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COMPETITIVE PATHWAYS IN THE DEHYDROCHLORINATION ROUTE TO CYCLOPROPA-ARENES

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Abstract—The dehydrochlorination route to cyclopropabenzene **4** from **2** yields t-butoxymethylbenzene **8** as the sole isolable by-product. The path by which the majority of **8** is produced does not involve solvolysis of **4**. The analogous route to cyclopropa[b]naphthalene **3** has been re-examined and the previously proposed 6-chlorobenzo[a]cyclohepta-1,3,5-triene **10** and 2-(t-butoxymethyl)naphthalene **9** have been reassigned as 1-(chloromethyl)naphthalene **5** and 1-(t-butoxymethyl)naphthalene **7**, respectively. Evidence is presented which supports the presence of competing pathways in both dehydrochlorination processes.

Following our recent discovery[1] of the presence of competing pathways in the synthesis of cyclopropa[b]naphthalene **3** from 7,7-dichlorobenzobicyclo[4.1.0]hept-3-ene **1** we have directed our attention to the analogous dehydrochlorination route to cyclopropabenzene **4** from **2**.[2] Whereas the product distribution from the reaction of **1** with potassium t-butoxide in THF[1] is strongly dependent on the base concentration,[1] no such dependence has been detected in the reaction of **2** with the same base in DMSO;[2] only **4** and t-butoxymethylbenzene **8** have been isolated. However, a more detailed investigation of this latter reaction, coupled with our revised product data from the behaviour of **1**, provides compelling evidence for the presence of a competing pathway in the synthesis of **4**.

Treatment of **2**[4] with 2·5 molar equivalents of potassium t-butoxide in dry DMSO resulted in an incomplete reaction even after 42 hr. On increasing the base quantity to 4 molar equivalents, **2** was completely consumed inside 18 hr and **4** and **8** were produced in yields of 56 and 8%, respectively (based on GLC analysis of product mixture). Increasing the amount of base to 8 molar equivalents caused a small increase in the yield of **8** (9%) at the expense of **4** (53%). Apart from **4** and **8** (and **2** in the first case above) only traces of uncharacterisable products were detected by GLC analysis. The reaction of **2** with four molar equivalents of base was subjected to more detailed investigation by withdrawing suitable aliquots and subjecting the worked-up organic phase to GLC analysis. After 0·5, 1·5 and 18·0 hr the ratio of **2**:**4**:**8** was determined as 5:82:9, 0:86:10 and 0:84:12, respectively. These data clearly demonstrate that **4** and **8** are rapidly produced with the yield of **8** being only slightly enhanced after a long reaction period. In order to assess the production of **8** from **4** under the reaction conditions believed to be prevalent after dehydrochlorination, cyclopropabenzene **4** was treated with potassium t-butoxide (two molar equivalents) and t-butanol (two molar equivalents) in dry DMSO. After 24 hr only a 6% conversion of **4** to **8** was recorded. From the rapidity by which **8** is generated and the observed reluctance of **4** to undergo solvolysis to **8**, it must be concluded that **8** arises not from **4** but from a reaction intermediate in the route to **4** *or by an alternative pathway*.

