357. *Homologous 9-Anthryl-1'-naphthylalkanes and a New Carbon–Carbon Cleavage occurring during Reduction by Lithium Aluminium Hydride.*

By Peter Rona and Uri Feldman.

The first three homologous 9-anthryl-1'-naphthylalkanes (I; $n = 1$—3) have been synthesised. Reduction of 9-1'-naphthoylanthracene and 9-benzoylanthracene by lithium aluminium hydride affords 9-anthryl-1'-naphthylmethane and 9-benzylanthracene, respectively, but the hydrogenolysis in each case is accompanied by another reaction involving cleavage of a carbon–carbon single bond. Thus, anthracene is formed in each case, accompanied by 1-naphthylmethanol and benzyl alcohol, respectively.

It was thought by Dr. O. Schnepp, of this Department, that in certain compounds containing aromatic nuclei separated by a chain of insulating (saturated) carbon atoms, a new type of energy transfer from one aromatic nucleus to the other should be observable. After the synthesis of the compounds reported in this communication, this expectation was indeed realised.[1]

Homologous compounds of structure (I) have been prepared. Friedel–Crafts reaction of 1-naphthoyl chloride with anthracene in nitrobenzene in the absence of catalyst afforded 9-1'-naphthoylanthracene, in analogy to the reaction of benzoyl chloride with anthracene.[2] Although Huang-Minlon reduction or catalytic hydrogenolysis of this ketone was unsuccessful, reduction of the ketone by lithium aluminium hydride afforded the desired

$$1\text{-}C_{10}H_7\cdot[CH_2]_n\cdot C_{14}H_9\text{-}9 \quad (Ia,\ n = 1;\ Ib,\ n = 2;\ Ic,\ n = 3)$$

9-anthryl-1'-naphthylmethane (I*a*), in 17% yield after chromatography of the reduction mixture. From the portion of the product which did not give the desired product (I*a*), anthracene was isolated in 65% yield and 1-naphthylmethanol in 51% yield; these results

---

* *Note added March 6th*, 1958.—Dornow and Furst (*Chem. Ber.*, 1957, **90**, 1774) reported a carbon-carbon cleavage under similar reduction conditions.

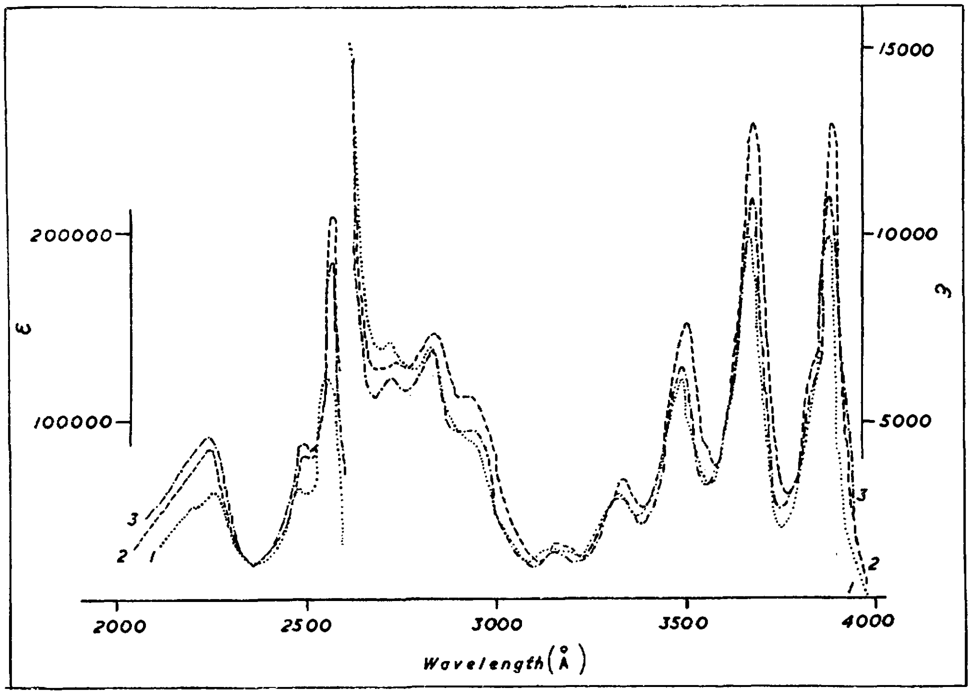
[1] Schnepp, *J. Chem. Phys.*, in the press.

