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CHEMISTRY OF STRAINED POLYCYCLIC COMPOUNDS—VII[1]

A BASE INDUCED HOMOALLYLIC REARRANGEMENT IN THE HOMOCUBANE AND CUBANE SYSTEM

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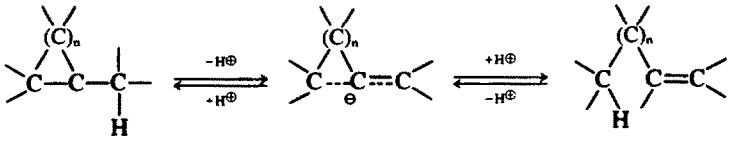
Abstract—The base induced homoallylic rearrangement in the highly strained homocubane and cubane cage systems has been studied. Under aprotic conditions using $LiN(iPr)_2$ as base, homocubane methylcyanide **3** and sulfone **5** are converted quantitatively into tricyclo [4.2.1.$0^{2,5}$]nonene derivatives by a regiospecific cleavage of C_4–C_7 and C_5–C_6 bond. This process is formulated as a double γ-homoallylic rearrangement. The homocubane acetate **7** does not give a homoallylic rearrangement under similar conditions. The cubane methylcyanides **18** and **31** show, when treated with $LiN(iPr)_2$ in THF, a facile regiospecific γ-homoallylic rearrangement leading to tricyclo[4.2.0.$0^{2,5}$]octene compounds. In contrast to the homocubane acetate **7** cubane acetate **21** is readily converted into the γ-homoallylic rearrangements products upon treatment with $LiN(iPr)_2$ in THF. The mechanism of the γ homoallylic rearrangement is discussed.

In a previous paper we described the stereospecific and regiospecific base induced homoketonization reaction of homocubane and 1,3-bishomocubane bridgehead alcohols.[1] In analogy with the concept of homoketonization/homoenolization a homoallylic rearrangement is formulated as depicted in Scheme 1. Such



Scheme 1

ring cleavage reactions of homoallylic carbanions have been reported[2] for monocyclic compounds with n being only 1 or 2. In polycyclic systems this type of reaction has rarely been observed. Dilling *et al.*[3] suggested a γ-homoallylic rearrangement to explain the formation of dicyclopentadiene as by-product during the reduction of perchlorobishomocubane with Li/t-BuOH. Eberbach and Prinzbach[4] observed a β-homoallylic rearrangement during the conversion of a tetracyclo[3.3.0.$0^{2,8}$.$0^{4,6}$]octane derivative into a tricyclo compound. Most likely relief of ring strain is the driving force in these ring-opening reactions.

This paper deals with the homoallylic rearrangement of the highly strained homocubane and cubane cage systems, having a carbanionic centre adjacent to the bridgehead position.

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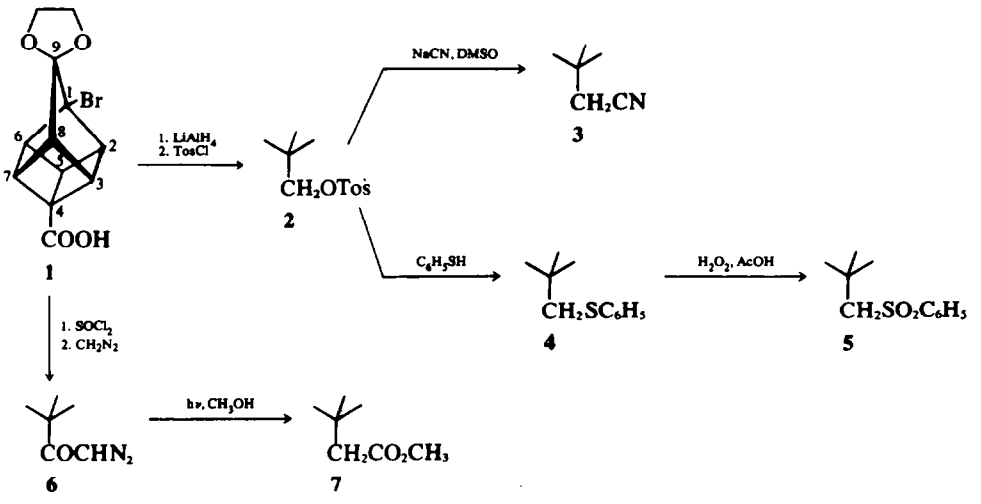
To study such a rearrangement in the homocubane cage system three substrates were selected, viz nitrile **3**, carboxylate **7** and sulfone **5** (Scheme 2). The electron withdrawing groups in these substrates are required to facilitate the formation of a carbanion in the desired position adjacent to the bridgehead C atom.

The substrates were all prepared using the homocubane carboxylic acid **1**[5] as the starting material (Scheme 2). Homologation of **1** by means of the Arndt–Eistert reaction gave the methyl ester **7** in an overall yield of 72%. It should be noted that the Wolff rearrangement of diazoketone **6** could only be accomplished by irradiation in MeOH. Attempts to achieve this rearrangement by treatment with Ag_2O in MeOH failed. The nitrile **3** was obtained in 90% yield by displacement of the tosylate **2** with NaCN. The sulfone **5** was prepared in 75% yield by treating the tosylate **2** with thiophenol and subsequently oxidizing the sulfide **4** with H_2O_2.

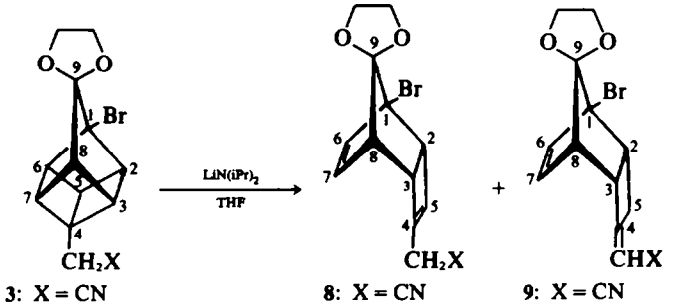
Treatment of nitrile **3** and sulfone **5** with NaOMe did not result in a rearrangement, neither at room nor reflux temperatures. Starting materials could be recovered almost quantitatively. Anion formation indeed had taken place as was shown by deuteration. Performing the base treatment in Me_3OD gave dideuterated nitrile **3** and sulfone **5**. Clearly, reprotonation of the initially formed carbanion is a much faster process than the anticipated homoallylic rearrangement. To circumvent this reprotonation the base treatment was carried out under aprotic conditions, viz in THF using $LiN(iPr)_2$ as the base. The use of this base is advantageous because it forms rather stable lithium complexes with a low tendency to undergo condensation reactions.[6–8]

The nitrile **3** indeed showed a smooth reaction upon treatment with $LiN(iPr)_2$ giving rise to an almost quantitative yield of a mixture of two alkenes. On the basis of spectral and chemical evidence structures **8** and **9** were assigned to these alkenes (Scheme 3).

