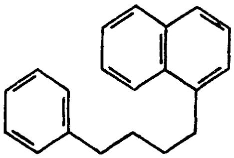
500. *The Formation of Aromatic Hydrocarbons at High Temperatures. Part III.* The Pyrolysis of 1-4′-Phenylbutylnaphthalene.*

By G. M. Badger and R. W. L. Kimber.

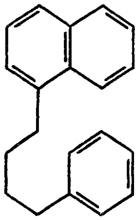
1-4′-Phenylbutylnaphthalene (I) has been synthesised. With palladium–charcoal at 360° it gives 1-phenylphenanthrene in good yield. Cyclodehydrogenation at higher temperatures, however, gives 1 : 1′-dinaphthyl, perylene, and 3 : 4-benzopyrene in small yield.

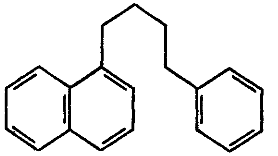
5-4′-Phenylbutyltetralin is a possible intermediate in the formation at high temperatures of 3 : 4-benzopyrene from simple products (Parts I and II). Two mechanisms are possible: the reaction may involve a primary cyclisation, followed by dehydrogenation of the tetralin ring; or the tetralin ring may suffer simple dehydrogenation to 1-4′-phenylbutylnaphthalene (I), which could then undergo cyclodehydrogenation. The latter has now been synthesised and its dehydrogenation studied.

(Ia)



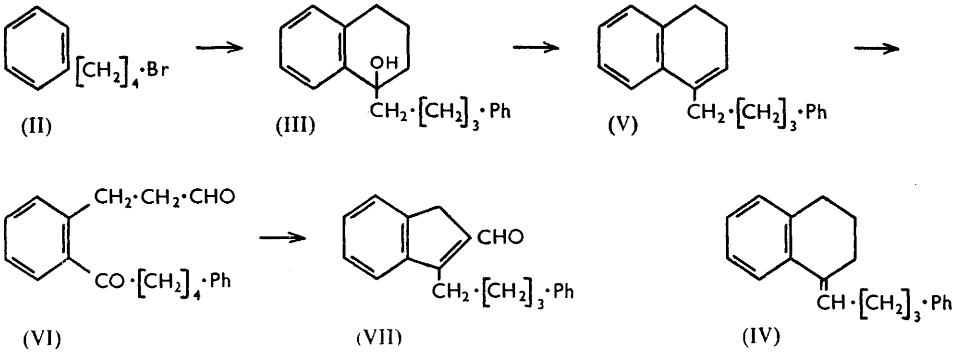
(Ib)





(Ic)

The cyclodehydrogenation of 1-4′-phenylbutylnaphthalene could occur in several ways: in the sense indicated by (Ia) to give 3 : 4-benzopyrene; in the sense indicated by (Ib) to give 1 : 1′-dinaphthyl and perylene; and in the sense of (Ic) to give 1-phenylphenanthrene. All these compounds have been identified as products of dehydrogenation under various conditions.



(II) (III) (V)

(VI) (VII) (IV)

When heated with palladium–charcoal at 360° 1-4′-phenylbutylnaphthalene was converted into 1-phenylphenanthrene in 63% yield. The same product was formed in small amount, together with a little perylene, at 360° with charcoal alone. Pyrolysis at 360° in absence of catalyst gave largely unchanged material, but the fluorescence spectra of some fractions indicated the presence of a little perylene and 3 : 4-benzopyrene. Pyrolysis at 600° was more complex, and gave small yields of 1 : 1′-dinaphthyl, perylene, and 3 : 4-benzopyrene. Some cracking also occurred under most conditions, and in various experiments toluene, naphthalene, and 1-methylnaphthalene were identified.

For the synthesis of 1-4′-phenylbutylnaphthalene, ethyl β-benzoylpropionate was

---

* Part II, preceding paper.

reduced to 4-phenylbutan-1-ol which was converted into the bromide (II). . Its Grignard complex, or lithio-derivative, was then added to α-tetralone to give the tertiary alcohol (III). No derivative of the alcoholic function could be prepared.

Dehydration of the alcohol, which occurred very readily, could conceivably give either (IV) or (V), but ozonisation gave no tetralone. The crude product [presumably (VI)] showed two carbonyl bands in the infrared region, but treatment with acidified 2 : 4-dinitrophenylhydrazine evidently resulted in intramolecular dehydration to the dinitrophenylhydrazone of the unsaturated aldehyde (VII). A similar intramolecular dehydration to indene-2-aldehyde has been reported by Braun and Zobel.[1]

The unsaturated compound is therefore believed to be a dihydronaphthalene derivative (V). It was dehydrogenated to the desired phenylbutylnaphthalene (I) by palladium–charcoal in *p*-cymene.