[2] Nenitzescu, Isacescu, and Ionescu, *Annalen*, 1931, **491**, 210.

indicate that cleavage of a carbon–carbon single bond occurred during the reduction. Although cleavage of ether bonds[3] and deamination[4] are known in such reductions, we are unaware of such cleavages previously in the case of a C–C single bond.*

The possibility that the basic conditions prevailing during this reduction are responsible for the observed cleavage at the ketone stage, though improbable *a priori*, was ruled out by refluxing 9-1′-naphthoylanthracene alternatively with excess of lithium amide in tetrahydrofuran or with saturated ethanolic potassium hydroxide for 4·5 hr. The ketone was recovered unchanged in each case, practically quantitatively.

9-Benzoylanthracene[2] was prepared and reduced with lithium aluminium hydride. It afforded 9-benzylanthracene[5] in 24% yield but this was again accompanied by anthracene and by benzyl alcohol. Again, in this case the ketone was quantitatively recovered after refluxing for 4·5 hr. under the above-mentioned basic treatments.



All spectra in *cyclo*hexane.
Curve 1, compound I*a*; curve 2, compound I*b*; curve 3, compound I*c*.

Several reasonable mechanisms can be envisaged for the observed carbon–carbon cleavage, taking into account various stages of the lithium aluminium hydride reduction process. The mechanistic problem and the scope of this apparently new type of cleavage are being studied further.

In order to prove the structure of 9-anthryl-1′-naphthylmethane it was prepared (45% yield) by an alternative route from 1-naphthylmethylmagnesium bromide and anthrone; the 2-9′-anthryl-1-1″-naphthylethane (I*b*) was prepared from 2-1′-naphthylethylmagnesium bromide and anthrone in 52% yield. 3-9′-Anthryl-1-1″-naphthylpropane (I*c*) was analogously prepared from 3-1′-naphthylpropylmagnesium bromide in 20% yield.

The ultraviolet absorption spectra of the above three hydrocarbons are given in the Figure.

[3] Freudenberg and Wilke, *Chem. Ber.*, 1952, **85**, 78.
[4] Adams and Moje, *J. Amer. Chem. Soc.*, 1952, **74**, 5557.
[5] E. Bergmann and Fujise, *Annalen*, 1930, **480**, 188.

EXPERIMENTAL

9-1′-*Naphthoylanthracene.*—A mixture of 1-naphthoyl chloride (18·7 g.), anthracene (8 g.), and nitrobenzene (16 g.) was heated at 180°. After several minutes vigorous evolution of hydrogen chloride started. Heating at 180° was continued for 1·5 hr. Next morning the ketone which crystallised was filtered off. Recrystallisation from acetic acid afforded the ketone (11·2 g., 71%), m. p. 205—206°. Chromatography of a 2 g. sample of this ketone dissolved in benzene (30 ml.) on basic alumina (40 g.; Fisher) and elution with benzene–hexane (1 : 1) yielded traces of anthracene; further elution with chloroform afforded 1·8 g. of *ketone* which, when recrystallised from acetic acid, was slightly yellow; it had m. p. 211—213° (Found: C, 90·0; H, 5·2. $C_{25}H_{16}O$ requires C, 90·3; H, 4·85%); $\nu_{max.}$ (in $CHCl_3$) 1660 cm.$^{-1}$ (C=O).

9-*Anthryl*-1′-*naphthylmethane.*—(*a*) The above chromatographed ketone (1·5 g.), dissolved in dry tetrahydrofuran (40 ml.), was added dropwise to a suspension of lithium aluminium hydride (1 g.) in dry tetrahydrofuran (20 ml.). The mixture was refluxed for 3·5 hr. (after 2 hr. it became dark brown and exhibited strong fluorescence in ultraviolet light). After being kept overnight at room temperature, the mixture was treated with ethyl acetate, then with Rochelle salt solution, and the solvents were removed under reduced pressure. Water, benzene, and ether were added, and the organic layer was separated, extracted with saturated salt solution, and dried ($MgSO_4$). After removal of solvents the yellow crystalline residue was thrice recrystallised from *cyclo*hexane–benzene, affording anthracene, m. p. 212° (400 mg.), identical (infrared spectrum and mixed m. p.) with an authentic sample.

