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COMPETITIVE PATHWAYS IN THE SYNTHESIS OF CYCLOPROPA[b]NAPHTHALENE

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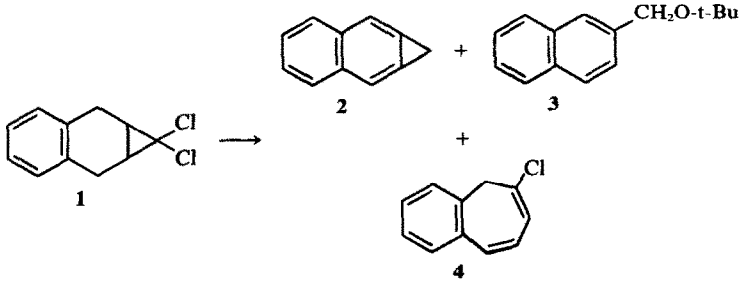
Abstract—The product distribution obtained from dehydrochlorination of the benzobicycloheptene **1** is dependent on the reaction conditions. In tetrahydrofuran at high base concentration cyclopropa[b]naphthalene (**2**) predominates, whereas at low base concentration 6 - chlorobenzo[a]cyclohepta - 1,3,5 - triene (**4**) is the major product. In dimethyl sulphoxide **2** and **4** are formed in low yields, the ether **10** being the major product.

Although the chemistry of cyclopropabenzene and its derivatives is well established,[1] there have been comparatively few reports concerned with other cyclopropa-arene ring systems and, of the early accounts[2,3] the addition of secondary diazo compounds to 1,4-naphthoquinone N,N' - di - benzenesulphonylimine, originally believed to afford cyclopropa[b]naphthalenes,[2] results in cyclopropane ring formation.[4] It is comparatively recently that the first authenticated synthesis of a cyclopropa[b]naphthalene was reported,[5] and in continuing our studies of cyclopropa-arene systems we, like Billups and Chow,[6] have found that the bicycloheptene **1** is a suitable precursor to cyclopropa[b]naphthalene (**2**). However, we have found that the dehydrochlorination reaction is not as simple as has been recently reported[6] and we now present evidence which demonstrates the presence of competing pathways in the base induced dehydrohalogenation of **1**.

The dehydrochlorination of **1** with sixteen molar equivalents of potassium t-butoxide in dry THF has been shown to give rise to **2** (38%) and its solvolysis product **3**. We have also found this to be the case but, in addition, we find that the product distribution is significantly altered when the base concentration is reduced. Thus addition of **1** to a chilled ($-10°$) solution of dry THF containing four molar equivalents of KO-t-Bu results in a complex mixture of products, the main components of which are separable by preparative TLC (Experimental). The major product, isolated as a colourless halogen-containing oil in a yield of 27%, has been identified as 6-chlorobenzo[a]cyclohepta-1,3,5-triene (**4**) mainly from its spectral data. The PMR spectrum of the compound exhibits a 2-proton singlet at 4·87 ppm and a 7-proton multiplet in the region 7·2–8·2 ppm, consistent with the proposed structure. The appearance of the methylene protons as a singlet precludes structures such as **6**, **7**, and **8** (Scheme) in which vicinal coupling between the methylene and adjacent vinylic protons is to be expected.[7] The mass spectrum of **4** shows molecular ions at *m/e* 176 and 178 (3:1) in agreement with a $C_{11}H_9Cl$ species, and fragment ions at *m/e* 141 (base; benzocycloheptatrienyl cation) and 115 (P-Cl-C_2H_2). An alternative formulation to **4** for the product would be 2-chloromethylnaphthalene (**5**) (Scheme), but a comparison of the IR and NMR data recorded for the product with those obtained from an authentic, and commercially available, sample of **5** eliminate this possibility. The other products obtained from the reaction of **1** with four molar equivalents of base were cyclopropa[b]naphthalene (**2**, 11%) and the ether **3** (17%).

In an analogous experiment using eight molar equivalents of base the same products were



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obtained, but the distribution was found to be intermediate between the two extreme cases outlined above with the yield of 2 (22%) increasing at the expense of that of 4 (16%).

The formation of 2 and 4 must arise from competing, concentration dependent, pathways. The route to 2 has been proposed[6] as involving 1,2-dehydrochlorination of 1 with subsequent rearrangement of the strained olefin formed, followed by a repetition of the process (path *a*, Scheme). If, however, base attack takes place at the benzylic position of 1, the cycloheptatriene 4 can arise by rearrangement and ring expansion, possibly as outlined in path *b* of the scheme, with the final step of the sequence involving a [1.5]hydrogen shift to place the chlorine substituent at the terminus of the conjugated system.* If base attack at the benzylic position of 1 resulted in 1,4-dehydrochlorination and formation of the chlorocycloheptatriene 7, then cyclopropa[a]naphthalene (9) could arise *via* a benzonorcaradiene (path *c*, scheme). However, no evidence for 9, either in this or the previously reported work, has been obtained.