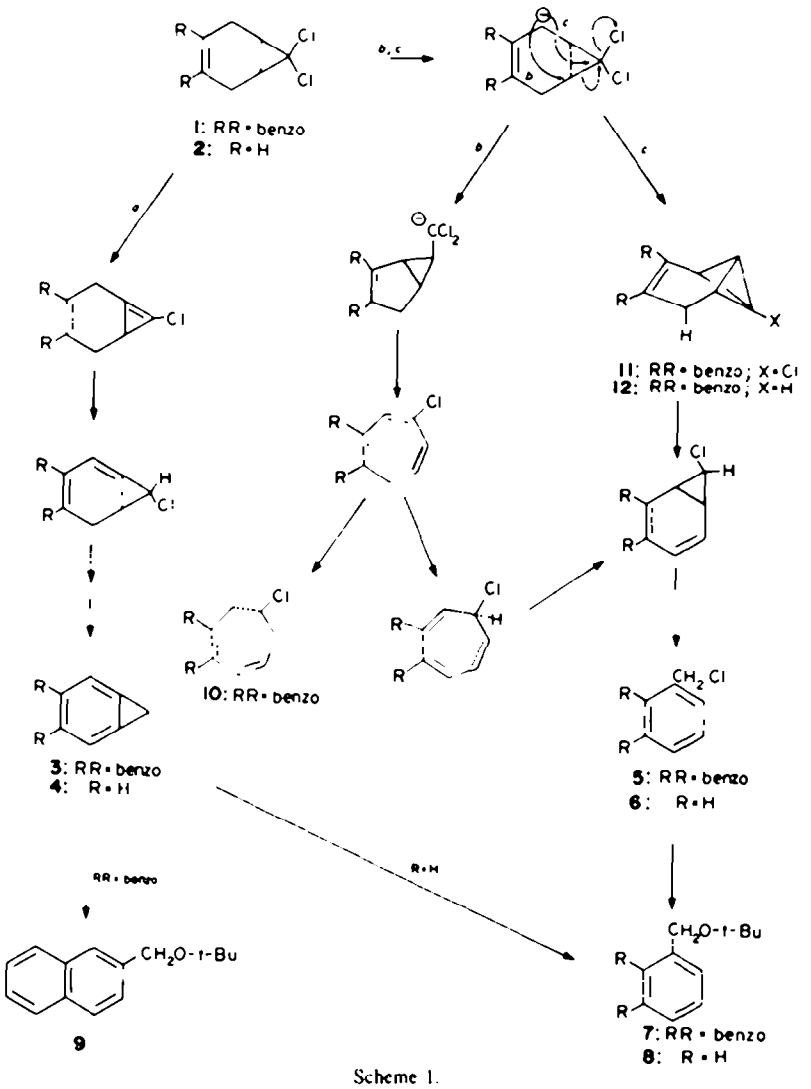
In view of the results described above, a re-examination of the behaviour of benzobicycloheptene **1** was instigated in an attempt to obtain meaningful evidence on the origin of the ether by-product. Furthermore, the structure of 6-chlorobenzo[a]cyclohepta-1,3,5-triene **10** previously proposed by us as the major product from **1** at low base concentration,[1] was placed in considerable doubt by the non-equivalence of its spectroscopic data with those recently recorded for the same compound synthesized from naphthalene.[5]

The reactions of **1** with 4, 8 and 16 molar equivalents of base (in THF) were repeated as described previously[1] and the major product at low base concentration has been re-assigned as 1-(chloromethyl)naphthalene **5** by comparison with an authentic and commercially available sample. The yields of cyclopropa[b]naphthalene **3** (11, 22 and 38%) and **5** (27, 16 and <1%) with 4, 8 and 16 molar equivalents of base, respectively, are fully consistent with those reported for **3** and **10** previously.

The unequivocal establishment of **5**, with a rearranged carbon skeleton, as a product from **1** raised serious doubts concerning the structure of the ether by-product in these dehydrochlorination reactions. We have found that the ether produced is not 2-(t-butoxymethyl)naphthalene **9** as proposed by Billups and Chow,[1] but the 1-isomer **7**. The compound is identical to an authentic sample prepared from **5**. Furthermore, under reaction conditions approximating to those present after dehydrochlorination, **5** is converted to **7** in a yield consistent with that obtained from the elimination reaction. Since **4** undergoes slow ring-cleavage and formation of ether **8** under the conditions present after its formation, cyclopropanaphthalene **3** should behave similarly. Indeed, we have found that **3** affords an 8% yield of ether **9** (identical to a sample prepared from 2-(chloromethyl)naphthalene) after 48 hours and consequently the presence of **9** in the product mixture from **1**, albeit in low yield, is to be expected. A careful examination of the ether component from the reaction of **1** in highest base concentration has revealed **9**, *ca.* 1%, as an impurity in **7** ($ArCH_2O$–: **7**, 4·83; **9**, 4·49 ppm).

Thus the dehydrochlorination of **1** affords **3** and **5** which give rise to their respectively solvolysis products **9** and **7** under the reaction conditions. At low base concentration (4 molar equivalents) the route to **5** (and **7**) competes with that to **3** (and **9**) to an extent of 4:1. At high (sixteen molar equivalent) base concentration the ratio is dramatically changed to 1:5.