EXPERIMENTAL

4-Phenylbutan-1-ol.—Ethyl β-benzoylpropionate [2] (100 g.), ethanol (100 c.c.), copper chromite (13 g.), and hydrogen (2000 lb./in.^{2}) were heated at 250° for 6 hr. After 1 hr. the autoclave was cooled and the hydrogen pressure was again raised to 2000 lb./in.^{2}. Removal of catalyst and solvent gave ethyl γ-phenylbutyrate [3] (72 g., 78%), b. p. 140°/17 mm.

This product (100 g.) in ether (100 c.c.) was added dropwise to lithium aluminium hydride (30 g.) in ether (500 c.c.). After being refluxed for 1 hr. the mixture was carefully decomposed with water and dilute sulphuric acid. 4-Phenylbutan-1-ol (76 g., 96%), b. p. 124—127°/9 mm., n_D^{24} 1·5188, was obtained. Its phenylurethane had m. p. 51—52° (Braun [4] gives b. p. 140°/14 mm.; and m. p. 51—52° for the phenylurethane).

4-Phenylbutyl Bromide.—The alcohol (50 g.) was added slowly, with stirring, to a slight excess of phosphorus tribromide, under anhydrous conditions. When the addition was complete the mixture was heated (steam-bath) until reaction was complete (1½ hr.). The bromide (49 g., 72%) had b. p. 132°/12 mm., n_D^{19} 1·5408 (lit.,[5] b. p. 132°/12 mm.).

1-Hydroxy-1-4′-phenylbutytetralin.—(i) α-Tetralone (21 g.) was added dropwise to a Grignard solution prepared from phenylbutyl bromide (30 g.), magnesium (4 g.), and anhydrous ether (45 c.c.). After being refluxed for ½ hr. the mixture was poured on ice (70 g.), and 10% hydrochloric acid (100 c.c.) added. The ethereal solution was thoroughly washed (water), the ether removed, and the product distilled; three fractions were collected: (*a*) b. p. 80—100°/30 mm. (10 g.), n_D^{25} 1·5040; (*b*) b. p. 120—140°/30 mm., and (*c*) b. p. 170—172°/0·1 mm. (15 g., 37%). Redistillation of fraction (*c*) gave *1-hydroxy-1-4′-phenylbutyltetralin*, b. p. 150°/0·01 mm., n_D^{17} 1·5760 (Found: O, 5·5. $C_{20}H_{24}O$ requires O, 5·7%). Unsuccessful attempts were made to prepare a *p*-nitrobenzoate, a 3 : 5-dinitrobenzoate, and a *p*-bromophenacyl ester. In some runs analysis of the product showed that partial dehydration had occurred. Fraction (*b*) was α-tetralone. Fraction (*a*) was largely *n*-butylbenzene; further fractionation gave the pure material, identified by its infrared spectrum.[6]

(ii) 4-Phenylbutyl bromide (35 g.) in ether (50 c.c.) was slowly added (during ½ hr.) to a stirred suspension of lithium (3·5 g.) in ether (75 c.c.) in an atmosphere of nitrogen. The first few drops were added at room temperature, the mixture then being cooled to −10° until the addition was complete. The stirred mixture was then allowed to warm to +10° during 2 hr. α-Tetralone (24 g.) in ether (20 c.c.) was added dropwise at 10—20°, and the mixture finally refluxed for ½ hr. It was then filtered (glass wool) and decomposed with water and dilute hydrochloric acid. Distillation gave *n*-butylbenzene, α-tetralone, and 1-hydroxy-1-4′-phenylbutyltetralin (27 g., 57%).

3 : 4-Dihydro-1-4′-phenylbutylnaphthalene.—The above alcohol (8 g.) was dehydrated by refluxing ethanol (100 c.c.) and concentrated sulphuric acid (1 c.c.) for 1 hr. Distillation gave the *dihydrophenylbutylnaphthalene*, b. p. 174—176°/0·1 mm., n_D^{23} 1·5809 (Found: C, 91·6; H, 8·6. $C_{20}H_{22}$ requires C, 91·6; H, 8·4%), in almost quantitative yield.

---

[1] Braun and Zobel, *Ber.*, 1923, **56**, 2139.

[2] Kindler, *Annalen*, 1939, **452**, 90.

[3] Adkins, *Org. Reactions*, 1954, **8**, 1.

[4] Braun, *Ber.*, 1911, **44**, 2867.

[5] Clutterbuck and Cohen, *J.*, 1923, **123**, 2507.