The IR spectrum of the mixture showed two cyanide absorptions at 2220 and 2250 cm^{-1} indicative of a conjugated and a nonconjugated nitrile function. An olefinic C–H absorption was observed at 3060 cm^{-1}. The NMR spectrum (100 MHz, C_6D_6) displayed a complex olefinic pattern between δ 5·5 and 6·0 ppm, which could be resolved by means of spin decoupling and INDOR



Scheme 2



Scheme 3

experiments. Olefinic proton H_7 in alkene **8** appeared as a doublet ($J_{7,6} \sim 6$ Hz) of doublets ($J_{7,8} \sim 4$ Hz) (part of an ABX system) at δ 5·68 ppm. INDOR experiments showed the expected doublet for proton H_6 in this compound coincides with the complex multiplet centered at δ 5·93 ppm for H_6 and H_7 in the alkene **9**. The remaining olefinic protons were found at δ 5·57 (H_5 in **8**) and δ 4·32 (olefinic proton adjacent to the nitrile function in **9**) as multiplets. The ethylene ketal protons and methine ring protons appeared between δ 2·6–4·0 ppm as a complex pattern. Proton H_8 in both **8** and **9** is found at δ 2·16–2·44 as a multiplet while the methylene protons adjacent to the nitrile function in **8** appeared at δ 1·97 as a broad singlet.

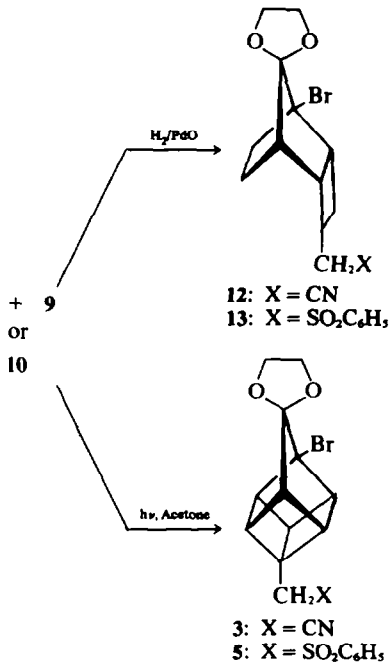
The relationship between the alkenes **8** and **9** was provided by treating the alkene mixture with $LiN(iPr)_2$. An allylic rearrangement changed, after quenching with H_2O, the ratio of **8** and **9** arbitrarily. Treatment of the mixture with a small excess of NaOMe in MeOH gave the exclusive formation of the thermodynamically more stable tricyclo[4.2.1.$0^{2,5}$]nonene **9**. Attempts to separate the mixture of isomers **8** and **9** by chromatographic methods were unsuccessful.

Important additional information about the structures of the alkenes was obtained from the two following experiments (Scheme 4). Firstly, hydrogenation of the alkene mixture with H_2/PdO quantitatively gave a single product to which structure **12** was assigned. The IR spectrum (KBr) showed a nitrile absorption at 2245 cm^{-1}. The NMR spectrum $CDCl_3$ displayed a symmetrical multiplet at δ 3·75–4·40 ppm for the ethylene ketal protons† and a complex pattern between δ 1·6 and 3·2 ppm for the remaining protons. Secondly, irradiation of the mixture of **8** and **9** in acetone gave the expected [$\pi^2 + \pi^2$] intramolecular photocyclization to the homocubane methylcyanide **3** (Scheme 4).

The sulfone **5** gave, when treated similarly with $LiN(iPr)_2$ in THF, a crystalline solid in almost quantitative yield. The spectral characteristics of this product were surely indicative of structure **10** (Scheme 3). Of its isomer **11** only trace amounts could be detected in the spectra of the initially obtained crude product. The IR spectrum of **10** showed sulfonyl absorptions at 1300 and 1140 cm^{-1}. The NMR spectrum ($CDCl_3$) displayed a multiplet at δ 7·3–8·0 ppm for the phenyl protons, a multiplet at δ 5·80 ppm for the olefinic protons H_5, H_6 and H_7, an asymmetric multiplet at δ 3·75–4·15 *ppm for the ethylene ketal protons, a narrow multiplet at* δ 3·55 ppm for the methylene protons adjacent to the sulfonyl group, a triplet ($J_{2,3} = J_{2,5} \sim 4$ Hz) at δ 3·35 ppm for H_2, a doublet ($J_{3,2} \sim 4$ Hz) at δ 3·1 ppm for H_3 and a multiplet at δ 2·45–2·65 ppm for H_8. Substantial support for the assignment of structure **10** was provided by its hydrogenation

*For sake of clearness the numbering of the C atoms is the same as in the starting material. The IUPAC numbering is applied in the Experimental.

†Although the tricyclo[4.2.1.$0^{2,5}$]nonane **12** does not contain a plane of symmetry the origin of asymmetry in the molecule is so remote from the ethylene ketal protons that they behave effectively as an AA'BB' system.



Scheme 4

with H_2/Pt giving the sulfone **13** in quantitative yield and by its irradiation in acetone producing the expected {(4-homocubyl)methyl}phenylsulfone **5** (Scheme 4).

The behaviour of ester **7** upon treatment with LiN(iPr)$_2$ was in sharp contrast with that observed for the nitrile **3** and sulfone **5**. After quenching with H_2O the starting carboxylate was recovered quantitatively. Anion formation had indeed taken place since quenching with D_2O resulted in mono and dideuterated **7** (Scheme 5). Furthermore, treatment of anion **14** with CO_2 afforded the malonic acid half ester which was converted into diester **15** with CH_2N_2 in an overall yield of 76% (Scheme 5). An explanation for this contrasting behaviour of ester **7** might well be due to the difference in stabilization of the intermediate α-carbanions. The anion of carboxylate **7** is predominantly present in its enolate form[6-8] having only a small negative charge at the α-C atom. Apparently, such an enolate anion is less prone to undergo the homoallylic rearrangement. On basis of the results shown it may be stated that in order to initiate the homoallylic rearrangement in the homocubane system a considerable negative charge is required at the α-C atom.

