Formation of 6,6'-(Butane-1,4-diyl)bis-(1,2,3,4-tetrahydronaphthalene) in the Reaction of Tetralin with Aluminium Chloride

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Abstract

It has been shown that the reaction of aluminium chloride with tetralin yields 6,6'-(butane-1,4-diyl)bis(1,2,3,4-tetrahydronaphthalene) as well as a number of other products. It is suggested that this compound is formed by protonation of tetralin, fragmentation of the alicyclic ring and then electrophilic attack of a further tetralin molecule. The positions of substitution in the product suggests that ion pairs are involved in the reaction. It is clear that intermediates have sufficient lifetime to undergo intermolecular substitution reactions in addition to intramolecular substitution or proton loss.

Polycyclic hydroaromatic compounds are components of coal tar derived by pyrolysis or hydrogenation. For a study of the effects of these materials on coal reactivity in the synthesis of fuels by hydrogenation, we needed to prepare large quantities of 1,2,3,4,5,6,7,8-octahydroanthracene (1) (see Scheme 1) and its corresponding phenanthrene isomer (2). Schroeter¹ reported the preparation of both these hydrocarbons and also perhydroanthracene (6) and 6-(4-phenylbutyl)-1,2,3,4-tetra-hydronaphthalene (7) or its isomer by the action of aluminium chloride on tetralin at 50–75°C. However, Dansi and Ferri,² using only slightly different conditions, obtained a different product and suggested that the main product from this reaction is 5,6,6a,6b,7,8,12b,12c-octahydrodibenzo[a,i]biphenylene (3). Small amounts of 1,4-diphenylbutane³ (4) and benzo[a]pyrene (5) have also been reported to be formed.^{3,4}

We have repeated the Schroeter¹ reaction and confirm that the products from this reaction are those claimed [i.e. benzene, 1,4-diphenylbutane (4), perhydroanthracene (6), octahydrophenanthrene (2), octahydroanthracene (1) and a tetrahydronaphthylbutane]. We have also isolated a further hydrocarbon, unreported by previous investigators of this reaction. This compound has been shown to be 6,6'-(butane-1,4-diyl)bis(1,2,3,4-tetrahydronaphthalene) (8) on the basis of its n.m.r. spectra and elemental analysis and by dehydrogenation to (9) or hydrogenation to (10). The

¹ Schroeter, G., Ber. Dtsch. Chem. Ges., 1924, 57, 1990.

² Dansi, A., and Ferri, C., Gazz. Chim. Ital., 1941, 71, 648.

³ Korshak, V. V., and Kolesnikov, G. S., Dokl. Akad. Nauk SSSR, 1951, 76, 69.

⁴ Phillips, D. H., Nature (London), 1983, 303, 468.



¹³C n.m.r. spectrum of the compound assigned as (8) contains resonances from six different CH_2 carbons, three protonated aryl carbons and three non-protonated aryl carbons. Quantitative determinations have demonstrated that these carbon types are in proportions consistent with (8). Similarly, the derivatives (9) and (10) are consistent in spectral properties and elemental composition with a derivation from (8).

The position of substitution in (7) and (8) has not previously been established and is of interest since attack of electrophiles in Friedel-Crafts reactions may be at either α or β positions. It has been suggested^{5,6} that the position of attack depends on whether a free carbocation or ion pair is the reactive entity. Attack occurs at the more sterically hindered α position when the carbocation is small and unhindered by a counter ion. Non-polar solvents such as tetralin should favour β -attack, and hence it can be predicted that in the reaction of tetralin with aluminium chloride the products (7) and (8) should be substituted at the β position. This was found to be the case. The ¹H spectrum of (8) clearly showed the typical ABC pattern expected for β substitution (J_{AB} 7.5 Hz, J_{AC} 0.4 Hz, J_{BC} 1.6 Hz, δ_A 6.96, δ_B 6.89, δ_C 6.87 ppm). Conclusive proof was obtained by dehydrogenation to (9) which had a ¹H spectrum with similar aromatic proton coupling patterns to 2-ethylnaphthalene, but unlike that of 1-ethylnaphthalene. The ¹³C spectrum was also consistent with β -substitution in (7) as β by dehydrogenation.



Although Schroeter believed that the reactivity of aluminium chloride was due to its ability to form organoaluminium compounds, more recent studies suggest that aluminium-chloride-catalysed dealkylations occur with the assistance of trace amounts of water.^{5,6} The [AlCl₃H⁺] OH⁻ species may protonate aryl rings to form carbocations. The isolation of compound (8) from the Schroeter reaction tells us much about the mechanism of the reaction. A scheme involving protonation by [AlCl₃H⁺] OH⁻ (see Scheme 1) accommodates almost all the products of the reaction and also accounts for the formation of compound (8). Electrophilic attack of tetralin on protonated tetralin gives the carbocation (11) (see Scheme 1), which on loss of a proton forms (7). Protonation of the phenyl ring in (7) and intramolecular displacement of the phenyl group releases benzene and produces the two octahydro derivatives (1) and (2). Compound (8) could be formed by protonation of the phenyl ring in (7) and electrophilic attack of tetralin (pathway *e*) or by attack of (7) on carbocation (11) (pathway *a*) followed by electrophilic attack of tetralin. In either case, it is clear that tetralin can displace phenyl groups from benzylic carbon, thereby producing

⁵ Olah, G. A., 'Friedel-Crafts Chemistry' p. 26, pp. 179-80 (John Wiley: New York 1973).

