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216. The Reaction of Bicyclo [3.2.1] octenyl Halides with Metal Hydrides

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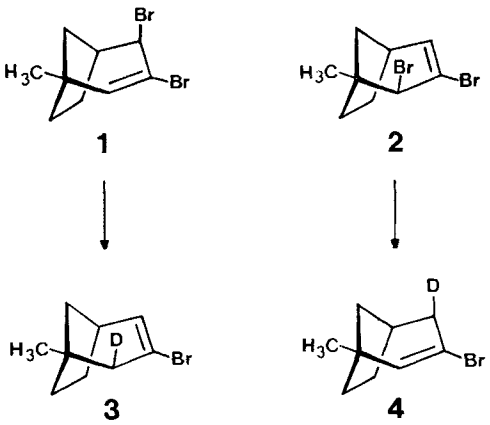
(2. V. 72)

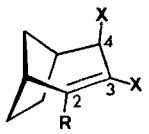
Summary. – Reduction of 2-phenyl- and 2-methyl-*exo*-3,4-dichlorobicyclo[3.2.1]oct-2-enes with lithium aluminium hydride (LAH) or tributyltin hydride (TBTH) gave *endo*-2-phenyl-3-chlorobicyclo[3.2.1]oct-3-ene, 2-phenyl-3-chlorobicyclo[3.2.1]oct-2-ene and their methyl analogues. The action of both reagents on 2-phenyl-*exo*-3,4-dibromobicyclo[3.2.1]oct-2-ene similarly resulted in reductive monodebromination to give normal and allylically rearranged products. Additionally, further reduction occurred to give *endo*-2-phenylbicyclo[3.2.1]oct-3-ene and 2-phenylbicyclo[3.2.1]-oct-2-ene. In all cases, LAH gave mainly the allylic rearrangement product whereas TBTH gave mostly unrearranged product. The reason for these differences could have been due either to the intervention of allylic radicals in the TBTH reduction or to differences in nucleophilicity. The results also show that LAH is equally efficaceous as TBTH in the reduction of these allylic halides and equally selective in the reduction of the vinyl bromides. The stereochemistry of the allylic rearrangement was shown to be *synfacial* in that hydride replaced halide on the same face of the molecule.

Introduction. – Bimolecular nucleophilic displacements on allylic halides have attracted continuing attention especially so in view of the problem of interpretation posed by the multiplicity of processes which may take place [1]. One of these processes which has been particularly difficult to unambiguously demonstrate is the S_N2' mechanism [2]. Examples are sparse and in each case there are points of contention or simply ambiguities [3]. In order to simplify the task of elucidating the stereochemistry of this mechanism we chose to study the reductive dehalogenation of bicyclo[3.2.1]octenyl halides with metal hydrides.

Our first attempt concerned the reaction of an equilibrium mixture of *exo*-1-methyl-3,4-dibromobicyclo[3.2.1]oct-2-ene (**1**) and *exo*-1-methyl-2,3-dibromobicyclo-[3.2.1]oct-3-ene (**2**) with lithium aluminium deuteride [4]. An 80:20 mixture of **1** and **2** on 15 hours treatment with an excess of reagent in boiling ether gave the *exo* deuteriated products **3** and **4** in a 84:16 ratio. These findings were interpreted in terms of an exclusive S_N2' process; namely that reactant **1** had given **3** and that **2** had formed **4**.



However, a second possibility cannot be ruled out, namely that the simultaneous operation of S_N2' and S_N2 processes at an incidence of about 80:20 on both reactants would also be compatible with these findings. In order to dispose of this particular ambiguity and to further see how substituents would affect the stereochemical outcome of the reduction we undertook the present study by selecting 2-phenyl- and 2-methyl-*exo*-3,4-dihalobicyclo[3.2.1]oct-2-enes (**5**, **6** and **7**) as substrates. The advantages are that compounds **5**, **6** and **7** exist as single isomers, that they possess a cyclohexenyl moiety disposed in a half-chair conformation, and they enjoy the useful features of conformational rigidity and dissymmetry which facilitate structure determination by NMR. spectroscopy [5]. If a minor S_N2 course were present it should be easily detected and moreover, the substituent at C(2) would be expected to exercise electronic control over the ratio of the S_N2' and S_N2 courses.