To gather information about the effect of cage strain on this homoallylic rearrangement in polycyclic compounds the far more strained cubane methylcyanide **18** and cubane carboxylate **21** were investigated. These compounds were prepared as outlined in Scheme 6. Alcohol **17**, obtained from acid **16** in high yield, was converted into its tosylate which upon treatment with NaCN gave a mixture of cubane methylcyanide **18** and homocubane bridgehead tosylate **19** in 80 and 15% yield, respectively. Despite several precautions it was impossible to avoid the formation of **19**. This spontaneous cage expansion reaction is inherent to the large strain in the cubane skeleton. Nitrile **18** and tosylate **19** could easily be separated by column chromatography. Ester **21** could be prepared from carboxylic acid **16** via an Arndt-Eistert reaction in an overall yield of 65% (Scheme 6).

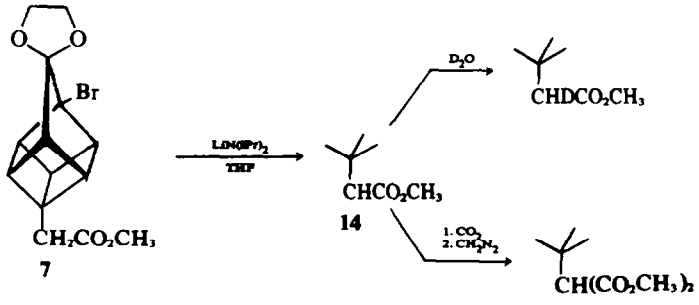
Treatment of cubane methylcyanide **18** with LiN(iPr)$_2$ gave in almost quantitative yield an oil consisting of a mixture of two alkenes to which the structures **22** and **23** were assigned on the basis of the following spectral and chemical evidence (Scheme 7).

The IR spectrum of the mixture showed cyanide bands at 2220 and 2250 cm^{-1} indicative of a conjugated and a non-conjugated nitrile function. Olefinic absorptions were observed at 3090, 3030, 1645 and 1620 cm^{-1}. The NMR spectrum (100 MHz, $CDCl_3$) displayed a complex multiplet between δ 5·7 and 6·6 ppm for the olefinic protons H_6 and H_7 of **22** and **23**, and H_8 of **23**, a multiplet* at δ 4·97 ppm for the vinylic proton adjacent to the nitrile function in **22**, a complex pattern at δ 2·2–4·2 ppm for the ring protons H_2, H_3 and H_5 in **22** and **23** and H_8 in **22**, a singlet at δ 2·92 ppm for the two methylene protons adjacent to the cyanide function in **23**, and two singlets at δ 1·23 and 1·24 ppm for the respective Me groups. The relation between **22** and **23** was proved by treating the mixture with LiN(iPr)$_2$. The ratio of **22** and **23** could be arbitrarily changed by an allylic rearrangement. Treatment of the mixture of **22** and **23** resulted in the exclusive formation of the thermodynamically more stable tricyclo[4.2.6.$0^{2,5}$]octene **22**.

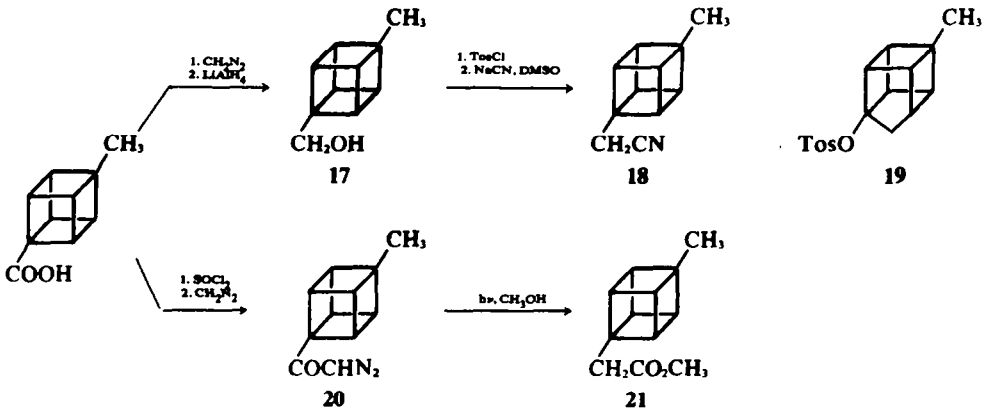
Substantial support for the proposed structure **22** and **23** (Scheme 7) was obtained from the thermolysis of the mixture in either refluxing benzene or carbontetrachloride. As expected[9,10] for these types of tricyclooctane systems compounds **22** and **23** showed a facile skeletal rearrangement leading to a mixture of cyclooctatriene **26** and cyclooctatetraene **27**, respectively (Scheme 7). The cyclooctatetraene **27** could be converted into the more stable cyclooctatriene isomer **26** by treatment with LiN(iPr)$_2$.

Upon thermolysis of pure tricyclooctene **22** only

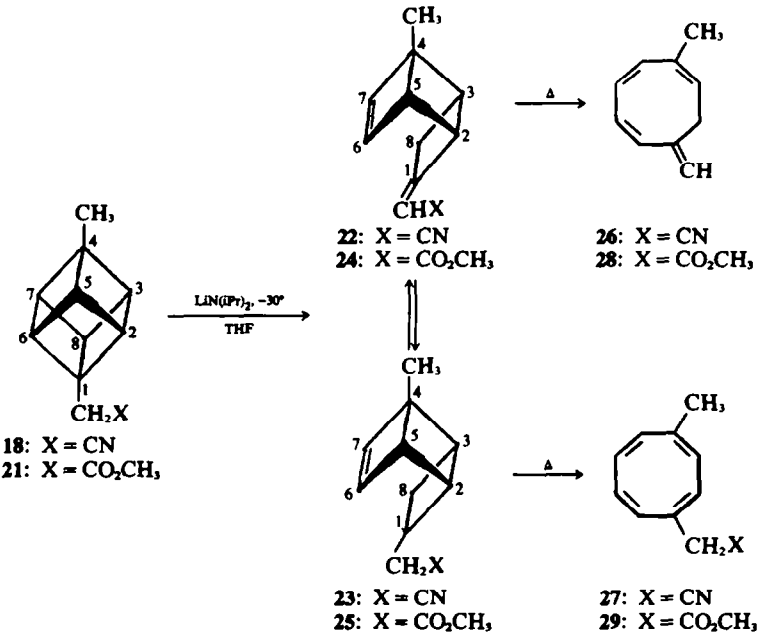
*The complexity of this signal is partly due to geometrical isomerism around the exocyclic double bond.



Scheme 5



Scheme 6

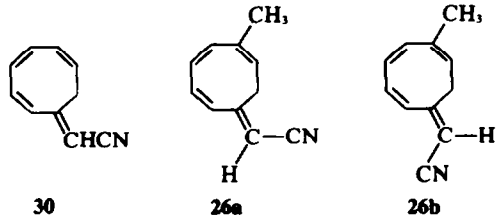


Scheme 7

cyclooctatriene **26** was obtained. The structure of **26** was proved unambiguously by its spectroscopical properties.