On the reasonable assumption that the ether 3 results from the addition of t-butanol to 2,† the total yield of isolable product from the reaction involving the smallest quantity of base demonstrates an almost even competition between the alternative routes (28% of 2 and 3 compared with 27% of 4). As the base concentration is increased, 1,2-dehydrochlorination of 1, resulting in the formation of 2 (and 3), clearly becomes the predominant pathway and emphasises a requirement for a large excess of base if viable yields of 2 are to be obtained.

The behaviour of 1 with an unspecified quantity of potassium t-butoxide in dimethyl sulphoxide has also been examined.[6] The major products of reaction were the ether 3 and β-vinylnaphthalene, although 2 was isolated in low (< 10%) yields. The formation of the first two compounds must involve reaction of 2 with t-butanol and the dimsyl anion, respectively, thus demonstrating an analogy with the reactions of 1 with a large excess of base in THF. Our investigations of the chemistry of 1 have also involved an examination of its behaviour with base in dimethyl sulphoxide. While our results indicate a distinct preference for the formation of products *via* 2, we again find that base attack at the benzylic position of 1 gives rise to a significant amount of product.

Treatment of 1 with three molar equivalents of KO-t-Bu in DMSO results in both 2 and 4 in low yield (8 and 9% respectively). In our hands, the major product of reaction (66%) is neither β-vinylnaphthalene nor 3, but di(2-naphthalenylmethyl) ether 10.[9] It is again reasonable to assume that the ether comes from 2 by a subsequent reaction and the result shows that base attack at the 1-position of 1 is clearly the preferred, but not the exclusive, mode of reaction; the product ratio for the two routes indicates competition to an extent of about 8·5 to 1. The absence of β-vinylnaphthalene from the product mixture is not too surprising in view of the quantity of base employed, but the conversion of 2 to 10 is not well understood. The possibility of reaction of 2 with moisture during the work-up to give 2-naphthalenyl alcohol which reacts with a second molecule of 2 does not appear to be involved since 2 is recovered unchanged after standing in moist dimethyl sulphoxide. Further aspects of cyclopropa-arene chemistry are under investigation in these laboratories.

EXPERIMENTAL

Microanalyses were performed by Dr. A. D. Campbell and associates of Otago University, Dunedin. IR spectra were recorded as thin films or in Nujol mulls on a Unicam SP200 or SP1000 spectrophotometer and ultraviolet spectra on a Shimadzu UV 200. PMR spectra were measured on a Hitachi Perkin–Elmer R20 60 MHz instrument operating at 34° and mass spectra were determined on an A.E.I. MS902 instrument. Preparative thin layer chromatography was performed using Merck Kieselgel GF254 on 1 m × 20 cm plates made to a thickness of 0·75 mm. Melting points are uncorrected. Light petroleum refers to the fraction b.p. 60–80°.

7,7-*Dichlorobenzobicyclo*[4.1.0]*hept*-3-*ene* (1)

