Electrochemical Reactions. Part XII.[1] Reduction of the 1,3-Dibromides, *endo*-2,*endo*-6- and *exo*-2,10-Dibromobornane

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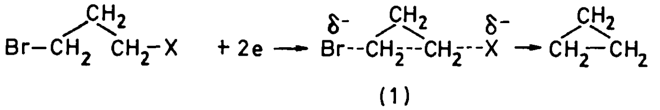
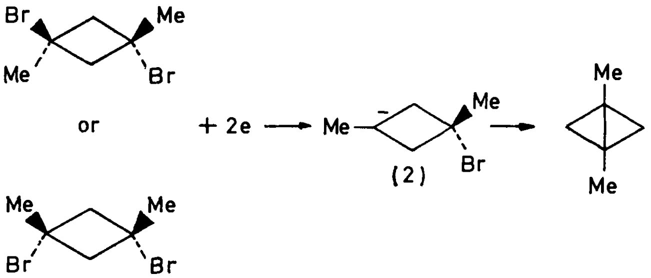
Electrochemical reduction of *endo*-2,*endo*-6-dibromobornane both in aqueous ethanol and in dimethylformamide gives tricyclene and bornane. *endo*-2-Bromobornane is intermediate in the formation of bornane. Reduction of *exo*-2,10-dibromobornane gives camphene and bornane. Bornane is formed by stepwise removal of the bromo-groups and camphene can be formed by solvolysis of the intermediate *exo*-2-bromobornane.

1,3-DIBROMO-COMPOUNDS on electrochemical reduction are usually converted in high yield into cyclopropanes. We felt that a study of the reduction of 1,3-dibromides of rigid stereochemistry could help elucidate the reaction pathway. Previous work has shown that cyclopropanes are formed from open-chain 1,3-dibromopropanes,[2,3] from both *cis*- and *trans*-1,3-dibromo-1,3-dimethylcyclobutane,[4] and from the dibromide (3) but not from 1,3-dibromoadamantane, which yields only adamantane.[5] The presence of water does not inhibit cyclisation of 1,3-dibromopropane. Reduction of 1,4- and 1,5-dibromo-compounds however gives only 25% of cyclobutane and no cyclopentane, respectively.[2] Some 1,3-dihalogenopropenes are thought to give cyclopropene derivatives on reduction.[6]





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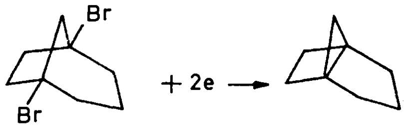

Rifi has suggested[4] that the reduction of acyclic 1-bromo-compounds with a suitable leaving group in the 3-position proceeds through a transition state (1) where elimination of the 1- and 3-substituents is concerted with addition of two electrons. 1-Bromo-3-chloropropane and 3-bromopropylammonium salts are reduced to cyclopropane, and polarography of these compounds shows only one wave at more positive potentials than that necessary for reduction of simple bromoalkanes. A carbanion mechanism with (2) as the carbanion intermediate is suggested for the reductive cyclisation of the *cis*- and *trans*-dibromocyclobutanes to bicyclobutane derivatives because, for these compounds, the polarographic wave is close to the wave for reduction of bromoalkanes. Fry and Britton[7] have shown that *meso*- and (±)-2,4-dibromopentanes are not reduced in a stereospecific manner and therefore favour a carbanion intermediate in this reduction rather than a concerted elimination. They suggest that dibromides claimed to be reduced in a concerted step are probably reduced in a stepwise manner, and that the lowering of half-wave potential in these cases is simply due to the inductive effect of a γ-bromine substituent. Cyclisation *via* a carbanion also occurs, for example, during the reaction of 3-chloropropene with phenyl-lithium to give some phenylcyclopropane. Here attack of the lithium reagent on the olefin generates a new carbanion centre which forms the cyclopropane by intramolecular displacement of chloride ion.[8]

We first examined the reduction of *endo*-2,*endo*-6-dibromobornane (4). This dibromide is obtained by bromination of pin-2-ene and its stereochemistry is assigned by analogy with the corresponding dichlorobornane.[9] As further proof of this stereochemistry, *endo*-2-bromobornane (5) is formed in substantial quantities during the electrochemical reduction discussed here. Reduction of the dibromide with zinc and alcohol gives tricyclene (7).[10] Our results from electrochemical reduction of the dibromide are summarised in Table 1. Tricyclene (7) and bornane (6) were the principal hydrocarbon products. An unidentified olefin (mol. wt. 136) was also obtained in very low yield by reduction in ethanol. The dibromobornane was stable in the absence of a polarised mercury cathode. Tricyclene was not accompanied by significant amounts of camphene (8) so it could not have been produced by solvolysis of *endo*-2-bromobornane, from which reaction camphene is the principal product.[11]

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[9] H. Kwart, *J. Amer. Chem. Soc.*, 1953, **75**, 5942; H. Kwart and G. Null, *ibid.*, 1956, **78**, 5943.