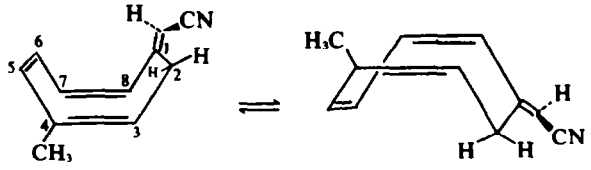
The IR spectrum showed strong olefinic absorptions at 1620 and 1585 cm^{-1}; a conjugated nitrile absorption was observed at 2215 cm^{-1}; the UV spectrum (C_2H_5OH) displayed two maxima at 243 nm (log ϵ 4·19) en 314 nm (log ϵ 3·95). Both the UV and IR data are consistent with the values reported by Cope *et al.*[11] for 2,4,6-cyclooctatrienylidene acetonitrile **30** (Scheme 8).

The NMR spectrum (100 MHz, $CDCl_3$), showing the presence of geometric isomers **26a** and **26b** (ratio: 1:1) (Scheme 8), exhibited a complex multiplet between δ 5·8 and 7·0 ppm for the olefinic ring protons H_5, H_6, H_7 and H_8, a triplet* at δ 5·54 ($J_{H_3,H_2} \sim 9$ Hz) for H_3 in **26a**, a triplet* at δ 5·43 ($J_{H_3,H_2} \sim 9$ Hz) for H_3 in **26b**, singlets at δ 5·16 and 4·90 ppm for the olefinic protons adjacent to the nitrile functions, a doublet centered at δ 3·26 ($J_{H_2,H_3} \sim 9$ Hz) for the methylene protons at C_2 in **26a**, a doublet at δ 3·02 ($J_{H_2,H_3} \sim 9$ Hz) for the methylene protons at C_2 in **26b** and a singlet at δ 1·74 for the Me groups. Conclusive information was obtained from low temperature proton NMR measurements which revealed the occurrence of ring inversion[12] in **26a** and **26b**. The nitriles **26a** and **26b** may undergo ring inversion as shown for **26a** in Scheme 9. At room temperature this inversion is sufficiently rapid to interchange the magnetic environment of the C_2 protons and a doublet (A_2X pattern) is observed. When the temperature is lowered the rate of ring inversion decreases, the methylene protons become unequal and an



Scheme 8

*Actually, a quartet is observed due to overlap of the two triplets which could be unravelled by means of spin decoupling experiments.



Scheme 9

ABX system should be observed. This indeed was found to be the case. At −10° to −15° the doublet at δ 3·26 ppm coalesces to a broad singlet, whereas the doublet at δ 3·02 ppm changes into a singlet at −31° to −32°. At −65° both isomers **26a** and **26b** showed an ABX pattern for the two methylene protons at C_2. The observed difference in activation energy of ring inversion in cyclooctatries **26a** and **26b** is due to a different steric interaction of the C_2 protons with either the nitrile function in **26a** or the proton in **26b**. Therefore, the doublets at δ 3·26 and δ 3·02 ppm could be assigned to the methylene protons at C_2 of **26a** and **26b**, respectively.

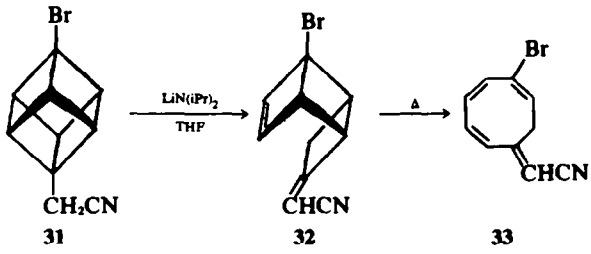
In a similar way cubane ester **21** was treated with $LiN(iPr)_2$. In contrast to the homocubane carboxylate **7** (Scheme 5) a homoallylic rearrangement took place readily and a mixture of tricyclo[4.2.0.$0^{2,5}$]octenes **24** and **25** was obtained in almost quantitative yield (Scheme 7).

Apparently, the increase of cage strain going from the homocubane cage system to the cubane system is sufficient to bring about the homoallylic rearrangement in the bridgehead carboxylate **21**. Analogous to the corresponding nitriles **22** and **23** (Scheme 7) tricyclooctene carboxylates **24** and **25** were smoothly converted into the tricyclooctatriene **28** and tricyclooctatetraene **29**, respectively, by refluxing them in benzene (Scheme 7).

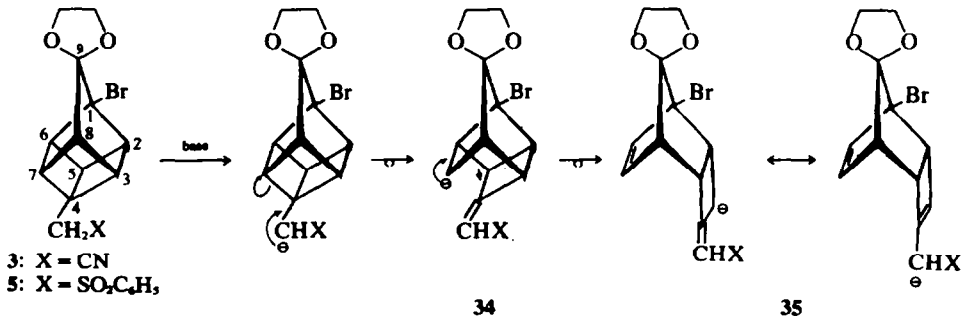
Finally, the homoallylic rearrangement was studied in a halogen substituted cubane derivative. The required 4-bromocubane methylcyanide **31** was prepared along the same route as outlined for nitrile **18** in Scheme 6. Treatment of compound **31** with $LiN(iPr)_2$ gave a dark-brown oil from which after careful chromatography tricyclo[4.2.0.$0^{2,5}$]octene **32** could be isolated as a single product in 70% yield (Scheme 10). At room temperature this compound appeared to be extremely unstable leading to polymeric products. Thermolysis gave only a minor amount of the expected cyclooctatriene **33** (Scheme 10). This result shows that the Br atom has a remarkable destabilizing effect on the tricyclo[4.2.0.$0^{2,5}$]octene system.

