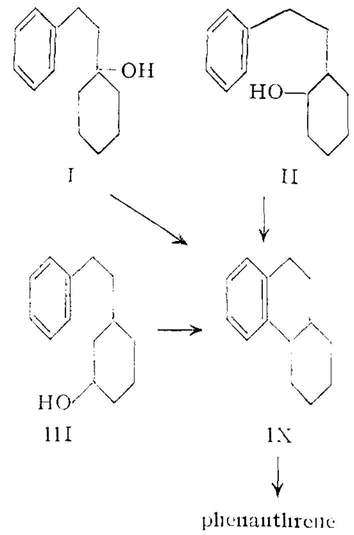
[1] M. T. Bogert and D. Perlman, THIS JOURNAL, **59**, 2534 (1937).

[2] M. T. Bogert, *Science*, **77**, 289 (1933).

[3] J. C. Bardhan and S. C. Sengupta, *J. Chem. Soc.*, **143**, 2520 (1932).

[4] J. C. Bardhan and S. C. Sengupta, *ibid.*, **143**, 2798 (1932).



rus pentoxide, readily furnished the 1,2,3,4,4a,9,10,10a-octahydrophenanthrene (IX), the physical properties of which agreed with those found by previous workers.[3] On being heated with selenium at 280–340° or with palladized charcoal at 210–270°, the octahydrophenanthrene readily furnished phenanthrene in good yield.

The absence of any unsaturated compound in the product of dehydration and the high yield of phenanthrene indicate that the $\Delta^2$-cyclohexene, under the acid conditions of the cyclization, may isomerize to $\Delta^1$-cyclohexene and then undergo cyclization to the octahydrophenanthrene (IX) or it may cyclize directly to the octahydrophenanthrene (IX).

Besides giving a more complete picture of the mechanism of Bardhan–Sengupta synthesis as shown on the Flow Sheet, this opens up a new line for the synthesis of phenanthrene. The study of the course of dehydration of β-phenylethylcyclohexanol-3 under the influence of different substituents is in progress and will be reported shortly.

## Experimental

**1-Styrylcyclohexan-3,5-dione.**—The method of Vorländer[5,6] and Groebel[7] was followed with some modifications. Sodium (4 g.) was dissolved in 70 ml. of absolute ethanol. Then diethyl malonate (28 g.) was added followed by cinnamylidene acetone (30 g.). The mixture was refluxed for 6 hours and the alcohol was distilled off and the residue was taken up in 225 ml. of water. Potassium hydroxide (18.75 g.) dissolved in a little water was added and refluxed for 20–25 minutes. The brown liquid was filtered through a plug of cotton to remove the small amount of tar formed during the alkali treatment. The filtrate was boiled again with 60 ml. of concentrated hydrochloric acid for about 20–25 minutes at which time the evolution of carbon dioxide was complete. The diketone, separated as a light yellow crystalline solid, was collected, washed with water and dried in vacuum; yield 31.2 g. (84%).

**1-Styryl-3-chloro-$\Delta^3$-cyclohexenone-5.**—The diketone (21.4 g.) was taken up in 50 ml. of dry chloroform and treated with phosphorus trichloride (7 g.) and refluxed for 3 hours. Chloroform was removed by distillation (water-bath) and, after decomposition with crushed ice, the residue was extracted with ether. The ethereal layer was washed with three 25-ml. portions of aqueous 4% sodium hydroxide solution to remove unreacted diketone. It was then washed with water, dried with calcium chloride and evaporated. The residue was distilled under reduced pressure and the chloroketone was obtained as a thick, pale yellow, viscous liquid, b.p. 185° (5 mm.), yield 10.7 g. (46%). The chloroketone did not keep well and was immediately converted to the monoketone.