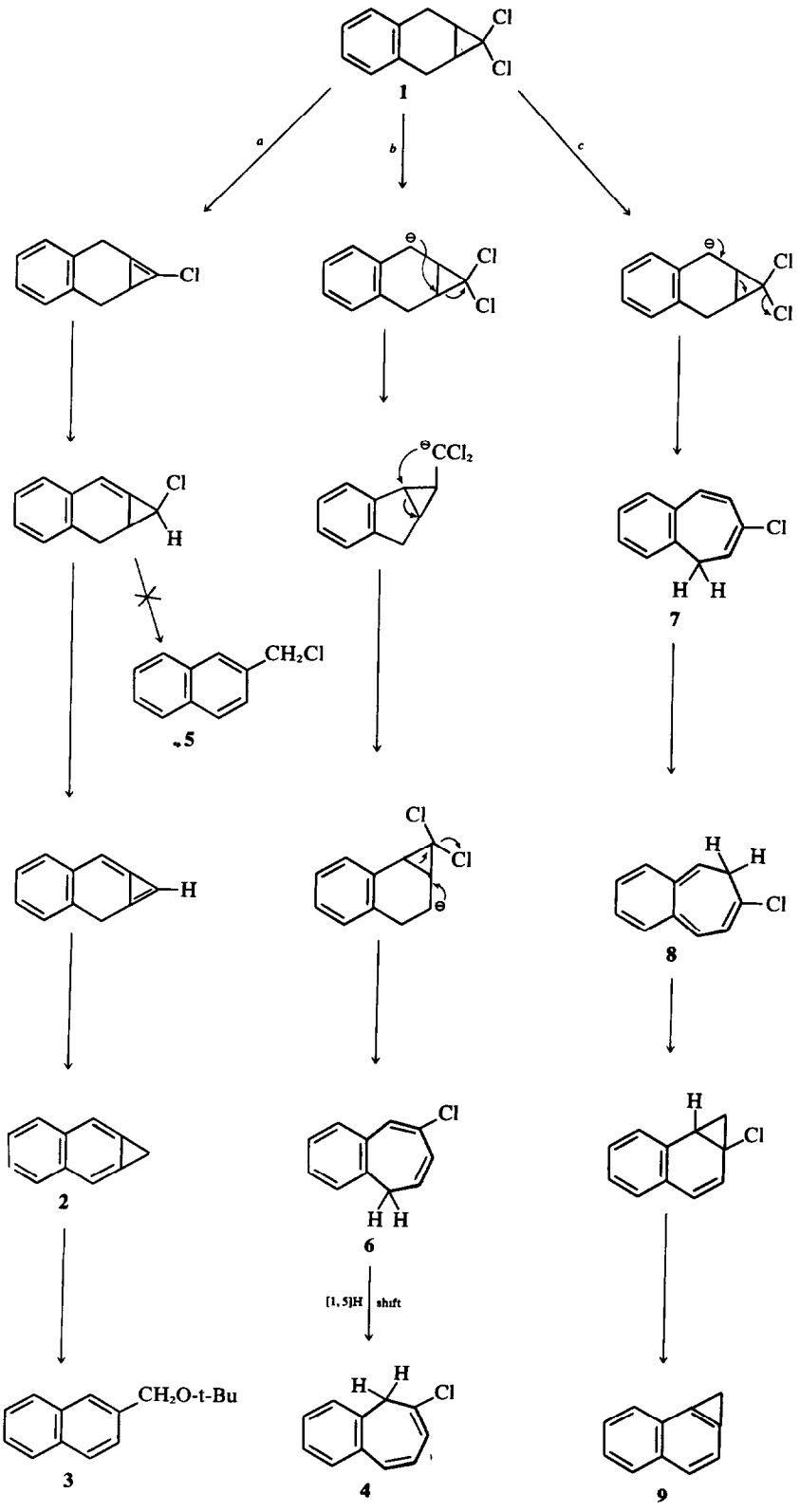
The compound was obtained by the addition of dichlorocarbene, prepared in the usual manner[10] from sodium trichloroacetate (25 g, 0·144 mol), to 1,4-dihydronaphthalene[11] (15 g, 0·115 mol). After separating, washing, and drying the organic phase, concentration in vacuum afforded a brown oil which was distilled to give 1,4-dihydronaphthalene (6·15 g, 41% recovery) b.p. 64–66° at 2 mm., and 7,7-*dichlorobenzobicyclo*[4.1.0.]*hept*-3-*ene* (1) (6·85 g, 47% based on the dihydronaphthalene used) b.p. 116–118° at 1 mm., m.p. 55–57°. (Found: C, 62·05; H, 4·76; Cl, 32·97. $C_{11}H_{10}Cl_2$ requires: C, 61·99; H, 4·76; Cl, 33·27%). ν_{max} 3030, 2900, 1590, 1500, 1460, 1435, 1222, 1073, 1042, 825, 805, 775, 748, 700 and 680 cm^{-1}. δ ($CDCl_3$) 2·03 (m, 2H), 2·73 (d, J_{gem} 16 Hz, 2H), 3·25 (m, J_{gem} 16 Hz, 2H, 7·06 (s, 4H).

Dehydrochlorinations of 1 *with potassium t-butoxide in tetrahydrofuran*

A soln of 1 (1·0 g, 4·69 mmol) in dry THF (20 ml) was added dropwise, with stirring, over a period of 0·75 h to a chilled (−10°) soln of t-BuOK in dry THF (50 ml). The mixture was allowed to stand, with continuous stirring at

*One referee has suggested that 2 could arise from 4 (or 6) by proton loss to give an antiaromatic chlorobenzocycloheptatrienyl anion which on losing chloride ion would produce a benzocycloheptatrienyl carbene. Carbene insertion could then afford 2. However, 4 is recovered unchanged when treated with sixteen molar equivalents of KO-t-Bu under the conditions for formation of 2.

†Cyclopropa-arene solvolysis has been shown to involve arocyclopropenium ions.[8]


Cl
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1
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7
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H H
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8
2
Cl
H H
6
[1, 5]H shift
H H
Cl
CH2O-t-Bu
3
4
9

room temp for 5 h and then evaporated to dryness *in vacuo*. The products were extracted with benzene (100 ml), washed with water (2 × 30 ml), dried ($MgSO_4$) and concentrated *in vacuo*. Subjection of the resultant oil to preparative TLC with light petroleum elution afforded 3 bands A–C with R_f values of 0·8, 0·5 and 0·0–0·4 respectively. The bands were extracted with benzene–chloroform (1:1), and band C was re-subjected to preparative TLC with benzene–light petroleum (1:1) elution to give band D (R_f 0·6) which was similarly extracted.