A mechanism for the observed base induced cage degradation reaction is proposed in Scheme 11 (shown for the homocubane system). The process can be formulated as a double γ-homoallylic rearrangement. Abstraction of a proton adjacent to the activating group initiates a γ-homoallylic rearrangement leading formally to the half cage carbanion **34**. Under the applied aprotic conditions a second γ-homoallylic rearrangement takes place affording the less congested mesomeric carbanion **35** (Scheme 11). No indication for the intermediacy of the half-cage carbanion **34** has been found. Therefore the formation of the carbanion **35** may well proceed via a synchronous process of bond cleavages (allowed cyclo reversion of a 6-electron system). It is interesting to note that the homoketonization of the corresponding bridgehead homocubane alcoholates[1] in protic media stops at the stage of the half cage structure, whereas under aprotic conditions also the second bond (viz C_5–C_6 bond) is cleaved.

The homoallylic rearrangement in the homocubane and cubane cage systems is a regiospecific process. In the

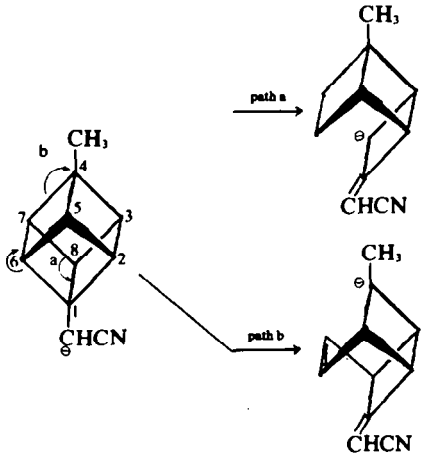


Scheme 10



Scheme 11

homocubane methylcyanide **3** and sulfone **5** homoallylic rearrangement proceeds by an initial specific cleavage of the C_4–C_7 (or the equivalent C_3-C_4) bond. Ring opened products derived from scission of the central C_4–C_5 bond in the homocubane system were not observed. In the 4-substituted cubane compounds, where all three C–C bonds around C_1 are equivalent, regiospecificity is observed in the second cyclobutane ring opening (Scheme 12) which proceeds by an exclusive cleavage of the C_7–C_8 bond (path a). Products arising from the C_4–C_7 bond scission were not observed (path b). The high selectivity in the direction of bond cleavage both in the homocubane and cubane system is most likely governed by relief of strain.



Scheme 12

EXPERIMENTAL

IR spectra were taken on a Perkin Elmer 257 grating spectrometer. NMR spectra were recorded on Varian HA-100 or T60 spectrometer, using TMS as internal standard. All m.ps are uncorrected and determined on a Kofler hot stage. Elemental analyses were carried out in duplicate (their average values are reported) in the micro-analytical department of the University of Nijmegen under supervision of Mr. J. Diersmann, and in the micro-analytical department of the University of Groningen, under supervision of Mr. D. Hamminga.

1 - *Bromopentacyclo*[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]*nonan* - 9 - *one ethylene ketal 4-methylcyanide* (**3**). A soln of **2** (0·2 g, 0·45 mmole), prepared in the usual way, and NaCn (0·2 g, 4 mmole) in DMSO was stirred at room temp for 3 days. The mixture was poured into water and extracted with $CHCl_3$. The chloroform phase was thoroughly washed with water and dried ($MgSO_4$). The $CHCl_3$ was removed *in vacuo* to give crude **3** (0·12 g, 90%) as a colourless oil which solidified on standing. Crystallization from hexane gave an analytically pure sample, m.p. 82·5–84·0°; IR ν_{max}^{KBr} 2245 (C≡N) cm^{-1}; NMR (CCl_4) δ 3·80–4·40 (sym.m., 4 H, ethylene ketal group), 3·5 (m, 5 H), 2·75–3·10 (m, 1 H, proton H_8), 2·56 (s, 2 H, $-CH_2CN$); *m/e* 294 (M^+, 1 Br). (Found: C, 53·06; H, 4·17; Br, 27·23; N, 4·72. Calc. for $C_{13}H_{12}BrO_2N$: C, 53·09; H, 4·11; Br, 27·16; N, 4·76%).

{4 - (1 - *Bromopentacyclo*[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]*nonyl* - 9 - *one ethylene ketal*)*methyl*}*phenyl sulfone* (**5**). To a soln of **2** (2·8 g, 6·4 mmole) in thiophenol (10 ml) was added a soln of NaOH (0·5 g) in water (1 ml). The mixture was heated under reflux for 5 hr. After cooling to room temp a soln of NaOH aq was added to neutralize excess thiophenol. The weak alkaline soln was extracted with ether. The ether phase was washed with dil NaOH aq and dried ($MgSO_4$). Solvent was removed yielding a mixture of **4** and diphenylsulfide. Pure **4** was obtained by column chromatography over silicagel. Elution with hexane afforded diphenyl sulfide. Further elution with benzene gave **4** (2·0 g, 83%) as an oil; NMR ($CDCl_3$) δ 7·1–7·6 (m, 5 H, phenyl protons), 3·85–4·40 (sym. m., 4 H, ethylene ketal protons), 3·45 (m, 5 H), 3·10 (s, 2 H, $-CH_2S-$), 2·7–3·0 (m, 1 H, proton H_8). H_2O_2 (15 ml, 40% aq. soln) was added to a soln of **4** in a mixture of AcOH (25 ml) and Ac_2O (7 ml). After stirring at room temp for 3 days, the mixture was poured into water and neutralized with dil NaOH aq. The ppt was filtered off, washed and dried to give **5** (2 g, 92%). Recrystallization from CCl_4 gave a pure sample, m.p. 144·5–145·0°; IR ν_{max}^{KBr} 1300, 1145 (SO_2) cm^{-1}; NMR ($CDCl_3$) δ 7·4–7·95 (m, 5 H, phenyl protons), 3·80–4·30 (sym.m. 4 H, ethylene ketal protons), 3·15–3·60 (m, 7 H, cage protons and $-CH_2-SO_2-$), 2·75–3·0 (m, 1 H, proton H_8). (Found: C, 52·48; H, 4·19; Br, 19·41; S, 7·91. Calc. for $C_{18}H_{17}BrO_4S$: C, 52·82; H, 4·19; Br, 19·53; S, 7·84%).