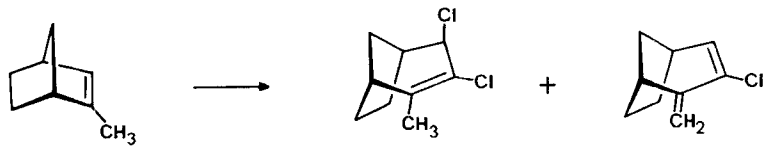


5 R = Ø , X = Br
6 R = Ø , X = Cl
7 R = CH_3, X = Cl

The substrates in question were prepared by the addition of dibromo and dichlorocarbene to 2-phenyl- and 2-methylnorbornene. The addition to 2-phenylnorbornene was quite straightforward [6]; however the reaction of dichlorocarbene with 2-methyl-

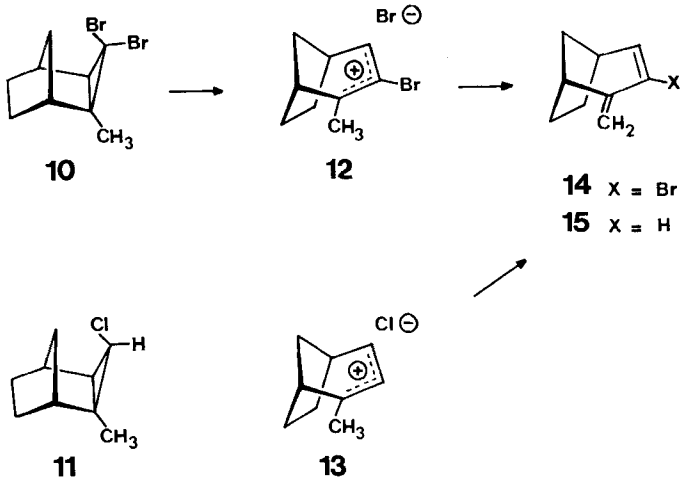
norbornene (**8**) gave results which necessitate a revision of our ideas concerning the rearrangement process of the intermediate cyclopropane adduct [7]. We discuss next appropriate experiments concerning this point.

Results and Discussion. – *A. Synthesis of Substrates* **5**, **6** *and* **7**. – The addition of dibromo and dichlorocarbene to 2-phenylnorbornene affords the *exo*-2-phenyl-3,4-dihalobicyclo[3.2.1]octenes-2 (**5** and **6**) [6]. The addition of dichlorocarbene, generated by the interaction of chloroform with 50% aqueous sodium hydroxide [8], to 2-methylnorborn-2-ene (**8**) gave the desired compound, *exo*-3,4-dichloro-2-methylbicyclo[3.2.1]-oct-2-ene (**7**) and its elimination product 2-methylene-3-chlorobicyclo[3.2.1]oct-3-ene (**9**).



8 **7** **9**

Compound **7** turned out to be quite stable. In 1,2,3-trimethylbenzene as solvent at 140° conversion of **7** to **9** was only partial. However, treatment of **7** with pyridine at 110° resulted in complete conversion after two hours. This result is surprising when compared to the behaviour of dibromocarbene and monochlorocarbene towards **8**. Here, elimination is exceptionally easy and is the sole process observed, the products of simple rearrangement not being isolable [4] [9]. To account for this result we previously suggested that the electrocyclic rearrangement of the first-formed cyclopropane adducts **10** and **11** proceeded directly to the corresponding ion pairs **12** and **13**, which promtly underwent proton loss to give the dienes **14** and **15**. In other words, rearrangement was by-passed by elimination. The present result now indicates that this interpretation needs to be revised. Rearrangement must occur prior to elimination.



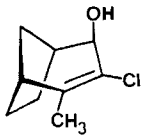
10 **12** **14** X = Br **15** X = H

11 **13**

The unusual stability of **7** not only permitted its separation from **9**, but was also reflected by a similar stability of the corresponding alcohol **16**. Treatment of **7** with

aqueous silver ion at reflux gave *exo*-3-chloro-4-hydroxy-2-methylbicyclo[3.2.1]oct-2-ene **16** and the diene **9** in ratio of 2:5. Clearly the intermediate allylic cation **17** has either shown an exclusive preference to be attacked by water at C(4) or that attack occurs at C(2) as well, but that the resulting tertiary alcohol **18** has effectively undergone 1,2 elimination to **9**. This latter possibility is likely since aqueous hydrolysis of **7** gave **16** and **18** in a ratio of 3:1.