The route from **2** to **4** is established[6] and **1** is presumed to behave similarly (path *a*, scheme) with the rate being



Scheme 1.

dependent on both substrate and base concentration. The route by which **5** is produced necessarily involves skeletal rearrangement but is less clear; a base independent process is compatible with the variations in the product distributions recorded. Loss of the benzylic proton of **1**† as proposed earlier is most reasonably invoked[1] and **5** could arise perhaps as illustrated by paths *b* and *c* of the scheme. Since **10** is not observed, we favour path *c* via the bicyclobutane **11**. Such a pathway is not without precedent as benzotricyclo[4.1.0.0^{2,7}]hept-3-ene **12** has recently been reported[8] and the rearrangement of **13** to **14** is known.[9]

13 **14**

The benzo-annelation present in **1** has provided a suitable label for monitoring the elimination and rearrangement to **5**. Were the same process to operate in **2** by loss of the allylic proton, benzyl chloride **6** and ether **8** would be produced. In none of the reactions of **2** was **6** detected as a product. However, under the elimination conditions **6** is converted quantitatively to **8** *in less than* 1.5 *hr* and thus its absence from the product mixture is not surprising. Ether **8** must arise by a route other than that from **2** and while we cannot distinguish between formation of **8** from an intermediate in the path to **4** (path *a*) and allylic proton loss (path *c*), we favour the latter.

Finally, it must be noted that dehydrochlorination of **2** is best effected with potassium t-butoxide in DMSO[2] while the most appropriate conditions for **1** involve the base in THF.[3] Since the former medium is more strongly basic than the latter, the essential independence of the product distribution from **2** with base strength is not unreasonable. Attempted dehydrochlorination of **2** with base (16 molar equivalents) in THF was incomplete even after 4 days. Product analysis proved to be more complex but ether **8** was the predominant product and only traces of **4** were detected throughout the reaction. This observation lends further support to the presence of competing pathways in the dehydrochlorination of **2**.

EXPERIMENTAL

Microanalyses were performed by Professor A. D. Campbell and associates of Otago University, Dunedin. IR spectra were

†The removal of a proton from the 2-position of 3,4,7,7-tetrachlorobicyclo[4.1.0]heptane has recently been reported.[7]

recorded as thin films or as nujol mulls on a Unican SP200 or SP1000 spectrophotometer. 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. GLC analyses were performed on a Pye 105 instrument using an E 30 column with nitrogen as carrier gas and a flow rate of 45 $cm^3 min^{-1}$. The oven temperature was programmed to remain at 60° for 35 min. after injection and then to increase at a rate of 45 deg. min^{-1} to a final temp of 150°. Mps are uncorrected.

7,7-Dichlorobicyclo[4.1.0]hept-3-ene **2**

To a stirred suspension of NaOMe (9·4 g, 0·174 mol) in pentane (65 ml) was added cyclohexa-1,4-diene (5·0 g, 0·063 mol). The resulting mixture was externally cooled in an ice-salt bath and ethyl trichloroacetate (24 g, 0·126 mol) added dropwise, over a period of 30 min. The mixture was stirred at ambient temp. for 6 hr, diluted with benzene (50 ml), and added to water (150 ml). The organic phase was washed with water (50 ml), dried over $MgSO_4$ (20 g) and concentrated to a brown oil which was diluted with petroleum ether (10 ml) and the resulting solid bis-addition product removed by filtration. The filtrate was concentrated and distilled to give **2** (4·8 g, 47%) as a colourless liquid, b.p. 88–90°/23 mmHg (lit.[4] 82–84°/12 mmHg). ν_{max} (film) 3020, 2885, 2820, 1427, 1322, 1218, 1115, 1070, 1005, 948, 800, 702 and 670 cm^{-1}. δ 1·77 (m, 2H), 2·23 (broadened s, 4H), 5·42 (s, 2H).