Methyl 4 - (1 - *bromopentacyclo*[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]*nonyl* - 9 - *one ethylene ketal*)*acetate* (**7**). A soln of **1**[5] (10 g, 3·3 mmol) in $SOCl_2$ (100 ml) was heated under reflux for 4 hr. The $SOCl_2$ was removed *in vacuo* to give the crude acid chloride of **1**. A soln of this acid chloride in anhd ether was added dropwise to a soln of CH_2N_2 in ether. After standing at room temp for 3 days, the solvent was removed *in vacuo* giving **6** as a yellow solid; IR ν_{max}^{KBr} 2100 ($-N\equiv N$) cm^{-1}. A soln of **6** in MeOH (about 600 ml) was irradiated with a 700 W Hanovia Q 700 medium pressure mercury vapor lamp (pyrex filter) for 2 hr (N_2 formation had stopped at that time). The MeOH was removed and the residue extracted with hexane. Evaporation of the solvent gave **7** (8 g, 72%) as an oil which solidified on standing. Crystallization from hexane gave an analytically pure sample, m.p. 65–73°. IR ν_{max}^{KBr} 1710 (C=O), 1255 (ester) cm^{-1}; NMR ($CDCl_3$) δ 3·78–4·35 (sym.m., 4 H, ethylene ketal protons), 3·65 (s, 3 H, OCH_3), 3·3–3·5 (m, 5 H), 2·7–3·0 (m, 1 H, proton H_8), 2·52 (s, 2 H, $-CH_2CO-$). (Found: C, 51·00; H, 4·69; Br, 24·30, Calc. for $C_{14}H_{15}BrO_4$: C, 51·39; H, 4·62; Br, 24·43%).

Rearrangement of cyanide **3** *with* $LiN(iPr)_2$ *in* THF. To a stirred ice-cooled soln of diisopropylamine (0·4 ml, 0·25 g, 2·5 mmole) in THF (10 ml) was added (N_2 atmosphere) 1·5 ml of 2 N Buli in hexane. After 15 min **3** (0·3 g, 1 mmole) was added. After stirring at 0° for 30 min water was added and the mixture ether extracted. The extracts were washed with dil HCl aq and dried ($MgSO_4$). Solvent was removed yielding a mixture (0·3 g) of **8** and **9**. Attempts to separate olefines **8** and **9** failed. NMR ($CDCl_3$) δ 6·27 (d, degenerated AB quartet, protons H_7 and H_8 in **9**), 6·02 (m, protons H_3, H_7 and H_8 in **8**), 5·08 (m, C=CHCN in **9**), 3·8–4·4 (m, ethylene ketal protons, 2·2–3·85 (complex pattern for the ring protons), 2·97 (broad s, CH_2CN in **8**).

1 - *Bromotricyclo*[4.2.1.$0^{2,5}$]*nonan* - 9 - *one ethylene ketal 4-methylcyanide* **12**. To a soln of a mixture of **8** and **9** (0·3 g) in EtOH (30 ml) PdO (0·1 g) was added. The mixture was shaken in a H_2 atmosphere (2 atm) for 2 days. The catalyst was filtered off and the solvent removed, affording **12** as a colourless oil (0·3 g, 100%) which solidified slowly on standing at 20°. Crystallization from hexane gave an analytical pure sample, m.p. 112–115°. *m/e* 298 (M^+, 1 Br), 218 (M^+–1 Br), 151 {M^+–(Br + CH_2=$CHCH_2CN$)}. (Found: C, 52·50; H, 5·53; Br, 26·70; N, 4·51. Calc. for $C_{13}H_{16}BrO_2N$: C, 52·36; H, 5·41; Br, 26·80; N, 4·70%).

Irradiation of **8** *and* **9** *in acetone.* A soln of a mixture of **8** and **9** (0·08 g) in acetone (75 ml) was irradiated with 80 W Hanovia medium pressure mercury vapor lamp (Pyrex filter) for 18 hr. Solvent was removed to give a brown oil. Extraction with hexane followed by column chromatography over silicagel gave **3** (0·02 g) as a colourless oil.

Rearrangement of sulfone **5** *with* $LiN(iPr)_2$ *in* THF. To an ice cold (0°) soln of $LiN(iPr)_2$ (2·5 mmole) in THF (10 ml) (prepared as described above) was added **5** (0·2 g, 4·9 mmole). After stirring at 0° for 10 min water was added and the mixture ether extracted. The extracts were washed with dil HCl aq and dried ($MgSO_4$). Solvent was removed to give an oil (0·2 g, ~100%) which solidified partly. Crystallization from CCl_4 gave **10**, m.p. 151–153°. IR ν_{max}^{KBr} 3045, 3060, 3080 (C=CH), 1300, 1140 ($-SO_2-$) cm^{-1}. *m/e* 409 (M^+, 1 Br). (Found: C, 52·37; H, 4·07; Br, 19·37; S, 7·70. Calc. for $C_{18}H_{17}BrO_4S$: C, 52·82; H, 4·19; Br, 19·53; S, 7·84%).

{4 - (1 - *Bromotricyclo*[4.2.1.$0^{2,5}$]*nonyl* - 9 - *one ethylene ketal*)*methyl*}*phenyl sulfone* **13**. The same procedure as for the hydrogenation of **8** and **9** was used. Sulfone **13** was obtained as a crystalline solid (100%). Recrystallization from EtOH gave an

analytically pure compound, m.p. 144–145°. IR ν_{max}^{KBr} 1300, 1140 (SO_2) cm^{-1}; NMR ($CDCl_3$) δ 7·3–7·95 (m, 5 H, phenyl protons), 3·75–4·40 (sym.m., 4 H, ethylene ketal protons), 2·8–3·5 (complex pattern, 4 H, protons H_2, H_3 and $-CH_2SO_2-$), 1·5–2·45 (complex pattern, 8 H). (Found: C, 52·31; H, 5·19; Br, 19·21; S, 7·70. Calc. for $C_{18}H_{21}BrO_4S$: C, 52·31; H, 5·13; Br, 19·34; S, 7·76%).

Irradiation of **10** *in acetone.* The same procedure as for the irradiation of **8** and **9** in acetone was used. A complex mixture of products was obtained in which **5** could be detected by means of GLC (column: SE $30_8^{1/2}$; temp: 280°) and TLC (silicagel, benzene/ether (10:1)).

Dimethyl{4 - (1 - *bromopentacyclo*[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]*nonyl* - 9 - *one ethylene ketal*)}*malonate* **15**. To an ice cooled (0°) soln of $LiN(iPr)_2$ (6·3 mmole) in THF was added **7** (1·0 g, 3·1 mmole). After stirring at 0° for 30 min, CO_2 was introduced into the mixture for 30 min, water was added and the mixture ether extracted. The water phase was acidified with dil HCl aq and ether extracted again. The ether soln was dried ($MgSO_4$) and treated with an ethereal CH_2N_2 soln. Solvent was removed to give **15** (0·9 g, 76%) as an oil. Crystallization from hexane gave an analytically pure sample: m.p. 78–80°; IR ν_{max}^{KBr} 1740 (split C=O) cm^{-1}; NMR ($CDCl_3$) δ 3·82–4·30 (sym.m., 4 H, ethylene ketal protons), 3·71 (s, 6 H, OCH_3), 3·4–3·6 (m, 6 H, cage protons and $-CH(CO_2R)_2$), 2·75–2·95 (m, 1 H, proton H_8). (Found: C, 49·85; H, 4·51; Br, 20·56. Calc. for $C_{16}H_{17}BrO_6$: C, 49·88; H, 4·45; Br, 20·75%).