The expected products of the simple rearrangement of the dichlorocyclopropane adduct **19** are the pair of allylic isomers **7** and **21**. Conceivable they could arise by a simple concerted isopolar rearrangement or *via* an intimate allylic ion pair such as **20** [10]. Whatever the precise nature of the rearrangement process, either isomer **7** is formed preferentially or is more stable than isomer **21**, or alternatively, **21** undergoes elimination to the diene **9** more readily than does **7**.



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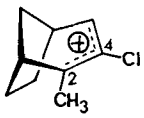

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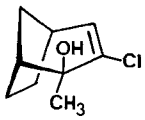

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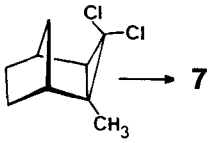

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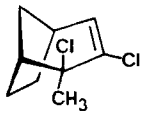

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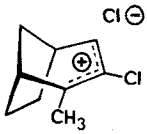

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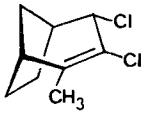


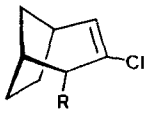
22

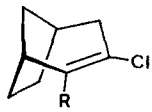
In an attempt to further investigate the course of elimination, the reverse process was studied viz., the addition of hydrogen chloride to the olefin **9**. The results are complex. The addition of excess hydrogen chloride in chloroform at 45° furnished **7** and what appeared to be its *endo* isomer **22** in the ratio 4:1. When the reaction was carried out in carbon tetrachloride at −10° a mixture of **7**, **22** and 2,3-dichloro-2-methylbicyclo[3.2.1]oct-3-ene (**21**) was obtained in the ratio 3:1:1. On letting the mixture stand at room temperature for 3 hours, the component **21** had disappeared leaving a mixture of **7** and **22**, the ratio of which was identical to that obtained in the first addition. Both mixtures proved impossible to separate, as all three products readily lost hydrogen chloride in the attempt. Nevertheless, evidence for the existence of **21** and **22** was forthcoming from a consideration of the NMR. spectra of the mixtures.

These findings can be conveniently rationalized by invoking the intermediacy of the allylic cation **17** formed by protonation of **9**. Cation **17** undergoes attack by chloride to give the *exo* chlorides **7** and **21** in the same ratios as the alcohols **16** and **18** obtained by hydrolysis of **7**. The easy passage of the tertiary chloride **21** to the secondary derivative **7** on heating merely reflects the traditional stability difference [1].

The formation of the *endo* chloro compound **22** is unprecedented in view of the known predisposition of the cation **17** and its radical equivalent to *exo* attack [11]. Nevertheless, simple cyclohexenyl chlorides, which are conformationally more flexible, have been reported to display departures from strict synfaciality on reaction with external nucleophile [12].

B. Reductive Dehalogenation of Substrates **5**, **6**, *and* **7**. – Treatment of **7** with an excess of lithium aluminium hydride (LAH) in boiling ether resulted in reductive dechlorination. Two isomers were formed in 73% yield in the ratio of 80:20 which on separation were identified as *endo*-2-methyl-3-chlorobicyclo[3.2.1]oct-3-ene (**23**) and 2-methyl-3-chlorobicyclo[3.2.1]oct-2-ene (**24**).



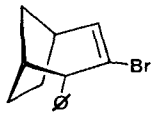


7 ⟶ (LAH) **23** R = CH_3 **24** R = CH_3

6 ⟶ (LAH) **25** R = Ø **26** R = Ø

At first sight, these results uncannily resemble those found with the mixture of 1-methylbicyclo[3.2.1]octenyl bromides (**1** and **2**). Equally astonishing was the result obtained with the phenyl analogue **6**. Excess LAH gave *endo*-2-phenyl-3-chlorobicyclo-[3.2.1]oct-3-ene (**25**) and 2-phenyl-3-chlorobicyclo[3.2.1]oct-2-ene (**26**) in the ratio 45:55 also in high yield (73%). For the bromo compound **5** reduction turned out to be more extensive. Treatment of **5** with excess LAH gave the two expected monobromo isomers **27** and **28**, but also the corresponding completely debrominated com-