The mother-liquors were combined and the solvents removed. The residual yellow oil was dissolved in hexane (10 ml.) and chromatographed on basic alumina (15 g.; Fisher). Elution gave anthracene (60 mg.), followed by 9-anthryl-1′-naphthylmethane (250 mg., 17%), eluted by hexane–benzene (1 : 1), which exhibited blue fluorescence in ultraviolet light, and finally an oil (300 mg.) eluted by chloroform–benzene (3 : 1). The slightly yellow *hydrocarbon* had m. p. 182—184° (sintering at 180°) (from *cyclo*hexane) (Found: C, 93·8; H, 5·6. $C_{25}H_{18}$ requires C, 94·3; H, 5·7%).

The oil obtained from the last fractions of the above chromatographic column solidified after distillation (b. p. 95—105°/0·3 mm., m. p. 58—60°). It was identical (infrared spectrum and mixed m. p.) with authentic 1-naphthylmethanol.

(*b*) The Grignard reagent was prepared under nitrogen from 1-bromomethylnaphthalene [6] (2 g.) and magnesium (220 mg.) in dry ether (20 ml.). Anthrone (550 mg.) in dry benzene (15 ml.) was added dropwise with stirring. The mixture was left overnight, refluxed for a further hour, cooled, and decomposed with 3M-sulphuric acid (20 ml.). The usual working-up gave a yellow oil (1·8 g.). Its hexane solution was chromatographed on basic alumina (40 g.; Fisher). The following fractions were obtained: anthracene (30 mg.); 1 : 2-di-1′-naphthylethane (450 mg.), m. p. 164—165° (from *cyclo*hexane); [7] 9-anthryl-1′-naphthylmethane (460 mg., 45%), m. p. 186—187° (from *cyclo*hexane), identical with the substance prepared by method (*a*).

9-1′-Naphthoylanthracene (200 mg.) was refluxed for 4·5 hr. with lithium amide (250 mg.) in dry tetrahydrofuran (10 ml.). Another portion of the ketone (200 mg.) was refluxed for 4·5 hr. with saturated ethanolic potassium hydroxide (20 ml.). In both cases the ketone was recovered nearly quantitatively.

9-*Benzoylanthracene.*—A mixture of anthracene (8 g.), benzoyl chloride (12 g.), and nitrobenzene (16 g.) was heated under reflux for 3 hr. and kept overnight at room temperature. The solid which separated (2·6 g.) was filtered off, and the mother-liquor steam-distilled to remove nitrobenzene. The black residue was dissolved in glacial acetic acid and afforded more of the product (4·8 g.; total yield 58%), m. p. 148—153° (from acetic acid). Chromatography of a solution of this product (3 g.) in benzene (100 ml.) on basic alumina (90 g.; Fisher), followed by elution with benzene–hexane (1 : 1), afforded anthracene (150 mg.). Further elution with benzene–chloroform (1 : 1) gave the yellow ketone (2·2 g.), m. p. 148—149° (from acetic acid). Nenitzescu *et al.*[1] report m. p. 148°, $\nu_{max.}$ (in $CHCl_3$) 1667 cm.$^{-1}$ (C=O).

9-*Benzylanthracene.*—A solution of the above purified ketone (1·5 g.) in dry tetrahydrofuran (40 ml.) was added dropwise to a suspension of lithium aluminium hydride (850 mg.) in the same solvent (20 ml.), an immediate vigorous reaction setting in. The mixture was fluorescent in

---

[6] Catch and Evans, *J.*, 1957, 2797.

[7] Bamberger and Lodter, *Ber.*, 1888, **21**, 54.

ultraviolet light whereas a solution of the starting material was not. Refluxing was continued for 4 hr., the mixture then being kept at room temperature for 36 hr. Working-up by the Rochelle salt procedure was followed by careful removal of the tetrahydrofuran through a 25 cm. Vigreux column so as to minimise loss of benzyl alcohol. The remaining solution was extracted with benzene, the extract dried (Na_2SO_4), and most of the benzene removed, again by careful distillation. The residual semicrystalline mass, not entirely free from benzene, was suspended in hexane (100 ml.) and applied to a column of basic alumina (30 g.; Fisher). Elution with hexane gave 9-benzylanthracene (360 mg., 24%), m. p. 130—132° (sinters at 127°) (from hexane) (Found: C, 93·85; H, 6·0. Calc. for $C_{21}H_{16}$: C, 94·0; H, 6·0%). Bergmann and Fujise [5] report m. p. 133°. Further elution with hexane–benzene (5 : 1—1 : 1) afforded authentic anthracene (210 mg., 20%). Elution with benzene–methylene chloride (1 : 1) then yielded a substance (200 mg.) which appears from its infrared spectrum to be an alcohol, m. p. 154—155° (from *cyclo*hexane).[8a] This by-product is regarded as α-9 : 10-dihydro-9-anthrylbenzyl alcohol (lit.,[8b] m. p. 156—157°) (Found: C, 87·6; H, 6·3. Calc. for $C_{21}H_{18}O$: C, 88·1; H, 6·3%).