4 - *Methylpentacyclo*[4.2.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]*octane* 1-*carboxylic acid* **16**. The same procedure as for the preparation of 4-bromopentacyclo[4.2.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]octane 1-carboxylic acid was used.[5] A 60% yield of **16** was obtained starting from 1 - bromo - 4 - methylpentacyclo[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]nonan - 9 - one. Crystallization from hexane gave an analytically pure sample, m.p. 139·5–141·0°; IR ν_{max}^{KBr} 1685 (C=O) cm^{-1}; NMR ($CDCl_3$): δ 4·0–4·25 (m, 3 H), 3·48–3·78 (m, 3 H), 1·28 (s, 3 H, Me). (Found: C, 74·01; H, 6·22. Calc. for $C_{10}H_{10}O_2$: C, 74·05; H, 6·21%).

1 - (4 - *Methylpentacyclo*[4.2.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]*octyl*)*carbinol* **17**. Carboxylic acid **16** was esterified with CH_2N_2 to give methyl 4 - methylpentacyclo[4.2.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]octane 1-carboxylate in almost quantitative yield. A soln of this ester (1·2 g, 7 mmole) in anhd ether (50 ml) was added to a suspension of LAH (0·3 g, 7·8 mmole) in anhd ether (50 ml). After stirring overnight, the mixture was diluted with water and extracted with ether. The ether layer was dried ($MgSO_4$) and concentrated to give crude **17** (1·0 g, 97%). Recrystallization from hexane and subsequent sublimation (70°/40 mm) gave a pure sample, m.p. 86–87°; IR ν_{max}^{KBr} 3300 (OH) cm^{-1}; NMR ($CDCl_3$) δ 3·75 (s, 2 H, $-CH_2O-$), 3·4–3·8 (m, 6 H), 1·47 (s, 1 H, OH), 1·26 (s, 3 H, Me). (Found: C, 81·34; H, 8·19. Calc. for $C_{10}H_{12}O$: C, 81·04; H, 8·16%).

4 - *Methylpentacyclo*[4.2.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]*octane* 1 - *methylcyanide* **18**. The same procedure as for the preparation of **3** was used, starting from the tosylate of **17**. A mixture of cyanide **18** and tosylate **19** was obtained, which could be separated by column chromatography over alumina. Elution with pentane and pentane/benzene (10:1) gave **18** in 80% yield. Crystallization from hexane gave an analytically pure sample: m.p.: ~25°; IR ν_{max}^{KBr} 2250 (C≡N) cm^{-1}; NMR ($CDCl_3$) δ 3·3–4·1 (m, 6 H), 2·62 (s, 2 H, $-CH_2CN$), 1·34 (s, 3H, Me). (Found: C, 84·21; H, 7·09; N, 8·72. Calc. for $C_{11}H_{11}N$: C, 84·08; H, 7·01; N, 8·92%). Further elution with benzene gave bridgehead tosylate **19** (15%) as an oil. IR ν(neat) 1360, 1190, 1170 cm^{-1}; NMR ($CDCl_3$) δ 7·1–8·0 (m, 4 H, phenyl protons), 2·9–3·5 (m, 6 H, cage protons), 2·4 (s, 3 H, Me), 2·0 (s, 2 H, methylene bridge protons), 1·1 (s, 3 H, Me).

Methyl 1 - (4 - *methylpentacyclo*[4.2.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]*octyl*) *acetate* **21**. The same procedure as for the preparation of **7** was used, starting from **16**. Acetate **21** was obtained as an oil in 65% yield. An analytically sample could be prepared by chromatography over silicagel (hexane/benzene: 10:1) and subsequent distillation *in vacuo* (100°/12 mm); IR ν(neat) 1730 (C=O) cm^{-1}; NMR (CCl_4) δ 3·4–3·9 (m, 6 H), 3·7 (s, 3 H, OCH_3), 2·65 (s, 2 H, $-CH_2CO_2-$), 1·35 (s, 3 H, Me). (Found: C, 75·56; H, 7·45. Calc. for $C_{12}H_{14}O_2$: C, 75·79; H, 7·37%).

Rearrangement of cyanide **18** *with* $LiN(iPr)_2$ *in* THF. To a cooled (−30°) soln of $LiN(iPr)_2$ (5 mmole) in THF (10 ml) was added **18** (0·25 g, 1·6 mmole). After stirring at −30° for 30 min water was added and the mixture ether extracted. The extracts were washed with dil HCl aq and dried ($MgSO_4$). Solvent was removed to give a mixture of **22** and **23**. Attempts to separate the mixture failed. **22** was obtained by treating the mixture with NaOMe in MeOH for 8 hr at room temp; IR ν(liquid) 3100, 3030 (=CH), 2220 (C≡N), 1650 (C=C) cm^{-1}; NMR ($CDCl_3$) δ 6·1–6·6 (m, 2 H, protons H_3 and H_4), 4·97 (m, 1 H, C=CHCN), 2·2–4·0 (m, 5 H), 1·24 (s, 3 H, Me).

Thermolysis of 7 - (2 - *methyltricyclo*[4.2.0.$0^{2,5}$]*octa* - 3 - *enylidene*) *acetonitrile* **22**. A soln of **22** in benzene was heated under reflux for 3 hr. Solvent was removed to give **26** as a single product. An analytically pure sample could be obtained by chromatography over silicagel (hexane/benzene 10:1) and recrystallization from hexane, m.p. <20°. (Found: C, 83·72; H, 7·14; N, 8·61. Calc. for $C_{11}H_{11}N$: C, 84·08; H, 7·01; N, 8·92%).