⁶ Olah, G. A., 'Friedel-Crafts and Related Reactions' Vol. II, p. 72, Vol. III, p. 64 (John Wiley: New York 1963).

a molecule which is composed of fragments of three tetralin molecules. Moreover, the intermediates in the formation of (1) and (2) in the Schroeter reaction have sufficient lifetime to undergo intermolecular substitution reactions as well as intramolecular substitution or proton loss.

Experimental

N.m.r. spectra were measured on a Jeol FX90Q spectrometer operating at 90 MHz for protons. The degree of carbon protonation was established in ¹³C spectra by use of INEPT⁷ and GASPE⁸ sequences. All ¹³C experiments were quantitative for signal integrals. Cr(acac)₃ (0.03 M) was used as relaxation reagent in CDCl₃ and inverse gated decoupling was used to obtain quantitative data.

Reaction of Aluminium Chloride with Tetralin

Tetralin (4.5 kg) purified of peroxide by shaking with 10% aqueous sodium bisulfite was dried (CaCl₂ and NaOH pellets) then treated in 1.5 kg lots with anhydrous, finely powdered aluminium chloride (30 g). The mixture was heated to $50-70^{\circ}$ (not exceeding 70°) for 5-7 h. After the addition of water (500 ml) and hydrochloric acid (100 ml), the tarry product dissolved slowly when stirred. Dissolution was completed by adding hot water. The organic layer was separated, washed with water $(2 \times)$ and dried $(CaCl_2)$. Benzene was removed under vacuum (c. 15 mm) by rotary evaporation. Unchanged tetralin (3.0 kg) was removed at lower pressure (<1 mm) at $< 100^{\circ}$. The distillation residue was vacuum distilled (c. 0.01 mm) at 90–120° to yield a mixture of perhydroanthracene (6) (c. 5 g, 0.3%), octahydroanthracene (1) (c. 220 g, 21%), octahydrophenanthrene (2) (c. 25 g, 2%) and 1,4-diphenylbutane (4) (c. 15 g, 1%), which were separated by high pressure liquid chromatography on a C-18 column with acetonitrile. Details of their identification are: 1,4-Diphenylbutane (4), m.p. 54°, lit.⁹ 52°. ¹H n.m.r.: δ_H (CDCl₃) 1 · 66, m, CH₂; 2 · 63, m, CH₂; 7.2, m, Ar. ¹³C n.m.r.: δ_{c} (CDCl₃) 31.1, CH₂; 35.9, CH₂; 125.7, CH; 128.3, CH; 128.4, CH; 142.5, C. 1,2,3,4,5,6,7,8-Octahydroanthracene (1), m.p. 72-73, lit.⁹ 78°. ¹H n.m.r.: δ_H (CDCl₃) 1 · 76, m, CH₂; 2 · 69, m, CH₂; 6 · 78, s, Ar. ¹³C n.m.r.: δ_C (CDCl₃) 23 · 5, CH₂; 29 · 0, CH₂; 129.5, CH; 134.2, C. Perhydroanthracene (6), m.p. 93°, lit.⁹ 93°. ¹H n.m.r.: $\delta_{\rm H}$ (CDCl₃) 0·8-1·65, m. ¹³C n.m.r.: δ_c (CDCl₃) 26·7, CH₂; 33·9, CH₂; 41·7, CH₂; 43·4, CH. 1,2,3,4,5,6,7,8-Octahydrophenanthrene (2), m.p. 16°, lit.⁹ 16·7°. ¹H n.m.r.: $\delta_{\rm H}$ (CDCl₃) 1·76, m, 2·72, m, 2·54, m, 6.83, s, Ar. ¹³C n.m.r.: δ_{c} (CDCl₃) 23.0, 23.6, 26.3, 30.1, 126.4, 134.2, 135.1.

Octahydroanthracene was obtained from the fraction boiling at 110–170° by recrystallization from ethanol but the main product of the reaction distilled between 160–190° and was 6-(4-phenyl-butyl)-1,2,3,4-tetrahydronaphthalene (7) (c. 450 g, 47%), b.p. 0·1 mm 175–178° (Found: C, 90·8; H, 9·2. C₂₀H₂₄ requires C, 90·9; H, 9·1%). ¹H n.m.r.: $\delta_{\rm H}$ (CDCl₃) 1·51–1·87, m, CH₂; 2·41–2·87, m, α -CH₂; 6·80–6·95, m, Ar; 7·10–7·32, m, Ph. ¹³C n.m.r.: $\delta_{\rm C}$ (CDCl₃) 23·3, CH₂; 29·0, CH₂; 29·4, CH₂; 31·2, CH₂; 35·4, CH₂; 35·8, CH₂; 125·6, CH; 128·2, CH; 128·3, CH; 129·0, CH; 134·2, C; 136·7, C; 139·5, C; 142·5, C.