(i) Reaction with 4 molar equivs of t-BuOK (2·1 g, 18·8 mmol).

Band A yielded a colourless solid which was recrystallised from pentane at −20° to give *cyclopropa*[b]*naphthalene* (**2**) as colourless needles (0·07 g, 11%), m.p. 86–87° (lit.[6] 86–87°). (Found: C, 94·46; H, 5·75. Calculated for $C_{11}H_8$: C, 94·24; H, 5·76%). ν_{max} 3040, 2950, 1673, 1600, 1525, 1465, 1383, 1260, 1237, 1143, 968, 943, 900, 845 and 745 cm^{-1}; λ_{max} (cyclohexane) 219 nm (log ϵ 4·73); δ ($CDCl_3$) 3·40 (s, 2H), 7·0–7·8 (complex m, 4H), 7·40 (s, 2H).

Band B gave 6 - chlorobenzo[a]*cycloheptа* - 1,3,5 - *triene* (**4**) (0·22 g, 27%) as a colourless oil (*m/e* 176·039034. $C_{11}H_9{}^{35}Cl$ requires: 176·039287; Δ = 1·39 ppm); ν_{max} 3040, 2950, 1603, 1515, 1460, 1280, 1263, 1173, 1017, 868, 798, 788, 775, 747, 708 and 688 cm^{-1}; λ_{max} (cyclohexane) 227 (4·4), 276 (3·5), 284 nm sh (log ϵ 3·4) δ ($CDCl_3$) 4·87 (s, 2H), 7·2–8·2 (complex m, 7H).

Band D gave 2-(*t-butoxymethyl*)*naphthalene* (**3**) as a pale yellow oil (0·17 g, 17%). (Found: C, 84·11; H, 8·41. Calculated for $C_{15}H_{18}O$: C, 84·05; H, 8·48%); ν_{max} 3040, 2970, 2920, 1600, 1515, 1473, 1465, 1395, 1370, 1195, 1105, 1060, 1017, 993, 790 and 775 cm^{-1}; δ ($CDCl_3$) 1·34 (s, 9H), 4·83 (s, 2H), 7·1–7·9 (complex m, 7H).

(ii) Reaction with 8 molar equivs of t-BuOK (4·2 g, 37·5 mmol).

Band A: **2** (0·14 g, 22%). Band B: **4** (0·13 g, 16%). Band D: **3** (0·14 g, 14%).

(iii) Reaction with 16 molar equivs of t-BuOK (8·4 g, 75mmol).

Band A: **2** (0·24 g, 38%). Band B: **4** in trace amounts (< 1%)

Band D: **3** (0·08 g, 8%).

Dehydrochlorination of **1** *with potassium t-butoxide in dimethyl sulphoxide*

A soln of **1** (1·0 g, 4·69 mmol) in dry DMSO (20 ml) was added dropwise, and with stirring, over a period of 0·5 h to a chilled (−10°) soln of t-BuOK (1·6 g, 14·3 mmol) in dry DMSO (50 ml). The mixture was allowed to stand, with continuous stirring, at room temp for 3 h by which time a deep red colour had developed. After the addition of chilled water (100 ml) the mixture was extracted with pentane (4 × 100 ml). The combined extracts were washed with water (2 × 400 ml), dried ($MgSO_4$) and evaporated *in vacuo* to give a yellow solid. Preparative TLC, in the manner described for the THF reactions above, gave rise to the 3 bands A–C R_f 0·8, 0·5, and 0·0–0·4, respectively which were extracted with benzene–chloroform (1:1). Band C was resubjected to preparative TLC eluting with benzene–light petroleum (1:1) to give band E R_f 0·5.

Band A afforded **2** (0·05 g, 8%), and *Band B* gave **4** (0·07 g, 9%). *Band D* yielded a pale yellow solid which was recrystallised from benzene–light petroleum (1:4) to give **10** as yellow plates (0·45 g, 66%), m.p. 123–124° (lit.[9] 123·5–124·5°). (Found: C, 88·51; H, 6·12. Calc for $C_{22}H_{18}O$: C, 88·56; H, 6·09%). ν_{max} 1602, 1330, 1178, 1132, 1115, 1032, 950, 898, 862, 820 and 738 cm^{-1}; δ ($CDCl_3$) 4·71 (s, 4H), 7·30–7·95 (complex m, 14H).

Note added in proof

The route from **1** to **2** has now been established as that shown in the Scheme: J. Prestien and H. Günther, *Angew. Chem.* Internat. edn., **13**, 276 (1974).

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