Finally a yellow oil (120 mg.) was eluted with chloroform. After removal of solvent, this was treated with *p*-nitrobenzoyl chloride. Chromatography of the hexane solution (10 ml.) of the product on acid-washed alumina (4 g.; Merck) and elution with hexane–benzene (5 : 1) afforded benzyl *p*-nitrobenzoate (30 mg.), identical (mixed m. p. and infrared spectrum) with an authentic specimen.

9-Benzoylanthracene (200 mg.) was refluxed for 4·5 hr. with (i) lithium amide (260 mg.) in dry tetrahydrofuran (10 ml.), (ii) saturated ethanolic potassium hydroxide (20 ml.). In both cases the ketone was recovered practically quantitatively.

2-9′-Anthryl-1-1″-naphthylethane.—The Grignard reagent was prepared under nitrogen from 2-1′-naphthylethyl bromide (9 g.) and magnesium (0·96 g.) in dry ether (45 ml.). Anthrone (2·5 g.) in dry benzene (45 ml.) was added. The usual working-up gave a solid residue (9·4 g.). Washing with light petroleum afforded greenish-blue fluorescent crystals (2·5 g., 52%), m. p. 169—170° (from hexane–benzene). The *ethane derivative*, m. p. 170—171°, was obtained by low-pressure sublimation; its m. p. was raised to 177—178° by repeated recrystallisation from benzene–hexane (Found: C, 94·0; H, 6·1. $C_{26}H_{20}$ requires C, 93·9; H, 6·1%).

3-9′-Anthryl-1-1″-naphthylpropane.—3-1′-Naphthylpropyl bromide, n_D^{16} 1·6269, was prepared in 84% yield by refluxing the corresponding primary alcohol with 48% hydrogen bromide. The alcohol (b. p. 130°/0·05 mm.) was prepared in 70% yield by lithium aluminium hydride reduction (in dry ether) of β-1-naphthylacrylic acid, m. p. 210°, prepared (50% yield) by condensation of 1-naphthaldehyde and malonic acid. The Grignard reagent was prepared under nitrogen from the above bromide (5·6 g.) and magnesium (0·54 g.) in dry ether (20 ml.). Anthrone (1·5 g.) in dry benzene (28 ml.) was added. Working-up gave a residual yellow oil which soon solidified. Chromatography on acid-washed alumina (Merck) afforded the desired *propane derivative*, m. p. 92° (from light petroleum–benzene) (20% yield) (Found: C, 93·2; H, 6·6. $C_{27}H_{22}$ requires C, 93·6; H, 6·4%). It was accompanied by 1 : 6-di-1′-naphthylhexane, m. p. 86° (from methyl*cyclo*hexane) (Found: C, 92·2; H, 7·65%; *M*, 360. Calc. for $C_{26}H_{26}$: C, 92·3; H, 7·7%; *M*, 338). Boelhouwer *et al.*[9] report m. p. 86·2—86·6°.

We are indebted to Dr. O. Schnepp for suggesting this problem and to Professor D. Ginsburg for encouragement and advice.

DEPARTMENT OF CHEMISTRY, ISRAEL INSTITUTE OF TECHNOLOGY,
HAIFA, ISRAEL.
[*Received, November 11th*, 1957.]

---

[8] (*a*) Julian, Cole, Diemer, and Schafer, *J. Amer. Chem. Soc.*, 1949, **71**, 2058, report m. p. 114° for α-9-anthrylbenzyl alcohol; (*b*) Horeau and Jacques, *Bull. Soc. chim. France*, 1946, 71.

[9] Boelhouwer, Nederbragt, and Verberg, *Appl. Sci. Res.*, 1950, *A*, 2, 249, report m. p. 86·2—86·6°.