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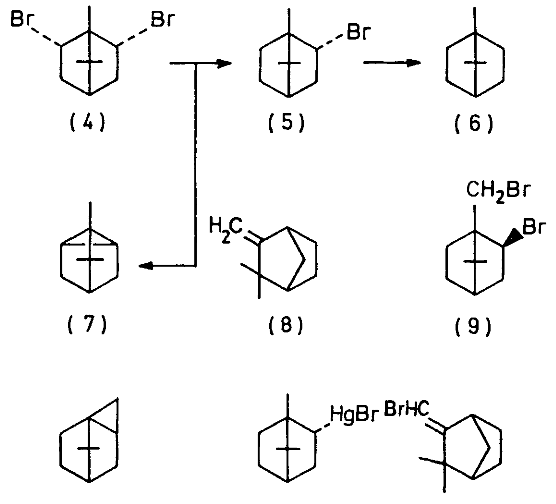
G.l.c. was used to monitor the formation of products as the reduction proceeded. A sample of the results is given in Table 2. *endo*-2-Bromobornane (5) is found as an intermediate in the reduction. Tricyclene and *endo*-2-bromobornane are both formed at a finite rate at zero time and so must be primary reduction products.



(4) (5) (6)

(7) (8) (9)

(10) (11) (12)

Table 1

Hydrocarbon products from reduction of *endo*-2,*endo*-6-dibromobornane

Solvent and electrolyte	Total yield (%)	Bornane	Tricyclene	Camphene
		(% in mixture)		
90% EtOH, sat. Pr_4NClO_4	76	30	70	0[a]
$Me_2N{\cdot}CHO$, 0·1M-Pr_4NClO_4	82	51	49	0
$Me_2N{\cdot}CHO$, sat. Me_4NBr	72	12	84	4

[a] A trace of an olefin with t_R (*B*) 16 min, *m/e* 136 (M^+) was also present.

Table 2

Progress of the reduction of *endo*-2,*endo*-6-dibromobornane in $Me_2N{\cdot}CHO$–0·1M-Pr_4NClO_4

Reaction time (h)	2,6-Dibromobornane	*endo*-2 Bromobornane	Bornane	Tricyclene
	(molar % of the initial dibromide)			
1	76	5	0	6
4	57	17	3	17
8	28	36	10	33
12	12	20	23	40
16	5	0	46	43

Bornane is formed at zero rate at zero time but its rate of formation increases as the concentration of 2-bromobornane in the reaction mixture increases. The concentration of 2-bromobornane reaches a maximum and then falls to zero. Thus bornane is only formed by the further reduction of 2-bromobornane.

This cyclisation of 1,3-dibromides is notably tolerant of stereochemistry of the leaving groups. We will discuss our example in terms of mechanisms which have been proposed for the reduction of bromoalkanes and 1,3-dibromoalkanes. Bromoalkanes are reduced first to give a radical and bromide ion. This radical is rapidly reduced further to a carbanion, which is protonated. The radical may react with mercury to give RHg• species which either give R_2Hg or are reduced to a carbanion and mercury.[12] Both *cis*- and *trans*-1,3-dibromo-1,3-dimethylcyclobutanes are reduced to the bicyclo[1.1.0]butane, and the carbanion (2) is considered to be an intermediate which inverts its stereochemistry, if necessary, at the carbanion site so as to undergo an internal displacement of bromide ion.[4] Such a reaction course is not open to *endo*-2,*endo*-6-dibromobornane (4) because the structure of the corresponding carbanion intermediate does not allow an internal nucleophilic displacement of bromide ion with inversion at the site of attack. It has been suggested [13] that, for some bromoalkanes, formation of an ion pair is promoted by the electrical field in the double layer around the cathode and that this ion pair undergoes reduction. A reaction between the carbanion centre from reduction of one C–Br bond in dibromobornane and an ion pair from the other C–Br bond to give tricyclene would be possible. However ion pair formation would also be expected to initiate a rearrangement to yield pin-2-ene, and pin-2-ene is not observed as a product.