[6] American Petroleum Institute Research Project 44, Infrared Spectral Data, Serial No. 468.

Position of unsaturation. The dihydro-naphthalene (2 g.) was ozonised in ethyl acetate (15 c.c.). Ethanol (20 c.c.) was added and the product hydrogenated over palladium–charcoal. Removal of the solvent gave a viscous oil which was separated into acid and neutral fractions. No pure derivative could be isolated from the acid fraction. The crude neutral fraction showed two peaks (5·80 and 5·93 μ) in the carbonyl region of the infrared spectrum; it gave a 2 : 4-dinitrophenylhydrazone as deep-red flat needles, (from chloroform), m. p. 210—211°. This is regarded as *3-4′-phenylbutylindene-*2*-aldehyde dinitrophenylhydrazone* (Found: C, 68·4; H, 5·3; O, 14·2; N, 12·4. $C_{26}H_{23}O_4N_4$ requires C, 68·6; H, 5·1; O, 14·05; N, 12·3%).

1-4′-*Phenylbutylnaphthalene*.—Dihydronaphthalene (14 g.) was dehydrogenated by 5 hours' refluxing with 10% palladium–charcoal (4·25 g.) in *p*-cymene (70 c.c.). Distillation gave 1-4′-*phenylbutylnaphthalene* (12·5 g., 90%), b. p. 164—166/0·3 mm., n_D^{22} 1·5990 (Found: C, 92·0; H, 8·0. $C_{20}H_{20}$ requires C, 92·3; H, 7·7%); $\lambda_{max.}$ (log ε) in *cyclo*hexane 226 (4·75), 240 infl. (3·32), 264 infl. (3·56), 273 (3·78), 283 (3·81), 290 mμ (3·52). No picrate or trinitrobenzene derivative could be obtained.

Pyrolysis of 1-4′-*Phenylbutylnaphthalene*.—(i) *At* 360°. Phenylbutylnaphthalene (2 g.) was refluxed for 20 hr. and the resulting mixture chromatographed on alumina (2½ × 20 cm.). Elution with hexane gave unchanged phenylbutylnaphthalene (1·5 g.); elution with benzene–hexane (1 : 1) then gave traces of yellow crystals. The fluorescence spectra of these fractions showed bands at 398, 404, 409, 417, and 427 mμ indicative of 3 : 4-benzopyrene, and at 445, 475, and 502 mμ indicative of perylene. Fractions showing 3 : 4-benzopyrene fluorescence were combined and extracted with cold concentrated sulphuric acid.[7] The hydrocarbon was reprecipitated with water, extracted into benzene, and the benzene evaporated. The ethanolic solution of this product showed absorption maxima at 365, 384, and 405 mμ, as expected for 3 : 4-benzopyrene, the other peaks being masked by impurities.

(ii) *At* 360° *with palladium–charcoal.* Phenylbutylnaphthalene (2 g.) was refluxed with 10% palladium–charcoal (0·5 g.) for 5 hr. Chromatography on alumina and elution with hexane gave 1-phenylphenanthrene (1·25 g.), prisms, m. p. 78—79° (lit.,[8] m. p. 78—79°) (from light petroleum) (Found: C, 94·6; H, 5·7. Calc. for $C_{20}H_{14}$: 94·5; H, 5·5%); $\lambda_{max.}$ (log ε) in ethanol 220 (4·46), 256 (4·72), 290 (4·08), 300 (4·16), 334 (2·64), 342 (2·49), and 350 mμ (2·52). Its picrate had m. p. 117—118° (lit.,[8] m. p. 117—118°) (Found: N, 8·8. Calc. for $C_{26}H_{17}O_7N_3$: N, 8·7%). Further elution of the column with benzene–hexane (1 : 2) gave fractions showing faint fluorescence spectra identical with those of 3 : 4-benzopyrene and of perylene.

(iii) *At* 360° *with charcoal.* Phenylbutylnaphthalene (2 g.) was refluxed with activated charcoal (0·5 g.) for 5 hr. Rearrangement of the apparatus for distillation gave some distillate (200 mg.), b. p. <220°. Recrystallisation gave naphthalene (100 mg.), m. p. and mixed m. p. 79·5—80°. The remainder of the product was chromatographed on alumina. Elution with hexane gave 1-phenylphenanthrene (150 mg.) identified by direct comparison with the specimen obtained above. Elution with benzene–hexane (1 : 2) of a blue fluorescent band and recrystallisation of the residue gave perylene as yellow prisms, m. p. and mixed m. p. 265°, further identified by comparison of its fluorescence spectrum with that of an authentic specimen. No benzopyrene was detected.