**β-Phenylethylcyclohexanone-3.**—A solution of chloroketone (27 g.) in 27 ml. of ethanol was shaken in an atmosphere of hydrogen at room temperature and pressure with 0.2 g. of palladous chloride. Almost the theoretical quantity of hydrogen was absorbed in about 8 hours. The catalyst was filtered, the solvent evaporated and the residue was distilled, yielding 21 g. of a product, b.p. 154–157° (5 mm.). The crude ketone was converted into semicarbazone which crystallized from alcohol in minute prisms, m.p. 179°.

*Anal.* Calcd. for $C_{15}H_{21}ON_3$: C, 69.5; H, 8.2. Found: C, 69.8; H, 8.0.

The ketone was regenerated from the semicarbazone by gently warming with dilute hydrochloric acid and extracting with ether. The solvent was removed and the residue distilled under reduced pressure. The ketone was obtained as a colorless mobile liquid with a characteristic, agreeable odor, b.p. 155° (5 mm.).

*Anal.* Calcd. for $C_{14}H_{18}O$: C, 83.2; H, 8.9. Found: C, 83.3; H, 8.7.

**β-Phenylethylcyclohexanol-3 (III).**—The ketone (10.1 g.) was dissolved in 50 ml. of ether and added to 50 ml. of water in a flat-bottomed flask fitted with a reflux condenser. The flask was cooled in ice-water and 10 g. of very thinly sliced sodium was added over a period of 4–5 hours. When all the sodium had dissolved, the ethereal layer was separated, washed with water until no longer alkaline, dried with anhydrous potassium carbonate and the ether removed. On distilling the residue under reduced pressure, a colorless viscous oil was obtained, b.p. 150–152° (5 mm.), yield 8.4 g. (82.3%).

*Anal.* Calcd. for $C_{14}H_{20}O$: C, 82.4; H, 9.8. Found: C, 82.7; H, 9.6.

**The 3,5-dinitrobenzoate** of the alcohol III, prepared in the usual way, crystallized from alcohol in small prisms, m.p. 120°.

**1,2,3,4,4a,9,10,10a-Octahydrophenanthrene (IX).**—Our method of dehydration of the alcohol (III) with phosphorus pentoxide was precisely the same as used by Bardhan and Sengupta.[3] Alcohol III (5.5 g.) was treated with 11 g. of phosphorus pentoxide and the product, upon distillation over sodium, gave 4.1 g. of octahydrophenanthrene (81.8%), b.p. 131° (5 mm.), $d^{31}_4$ 0.9974, $n^{31}_D$ 1.5486 (lit.[3] $d^{32}_4$ 0.9973, $n^{32}_D$ 1.5486). Tests for the presence of unsaturated compounds using potassium permanganate in acetone and bromine in carbon tetrachloride gave negative results.

**Phenanthrene.** (a).—Octahydrophenanthrene (4 g.) was heated with 8 g. of selenium powder at 280–340° for 24 hours, then cooled and thoroughly extracted with ether. The solvent was removed and the residue of crude phenanthrene was converted to its picrate, long yellow needles, m.p. 145° after repeated crystallization. The regenerated phenanthrene melted at 100°. The identities of phenanthrene and its picrate were established by mixed melting points with authentic specimens.

*Anal.* Calcd. for $C_{14}H_{10}$: C, 94.4; H, 5.6. Found: C, 94.6; H, 5.3.

(b).—Octahydrophenanthrene (IX) (4 g.) was dehydrogenated by heating with 4 g. of 10% palladized charcoal at 210–270° for about 4 hours in a slow stream of carbon dioxide, using the technique of Linstead and co-workers.[8] The mass was cooled and thoroughly extracted with ether. The solvent was removed and the residue (3.5 g.) of crude phenanthrene was purified through its picrate, yielding 3 g., m.p. 100° (78.4%).

The author is grateful to Prof. R. Chatterjee for laboratory facilities.

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(6) D. Vorländer, *ibid.*, **294**, 312 (1897).

(7) P. Groebel, *ibid.*, **345**, 208 (1906).

(8) R. P. Linstead and co-workers, *J. Chem. Soc.*, 1146 (1937); 1127, 1134, 1139 (1940).