Dehydrochlorinations of **2** *with potassium t-butoxide in dimethyl sulphoxide*

(i) Using 4 molar equivalents of base. A soln of **2** (1·75 g, 10·7 mmol) in dry DMSO (25 ml) was added dropwise, over a period of 30 min, to a stirred soln of t-BuOK (4·80 g, 42·8 mmol) in dry DMSO (50 ml). The resulting black soln was stirred at ambient temp. for 18 hr and then poured into chilled (0°) water (300 ml) and extracted with pentane (3 × 100 ml). The extract was washed with water (2 × 80 ml) and dried over $MgSO_4$ (40 g). Concentration to dryness at 0° gave a pale yellow oil (0·68 g) which afforded two major products separated by preparative GLC and identified as: **4**[10] (56%). ν_{max} (film) 3030, 2970, 1665, 1450, 1186, 1142, 1095, 828, 725 cm^{-1}. δ 3·11 (s, 2H), 7·02 (s, 4H); and **8** (8%) identical to an authentic sample prepared from **6**.

The reaction was repeated on the same scale and samples of the mixture (1 ml^3) were withdrawn at 0·5, 1·5 and 18 h, shaken with water (3 ml) and pentane (2 ml). The percentage compositions of the pentane phase as analysed by GLC were:

Compound	0·5 hr	1·5 hr	18 hr
6	--	—	--
4	82	86	84
2	5	--	—
8	9	10	12
Others	4	4	4

(ii) Using 8 molar equivalent of base. The reaction was repeated as above with 8 molar equiv. of t-BuOK (9·59 g, 85·6 mmol), with a reaction time of 18 hr. Analysis of the product mixture by GLC showed the presence of **2** (53%) and **8** (9%).

Reaction of **4** *with potassium t-butoxide and t-butanol in dimethyl sulphoxide*

A soln of **4** (0·20 g, 2·2 mmol) in dry DMSO (5 ml) was added to a stirred suspension of t-BuOK (0·50 g, 4·5 mmol) and t-BuOH (0·33 g, 4·5 mmol) in dry DMSO (10 ml). The mixture was stirred at ambient temp. for 24 hr and then poured into water (50 ml) and extracted with pentane (3 × 50 ml). The extract was washed with water (2 × 50 ml) and dried over $MgSO_4$ (20 g). Concentration to dryness at 0° gave a pale yellow oil. GLC analysis revealed a product composition of **8** (6%) and **4** (94%).

Reaction of **6** *with potassium t-butoxide and t-butanol in dimethyl sulphoxide*

A soln of **6** (1·00 g, 7·9 mmol) in dry DMSO (25 ml) was added dropwise, over a period of 30 min, to a stirred suspension of t-BuOK (2·20 g, 19·6 mmol) and t-BuOH (1·45 g, 16·6 mmol) in dry DMSO (50 ml). After stirring for 1·5 hr, a sample of the mixture (1 ml) was shaken with water (3 ml) and pentane (2 ml). GLC analysis of the pentane phase revealed only **8** with no evidence for **6**. The mixture was subsequently poured into water (250 ml) and extracted with pentane (2 × 100 ml). The extract was washed with water (100 ml) and dried over $MgSO_4$ (30 g). Concentration gave a colourless oil which was distilled to give **8** (1·19 g, 92%), b.p. 98–100°/15 mm (lit.[11] 90–92°/10 mm). ν_{max} 3060, 3020, 2970, 1600, 1582, 1456, 1393, 1367, 1200, 1092, 1067, 1025, 888, 737, 726 and 700 cm^{-1}. $\delta(CDCl_3)$ 1·22 (s, 9H), 4·41 (s, 2H) and 7·18 (s, 5H).

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

The dehydrochlorinations of **1** were performed, and the products isolated, as described previously.[1] The percentage yields in parenthesis refer to reactions with 4, 8 and 16 molar equivs. of base, respectively.

Band A (R_f 0·8) gave **3** (11, 22, 38%) m.p. 86–87° (lit.[1] 86–87°).

Band B (R_f 0·5) gave **5** as a colourless oil (27, 16, <1%) (*m/e* measured 176·039034. Calc. for $C_{11}H_9{}^{35}Cl$ 176·039287, Δ 1·39 ppm) identical to a commercially available sample. δ ($CDCl_3$) 4·87 (s, 2H) 7·20–8·20 (complex m, 7H).