There is a similarity between the electrochemical reduction of *endo*-2,*endo*-6-dibromobornane and the reduction [9] of the dichlorobornane with sodium amalgam. The dichlorobornane is reduced in ether to tricyclene and for this process Kwart and Null have suggested a concerted reduction step involving both chlorine groups. Reduction in ethanol gave *endo*-2-chlorobornane and bornane in a stepwise process. In cases such as (1) where a concerted reduction of dibromides is proposed by Rifi,[2,4] the half-wave potential for reduction of the dibromide is more positive than that for reduction of a monobromide. The half-wave potential for reduction of *endo*-2,*endo*-6-dibromobornane has a high negative value (see Table 5) and this argues against the concerted process for the reaction.

As an alternative to the foregoing mechanisms, the cyclisation of *endo*-2,*endo*-6-dibromobornane and the dichloro-compound can be considered to proceed by reduction of the halide groups in rapid succession to give a diradical which then cyclises. The 2- and 6-positions in bornane are suitably positioned to facilitate this cyclisation of a diradical. Such a reaction sequence must of course compete with the reduction of a single halide group to a carbanion which is then protonated, and both tricyclene and the *endo*-2-halogenobornane are primary reduction products.

Reduction of *exo*-2,10-dibromobornane (9) was also examined. This dibromide was obtained by bromination of camphene (84% racemic) and is assumed to have

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exo-stereochemistry by analogy with the reaction of camphene and hydrogen bromide to give *exo*-2-bromobornane. The ^{1}H n.m.r. signals due to the methyl groups and the 2-proton confirm that only one isomer is present in the crystalline dibromide. Reduction afforded bornane and camphene as the major products (Table 3).

TABLE 3

Hydrocarbon products from reduction of *exo*-2,10-dibromobornane

Solvent and electrolyte	Total yield (%)	Bornane (% in mixture)	Camphene (% in mixture)
90% EtOH, sat. Pr_4NClO_4	62	26	74
$Me_2N{\cdot}CHO$, 0·1M-Pr_4NClO_4	70	60	40
$Me_2N{\cdot}CHO$, sat. Me_4NBr	76	10	90

No unidentified hydrocarbon product which could have been 8,8-dimethyltricyclo[3.2.1.$0^{1,3}$]octane (10) was detected. If this hydrocarbon was present at all the amount was less than 3% of the total product. It may be formed and rearranged to camphene but this possibility cannot be tested since camphene is also formed in an alternative way.

A trace of some alkylmercury compound was also isolated as the alkylmercury(II) bromide after reaction with mercury(II) bromide. This alkylmercury bromide showed a molecular ion $C_{10}H_{17}HgBr$ with fragmentation to Hg^+ and $C_{10}H_{17}{}^+$ ions. The n.m.r. spectrum showed two methyl peaks in a ratio of 2 : 1, which leads us to identify this salt as *endo*-2-bornylmercury(II) bromide (11). Radical intermediates from reduction of alkyl halides can attack mercury to give the alkylmercury radical which eventually forms dialkylmercury. The alkylmercury radical intermediates rapidly invert their stereochemistry about the mercury–carbon bond.[14] Thus in the foregoing reaction the more stable *endo*-stereochemistry is suggested for the product.

An examination of samples (see Table 4) taken during the reduction of 2,10-dibromobornane in dimethylformamide revealed small amounts of *exo*-2- and *endo*-2-bromobornane (5) and two unidentified compounds present in the intermediate stages. ω-Bromocamphene (12) was not detected. The solvolysis of *exo*-2-bromobornane to give camphene is fast and will be extremely rapid during work-up when water is added, so the proportion of this actually detected does not represent its true concentration as an intermediate in the reduction. *endo*-2-Bromobornane is solvolysed so slowly that small amounts can be easily detected. The rate of formation of bornane was zero at zero time and increased as the reaction progressed, so this hydrocarbon is formed by the stepwise reduction of C–Br bonds. Camphene was formed at a finite rate at zero time but most, if not all, of this hydrocarbon will arise by solvolysis of any *exo*-2-bromobornane formed.