Rearrangement of acetate **21** *with* $LiN(iPr)_2$ *in* THF. The same procedure as described for the rearrangement of **3** was used giving a mixture of **24** and **25** in almost quantitative yield. Attempts to separate the isomers by chromatographic methods were unsuccessful; IR ν(liquid) 3090, 3020 (=CH), 1720 (broad C=O) cm^{-1}; NMR ($CDCl_3$) δ 5·7–6·6 (m, protons H_3 and H_4 of **24** and **25**, and proton H_8 of **25**, 5·4 (m, $C=CHCO_2-$ in **24**), 3·62 (s, OCH_3), 1·5–3·4 (complex pattern), 1·25 (broad s, Me). Pure **24** was obtained by treating the mixture with NaOMe in MeOH for 8 hr at room temp; IR ν(liquid) 3090, 3020 (=CH), 1710 (C=O) cm^{-1}; NMR (CCl_4) δ 6·1–6·45 (m, 2 H, protons H_3 and H_4), 5·45 (m, 1 H, $=CHCO_2$), 3·60 (s, 3 H, OCH_3), 2·2–3·4 (m, 5 H, 1·23 (s, 3 H, Me).

Thermolysis of 7 - (2 - *methyltricyclo*[4.2.0.$0^{2,5}$]*octa* - 3 - *enylidene*) *acetate* **24**. The same procedure as for the thermolysis of **22** was used. Compound **28** was obtained as an oil in almost quantitative yield. A pure sample could be obtained by column chromatography over silicagel (hexane); IR ν(liquid) 3010 (=CH), 1710 (C=O), 1620, 1590 (C=C) cm^{-1}; UV (96% EtOH) λ_{max} 249 (log ϵ 4·08), 323 (log ϵ 3·89) nm; NMR (C_6D_6) δ 5·0–6·3 (complex pattern, protons H_3, H_5, H_6, H_7 and H_8), 5·78 (s, $CHCO_2-$), 5·50 (s, $CHCO_2-$), 3·82 (d, $J_{H_2,H_3} \sim 9$ Hz, protons H_2), 3·45 (s, OCH_3), 2·86 (d, $J_{H_2,H_3} \sim 9$ Hz), protons H_2), 1·53 (s, Me); *m/e* 190 (M^+).

4 - *Bromopentacyclo*[4.2.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]*octane* 1 - *methylcyanide* **31** was prepared as described for **18**, starting from 4 - bromopentacyclo - [4.2.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]octane 1-carboxylic acid.[5] This acid was converted into 1 - (4 - bromopentacyclo[4.2.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]octyl) carbinol by reduction with LAH, as described for the preparation of **17**. Crystallization from hexane gave pure carbinol (80% yield), m.p. 124·6–126·6°; IR ν_{max}^{KBr} 3420, 3360 (OH), 1205, 1190, 1030 cm^{-1}; NMR ($CDCl_3$) δ 3·8–4·3 (m, 6 H), 3·8 (s, 2 H, $-CH_2O-$), 1·37 (s, 1 H, OH). (Found: C, 50·45; H, 4·27; Br, 37·38; Calc. for C_9H_9BrO: C, 50·73; H, 4·26; Br, 37·51%). A mixture of the tosylate of this alcohol, prepared in the usual way, and NaCN in DMSO was stirred at room temp for 3 days. Water was added and the soln extracted with ether. The ether phase was thoroughly washed with water and dried ($MgSO_4$). Solvent was removed to give **31** (90%) as an oil, which solidified on standing. Recrystallization from hexane gave an analytically pure sample: m.p. 80–82°. IR ν_{max}^{KBr} 3040 (C–H), 2250 (C≡N) cm^{-1}; NMR (CCl_4) δ 3·8–4·4 (m, 6 H), 2·65 (s, 2 H, $-CH_2CN$). (Found: C, 54·06; H, 3·62; N, 6·34; Br, 36·08. Calc. for $C_{10}H_8NBr$: C, 54·05; H, 3·60; N, 6·31; Br, 36·04%).

Rearrangement of cyanide **31** *with* $LiN(iPr)_2$ in THF. The same procedure as for the rearrangement of **18** was used giving almost exclusively **32** as a dark brown oil. Chromatography over silicagel (hexane/benzene: 5:1) gave a pure sample (70%); IR ν(liquid) 3100, 3060 (=CH), 2220 (C≡N), 1650 (C=C) cm^{-1}; NMR ($CDCl_3$) δ 6·25–6·65 (m, 2 H, protons H_3 and H_4), 5·15 (m, 1 H, =CHCN), 2·4–4·2 (complex pattern, ring protons).

Thermolysis of 7 - (2 - *bromotricyclo*[4.2.0.$0^{2,5}$]*octa* - 3 - *enylidene acetonitrile* **32**. The same procedure as for the thermolysis of **22** was used, leading to a complex mixture of several products. Column chromatography over silica with benzene as eluens gave a small amount of **33**; IR ν(liquid) 3060 (=CH), 2210 (C≡N), 1615, 1580 (C=C); UV (96% C_2H_5OH) λ_{max} 293, 345 nm; NMR ($CDCl_3$) δ 5·8–6·6 (m, protons H_3, H_5, H_6 and H_8), 5·37 (s, =CHCN), 5·06 (s, =CHCN), 3·40 (d, $J_{H_2,H_3} \sim 9$ Hz, protons H_2), 3·17 (d, $J_{H_2,H_3} \sim 9$ Hz) protons H_2).

REFERENCES

[1]Part VI: A. J. Klunder and B. Zwanenburg, *Tetrahedron* **29**, 1683 (1973).
[2]D. J. Cram, *Fundamentals of Carbanion Chemistry* pp. 211–222. Academic Press, New York (1965).
[3]W. L. Dilling, H. P. Braendlin and E. T. McBee, *Tetrahedron* **23**, 1211 (1967).
[4]W. EBerbach and H. Prinzbach, *Chem. Ber.* **102**, 4164 (1969).
[5]A. J. H. Klunder and B. Zwanenburg, *Tetrahedron* **28**, 4131 (1972).
[6]M. W. Rathke and A. Lindert, *J. Am. Chem. Soc.* **93**, 2318 (1971).
[7]S. Reiffers, H. Wijnberg and J. Strating, *Tetrahedron Letters* 3001 (1971).
[8]H. O. House, *Modern Synthetic Reactions*, (2 Ed) Chaps 9, 10. Benjamin, California, (1972).
[9]K. B. Wiberg, *Chapter on Small Ring Bicyclo[n,m,o]alkanes in Advances in Alicyclic Chemistry* (Edited by H. Hart and G. I. Karabatsos), Vol. 2, pp. 185–254. Academic Press, New York (1968).
[10]M. Avram, I. G. Dinulescu, E. Marica, G. Mateescu, E. Sliam and D. Nenitzescu, *Chem. Ber.* **97**, 382 (1964).
[11]A. C. Cope, R. M. Pike and D. F. Rugen, *J. Am. Chem. Soc.* **76**, 4945 (1954).
[12]G. Ganter, S. M. Pokras and J. D. Roberts, *ibid.* **88**, 4235 (1966).