Band C (R_f 0·0–0·4) was rechromatographed eluting with benzene light petroleum (1:1) to give:

Band D (R_f 0·6) which gave *1-(t-butoxymethyl)naphthalene* **7** as a pale yellow oil (17, 14, 8%). (Found: C, 84·11; H, 8·41. $C_{15}H_{18}O$ requires: 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) 7·10–7·90 (complex m, 7H).

1-(t-Butoxymethyl)naphthalene **7** *and 2-(t-butoxymethyl)-naphthalene* **9**

A soln of appropriate chloromethylnaphthalene (1·0 g, 5·7 mmol) in dry DMF (20 ml) was added dropwise, over a period of 30 min, to a stirred soln of t-BuOK (2·0 g, 17·6 mmol) in dry DMF (40 cm^3) and the resulting soln stirred at ambient temp. for 24 hr. The resultant soln was poured on to 5% HCl (150 ml), extracted with ether (3 × 75 ml) and the organic extract washed with water (100 ml), dried over $MgSO_4$ (25 g) and concentrated in vacuum to give an oil.

1-(t-Butoxymethyl)naphthalene **7** (0·82 g, 67%) was isolated as a pale yellow oil after preparative TLC of the crude oil eluting with benzene-light petroleum (1:1) (R_f 0·6) and was identical to the sample obtained above.

2-(t-Butoxymethyl)naphthalene **9** (0·53 g, 43%) was obtained by cooling the crude oil from above and recrystallising the solid thus obtained from light petroleum at −20° to give colourless needles m.p. 59–61° (Found: C, 84·07; H, 8·57. $C_{15}H_{18}O$ requires: C, 84·05; H, 8·48%) ν_{max} 1595, 1505, 1465, 1390, 1362, 1195, 1082, 948, 853, 825 and 738 cm^{-1}. δ ($CDCl_3$) 1·32 (s, 9H), 4·49 (s, 2H), 7·10–7·80 (complex m, 7H).

Reaction of **5** *with potassium t-butoxide and t-butanol in THF*

A soln of **5** (1·1 g, 6·25 mmol) in dry THF (25 ml) was added dropwise, over a period of 30 min, to a stirred suspension of t-BuOK (4·2 g, 37·5 mmol) and t-BuOH (0·92 g, 12·5 mmol) in dry THF (50 ml), externally cooled in an ice-water bath. The mixture was stirred at ambient temp. for 5 hr and then concentrated to dryness. The products were extracted with benzene (100 ml), washed with water (2 × 30 cm^3), dried over $MgSO_4$ (20 g) and concentrated to a yellow oil. The resultant oil was subjected to preparative TLC, eluting with benzene-light petroleum (1:2) to give two bands A-B with R_f values of 0·9 and 0·4 respectively.

Band A (R_f 0·9) was extracted with chloroform (100 ml) and concentrated to give **5** (0·67 g, 65% recovery).

Band B (R_f 0·4) was extracted with chloroform (100 ml) and concentrated to give **7** (0·52 g, 35%).

Reaction of cyclopropa[b]naphthalene **3** *with potassium t-butoxide and t-butanol in tetrahydrofuran*

A soln of **3** (200 mg, 1·43 mmol) in dry THF (10 ml) was added dropwise, over a period of 10 min, to a stirred suspension of t-BuOK (0·64 g, 5·71 mmol) and t-BuOH (0·21 g, 2·86 mmol) in dry THF (25 ml). The mixture was stirred at ambient temp. for 48 hr and then concentrated to dryness. The products were extracted with benzene (40 ml), washed with water (2 × 20 ml) and concentrated to a pale yellow oil which was subjected to preparative TLC, eluting with benzene-light petroleum (1:1). The two bands, R_f 0·9 and 0·6 respectively, were extracted with chloroform (80 ml).

Band A (R_f 0·9) gave **3** (150 mg, 75% recovery).

Band B (R_f 0·6) gave **9** (25 mg, 8%), identified by comparison of IR and NMR spectra with an authentic sample.

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