TABLE 4

Progress of the reduction of *exo*-2,10-dibromobornane in $Me_2N{\cdot}CHO$–0·1M-Pr_4NClO_4

Reaction time (h)	2,10-Dibromobornane	Bornane	Camphene
	(molar % of the initial dibromide)		
1	78	0	4
5	38	4	18
10	14	19	30
15	4	40	37

TABLE 5

Polarographic half-wave potentials in $Me_2N{\cdot}CHO$–0·1M-Pr_4NClO_4

Compound	$-E_{\frac{1}{2}}$/V *vs.* s.c.e.
endo-2,*endo*-6-Dibromobornane	2·48
exo-2,10-Dibromobornane	2·35
trans-1-Bromo-4-t-butylcyclohexane	2·56 [a]

[a] Lit.,[13] $E_{\frac{1}{2}} = -2{\cdot}45$ V (*vs.* s.c.e.).

A rate constant for the solvolysis of *exo*-2-bromobornane does not appear to have been recorded. The solvolysis of *exo*-2-chlorobornane (k_1 $1{\cdot}4 \times 10^{-4}$ s^{-1} at 35° in 9 : 1 MeOH–H_2O) [11] is $1{\cdot}5 \times 10^5$ faster than the reaction of *endo*-2-chlorobornane and the rate for the bromide is expected to be greater still by a factor of 25—60.[15] Solvolysis yields camphene as the hydrocarbon product and the foregoing figures give a half life of 80—200 s for *exo*-2-bromobornane. The *endo*-2-bromobornane found in the reaction in dimethylformamide may arise by equilibration of an *exo*-2-compound. Equilibration of *exo*-2- and *endo*-2-chlorobornanes has been observed in aprotic solvents such as liquid sulphur dioxide and chlorobenzene, catalysed by tin(IV) chloride.[16] Here the *endo*-isomer is favoured but the attainment of equilibrium is slow.

EXPERIMENTAL

^{1}H N.m.r. spectra were recorded with [^{2}H]chloroform as solvent and tetramethylsilane as internal lock. Unless otherwise stated, the following conditions were used for g.l.c. A Perkin-Elmer F_{11} instrument with flame ionisation detector was fitted with the following columns (2 m × 1/8 in diam): *A*, Apiezon L (15%), temp. 120°; *B*, silver nitrate in dihydroxyethane (30%) on Chromosorb P, temp. 45°; *C*, silicone gum rubber (1·5%), temp. 55°. An Autoprep Aerograph A-700 instrument with thermal conductivity detector was fitted with 1/4 in diam. columns: *D*, 20 ft Apiezon L (30%), temp. 130°; *E* 9 ft silver nitrate–phenylacetonitrile (20%), temp. 45°.

Polarography.—The bromo-compound ($1{\cdot}0 \times 10^{-3}$M) and tetrapropylammonium perchlorate (0·1M) were dissolved in dimethylformamide which had been dried ($CuSO_4$) and distilled (b.p. 43° at 2 mmHg). A three-electrode cell was used with the reference salt bridge train of saturated calomel electrode|1·0M-$NaNO_3$|0·1M-Pr_4NClO_4 in $Me_2{\cdot}NCHO$, and polarograph previously described.[17] $E_{\frac{1}{2}}$ Values at a dropping mercury electrode are given in Table 5.

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[14] R. E. Dessy, W. Kitching, J. Pharras, R. Salinger, A. Chen, and T. Chivers, *J. Amer. Chem. Soc.*, 1966, **88**, 460.

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[16] H. Meerwein and K. van Emster, *Ber.*, 1922, **55**, 2500.

[17] K. Alwair, J. F. Archer, and J. Grimshaw, *J.C.S. Perkin II*, 1972, 1663.

Electrochemical Reduction.—A conventional H-type cell [18] was used with a mercury cathode and either a carbon or a platinum anode. The potential for reduction was close to the decomposition potential of the electrolyte and so a controlled cathode potential was not used. A stationary nitrogen atmosphere was maintained over the catholyte and precautions were taken to avoid loss of products by evaporation at other stages.

Identification of Products.—Hydrocarbon mixtures from a reduction were separated by preparative g.l.c. Column *D* resolved tricyclene (t_R 16 min) and a mixture of camphene and bornane (t_R 23 min). Further g.l.c. on column *E* separated bornane (t_R 15 min) and camphene (t_R 20 min). The samples were then characterised by analytical g.l.c. and mass and ^1H n.m.r. spectroscopy.