(iv) *At* 360° *with palladium–asbestos.* Phenylbutylnaphthalene (2 g.) was refluxed with 5% palladium–asbestos (1 g.) for 5 hr. A low-boiling fraction was mainly toluene, b. p. 110°, n_D^{25} 1·4913 (infrared spectrum). Chromatography on alumina (3 × 15 cm.) and elution with hexane gave 8 fractions (each of 70 c.c.). Further elution with benzene–hexane (1 : 2) gave fractions 9—18 (each of 70 c.c.). Fraction 1 yielded unchanged phenylbutylnaphthalene. Fractions 2—7 showed diffuse fluorescence at 400—480 mμ. The later fractions showed fluorescence bands indicative of 3 : 4-benzopyrene and perylene. Fraction 8 gave an ultraviolet spectrum similar to that of a chrysene derivative. Fractions 9 and 10 showed some of the same maxima as fraction 8 and also bands suggestive of perylene and 3 : 4-benzopyrene.

(v) *At* 600°. Phenylbutylnaphthalene (5 g.) was vapourised at the rate of 1 drop/15 sec. and passed with nitrogen (1 c.c./sec.) through a silica tube (36 × 1 in.) packed with porcelain chips (3/8—1/4 in.) heated to 600°. Distillation of the resulting tar gave (*a*) b. p. 110—120° (1·25 g.), (*b*) b. p. 90—120°/28 mm. (1·5 g.), and (*c*) the residue (1·5 g.).

Fraction (*a*) was mainly toluene, identified by refractive index and infrared spectra. Fraction (*b*) was heated (boiling-water bath) at atmospheric pressure and naphthalene (0·1 g.),

---

[7] Berenblum, *Nature*, 1945, **156**, 601.

[8] Bachmann and Wilds, *J. Amer. Chem. Soc.*, 1938, **60**, 624.

m. p. and mixed m. p. 80°, sublimed. The yellow liquid remaining was redistilled, yielding 1-methylnaphthalene, identified by ultraviolet and infrared spectroscopy and by refractive index. The picrate had m. p. and mixed m. p. 140—142°.

Fraction (*c*) was chromatographed on alumina ($2\frac{1}{2} \times 20$ cm.). A blue fluorescent band was eluted with hexane (fractions 4—8; each of 70 c.c.), then an orange fluorescent band with benzene–hexane (1 : 1) (fractions 9—10; each of 70 c.c.), and finally a yellow fluorescent band with benzene (fractions 11—12; each of 70 c.c.).

Fractions 4 and 5 were combined and rechromatographed in hexane. Evaporation of the first fractions yielded a solid (20 mg.), with ultraviolet absorption spectrum identical with that of 1 : 1′-dinaphthyl; but it could not be obtained pure, having m. p. 143—146° alone, and 145° mixed with an authentic specimen (m. p. 145°). Further elution of this chromatogram with benzene–hexane (1 : 2) gave a pale yellow solid (10 mg.), $\lambda_{max.}$ in ethanol 240, 261, 272, 304, 319, and 334 mμ, indicative of pyrene.[9]

Fractions 6—9 were combined and twice rechromatographed on a large column of alumina, hexane and benzene–hexane being used as eluants. The first fractions contained a mixture of perylene and 3 : 4-benzopyrene. The fluorescence spectra showed bands associated with both hydrocarbons: $\lambda_{max.}$ in ethanol 434, 429 infl., 408, and 386 mμ associated with perylene,[9] and at 225, 296, 348, and 364 mμ associated with 3 : 4-benzopyrene.[9] Later fractions contained more 3 : 4-benzopyrene; one showed maxima at 226, 255, 266, 273, 284, 296, 330, 347, 364 infl., 378, 384, 404 mμ as expected for 3 : 4-benzopyrene;[9, 10] and also gave a 3 : 4-benzopyrene fluorescence spectrum. Evaporation of the solvent gave almost pure 3 : 4-benzopyrene, m. p. and mixed m. p. 170—172° (lit.,[9] m. p. 176·5—177·5°). The total estimated quantity of perylene was 3 mg. and of 3 : 4-benzopyrene 10 mg.

Similar results were obtained following pyrolysis of phenylbutylnaphthalene at 700°, except that the yield of naphthalene (2 g.) was much greater. Pyrolysis at 500° was much less effective and gave 3·5 g. of unchanged material (from 5 g.).

UNIVERSITY OF ADELAIDE, SOUTH AUSTRALIA.

[*Received, January 24th*, 1958.]

---

[9] Clar, " Aromatische Kohlenwasserstoffe," 2nd edn., Springer, Berlin, 1952.

[10] Mayneord and Roe, *Proc. Roy. Soc.*, 1935, *A*, **152**, 323.