From the high boiling distillate (b.p. 0 · 1 mm, 190–240°) 6,6'-(*butane-1,4-diyl*)bis(1,2,3,4-tetrahydronaphthalene) (8) crystallized after dilution with acetone and cooling to -25° . This compound has been claimed¹⁰ to be formed from trimerization of diacetylenes but was poorly characterized. Recrystallization from ethanol gave colourless plates (c. 25 g, 2%), m.p. 68–69° (Found: C, 90 · 3; H, 9 · 4. C₁₄H₃₀ requires C, 90 · 5; H, 9 · 5%). ¹H n.m.r.: $\delta_{\rm H}$ (CDCl₃) 1 · 63, m, CH₂; 1 · 77, m, CH₂; 2 · 55, m, CH₂; 2 · 72, m, CH₂; 6 · 87, 6 · 89, 6 · 96, J 7 · 5, 0 · 4, 1 · 6 Hz, see text. ¹³C n.m.r.: $\delta_{\rm C}$ (CDCl₃) 23 · 3, CH₂; 23 · 4, CH₂; 29 · 0, CH₂; 29 · 4, CH₂; 31 · 4, CH₂; 35 · 5, CH₂; 125 · 6, CH; 129 · 0, CH; 129 · 1, CH; 134 · 3, C; 136 · 8, C; 139 · 7, C.

Dehydrogenation of 6,6'-(Butane-1,4-diyl)bis(1,2,3,4-tetrahydronaphthalene)

The bis-naphthalene (8) (1.6 g) and methyl *trans*-cinnamate (0.8 g) were melted together and mixed with vacuum dried palladium on charcoal (5%) catalyst (200 mg). The mixture was heated

⁹ 'Dictionary of Organic Compounds' 4th Edn, p. 1274 (Eyre & Spottiswoode: London 1965). ¹⁰ Huber, A. J., J. Chem. Soc. C, 1967, 6.

⁷ Bendall, M. R., Pegg, D. T., and Doddrell, D. M., J. Magn. Reson., 1981, 45, 8.

⁸ Cookson, D. J., and Smith, B. E., Org. Magn. Reson., 1981, 10, 111.

at 270° for 30 min. After cooling, the product was dissolved in chloroform and filtered. The solvent was evaporated and dihydrocinnamate was removed by washing with ethanol to yield crude 2,2'-(*butane-1,4-diyl*)*bisnaphthalene* (9) which was crystallized from ethanol (1 · 2 g, 77%), m.p. 153-154° (Found: C, 92 · 9; H, 7 · 1. C₂₄H₂₂ requires C, 92 · 9; H, 7 · 1%). ¹H n.m.r.: $\delta_{\rm H}$ (CDCl₃) 1 · 78, m, CH₂; 2 · 81, m, CH₂; 7 · 24-7 · 84, m, Ar. ¹³C n.m.r.: $\delta_{\rm C}$ (CDCl₃) 30 · 9, CH₂; 35 · 9, CH₂; 125 · 0, CH; 125 · 8, CH; 126 · 3, CH; 127 · 4, 2 × CH; 127 · 6, CH; 127 · 8, CH; 131 · 9, C; 133 · 6, C; 140 · 0, C.

Hydrogenation of 6,6'-(Butane-1,4-diyl)bis(1,2,3,4-tetrahydronaphthalene)

The bis-naphthalene (8) (3 g) was suspended in acetic acid (75 ml) in a glass vessel and hydrogenated at 6.8 MPa at 120–150° for 3 h. After cooling, the product was diluted with 500 ml of water, neutralized with ammonia solution and extracted with carbon tetrachloride. After filtering, the carbon tetrachloride extract was evaporated to yield an oil which crystallized after standing for several days. Recrystallization from hexane gave 2,2'-(*butane-1,4-diyl*)*bis*(*decahydronaphthalene*) (10) (2.8 g, 90%), m.p. 52° (Found: C, 87.2; H, 12.6. C₂₄H₄₂ requires C, 87.3; H, 12.7%). ¹H n.m.r.: $\delta_{\rm H}$ (CDCl₃) 0.9–1.8, m. ¹³C n.m.r.: $\delta_{\rm C}$ (CDCl₃) 21.0, CH₂; 25.9, CH₂; 27.2, CH₂; 27.3, CH₂; 27.9, CH₂; 32.5, CH₂; 32.6, CH₂; 32.8, CH₂; 36.1, 2×CH; 37.8, CH₂; 38.5, CH.

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