Camphene (84%) and tricyclene (16%) were separated from commercial camphene by g.l.c. on column *D*. Bornane was obtained by Wolff reduction of camphor hydrazone.[19] Camphene had m.p. 49—51°, t_R (*A*) 12·5 min, (*B*) 11·5 min, τ 5·29 (1H, olefinic), 5·50 (1H olefinic), 8·96 (Me), and 8·98 (Me). Tricyclene had m.p. 67—68°, t_R (*A*) 9·5 min, (*B*) 2·0 min, τ 9·00 (Me) and 9·18 (2Me). Bornane had m.p. 158—159°, t_R (*A*) 13·0 min, (*B*) 2·0 min, τ 9·17 (3Me).

ω-Bromocamphene, b.p. 78—79° at 3 mmHg (lit.,[20] 87—88° at 5 mmHg) t_R (*C*) 12·1 min, *endo*-2-bromobornane, m.p. 92° (lit.,[21] 90°) t_R (*C*) 10·0 min, and *exo*-2-bromobornane, m.p. 133—134° (lit.,[22] 133°) t_R (*C*) 11·0 min, were prepared as described in the literature.

Reduction of endo-2,endo-6-*Dibromobornane.*—A solution of 2,6-dibromobornane [23] (5·92 g, 0·02 mol) in the electrolyte (140 ml; see Table 1) was reduced at a mercury cathode (area 18 cm^2; initial current 0·06 A) for 27—44 h until the current had fallen to a small value and g.l.c. indicated no remaining dibromide. The catholyte was then diluted with water and the products were extracted with ether and dried ($MgSO_4$). The volume was reduced to 20 ml and a solution of mercury(II) bromide (15 g) in ethanol (150 ml) was added. No alkylmercury(II) bromide precipitated and in repeat runs this step was omitted. The products were again isolated in ether, after dilution with water, and identified by g.l.c. The total yield was determined by g.l.c. (column *C*, temp. 165°) with naphthalene (t_R 70 min) as standard and a thermal conductivity detector. The proportions of products were determined by use of columns *A* and *B*.

Reduction of exo-2,10-*Dibromobornane.*—A solution of the dibromide [20,22] (0·02 mol) in the electrolyte (Table 3) was reduced as in the previous example. The total product with mercury(II) bromide (15 g) in ethanol (150 ml) precipitated an alkylmercuric bromide (0·09—0·25 g), m.p. 255—258° (from ethanol) (Found: C, 28·5; H, 4·2. Calc. for $C_{10}H_{17}BrHg$: C, 28·8; H, 4·1%), *m/e* 418 (M^+, $C_{10}H_{17}{}^{202}Hg^{79}Br$, $C_{10}H_{17}{}^{200}Hg^{81}Br$) and isotope pattern, τ 9·15 (2Me) and 9·17 (Me). Optically active bornylmercuric bromide has m.p. 186°.[24] The filtrate was worked up as for the previous example and analysed by g.l.c.

Detection of Reaction Intermediates.—The dibromide (5·92 g, 0·02 mol), together with hexadecane (1·48 g) and durene (2·72 g) as internal standards, was dissolved in dimethylformamide (150 ml) containing tetrapropylammonium perchlorate (3·75 g) and reduced over a mercury cathode (area 18 cm^2; initial current 0·08 A). A platinum anode in dimethylformamide–0·1M-tetrapropylammonium perchlorate was used. Samples (5 ml) were withdrawn from the catholyte at 2 h intervals and taken into ether; the solutions were washed with dilute hydrochloric acid and water, dried ($MgSO_4$), and evaporated to 0·75 ml.

(a) endo-2,endo-6-*Dibromobornane*. The formation of tricyclene and bornane was followed on column *D* (durene t_R 31 min) and of *endo*-2-bromobornane on column *C* (durene t_R 5·0 min). The loss of 2,6-dibromobornane was followed on column *C*, temp. 100°, t_R 14·3 min (hexadecane t_R 20·4 min). Appropriate calibration factors were determined.

(b) exo-2,10-*Dibromobornane*. The total yield of bornane and camphene was determined on column *D* and the ratio on column *B*. 2,6-Dibromobornane (temp. 100°, t_R 13·8 min), *endo*-2-bromobornane, and *exo*-2-bromobornane were detected on column *C*; no ω-bromocamphene was detected.

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