5 ⟶



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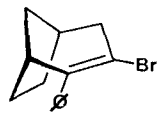

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29

30

pounds **29** and **30** in a percentage ratio of 87.7, 8.7, 3.0, 0.6. The second reductive debromination took place without allylic rearrangement; separate treatment of **27** and **28** with LAH gave simply the hydrocarbons **29** and **30**, respectively. Thus the overall reaction in all cases is a reduction in which allylic halogen has been replaced by hydride ion. Without specifying the nature of the substitution the exchange of one group by the other has occurred on the same face of the molecule. Significantly, both allylic rearranged and unrearranged products are observed.

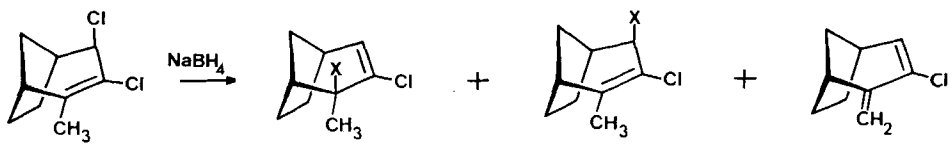
In view of the nucleophilic character of LAH it can be supposed that the rearranged and unrearranged monodehalogenated products arise by hydride ion attack on the contact ion pair, rather than the covalent species (*v. infra*).

Both the rearranged and unrearranged reduction products turned out to be stable under the reaction conditions. Stability was tested by separating *endo*-2-methyl-3-chlorobicyclo[3.2.1]oct-3-ene (**23**) and its allylic isomer **24**. Both were stable at 135° with no interconversion. Similar stability was displayed towards excess sodium methoxide at 40° for 18 hours. The two phenyl isomers **27** and **28** were similarly stable at 168° for 24 hours.

In order to see if the reagent has any effect on the ratio of isomers, it was decided to repeat the reductions with tributyltin hydride (TBTH). Organotin hydrides enjoy a considerable vogue as reagents for reductive replacement of halogen in organic halides [13]. The mechanism is commonly reputed to involve the radical intermediate of the substrate hydrocarbon [14]. In the present case allylic radicals should form which would eventually capture hydrogen to give the isomeric parent hydrocarbons in ratios which might be expected to give some indication of the species involved in the LAH reduction. Thus the behaviour of the allylic radicals could be taken as a model for the corresponding free allylic cations.

With excess TBTH, *exo*-3,4-dichloro-2-methylbicyclo[3.2.1]oct-2-ene (**7**) gave the rearranged **23** and unrearranged **24** reduced products in the ratio 20 : 80. Under the same conditions, *exo*-3,4-dichloro-2-phenylbicyclo[3.2.1]oct-2-ene (**6**) gave the rearranged *endo*-phenyl product **25** and the unrearranged product **26** in the ratio 10:90. The action of TBTH on the dibromo compound **5** resulted in more profound reductive dehalogenation; the rearranged and unrearranged monobromo products **27** and **28** and their corresponding further reduced derivatives **29** and **30** were found in a ratio of 9.9, 89.0, 0.15 and 0.95%. Curiously enough, these ratios are the inverse of those found for the LAH reductions.

As a further check on the possible mechanism, it was decided to carry out the reduction in an ionizing medium. As an example **7** was submitted to the action of



7

23 X=H, 28% **24** X=H, 14% **9** 10%

18 X=OH, 16% **16** X=OH, 32%

Scheme. *Reaction of* **7** *with sodium borohydride in 80% aqueous diglyme*

sodium borohydride in 80% aqueous diglyme. The results are summarized in the scheme.

The formation of the isomeric *exo* alcohols **16** and **18** and the diene **9** in addition to the expected reduction products **23** and **24** clearly demonstrate the intermediacy of the allylic cation **17** or at least its ion-pair **13**.

Mechanistic Conclusions. – It is immediately seen that the macroscopic chemical behaviour of LAH and TBTH is the same, in that they both effect reductive dehalogenation of the bicyclo[3.2.1]octenyl halides. Moreover, as far as the allylically rearranged product is concerned, the stereochemical result is the same, namely that hydride ion has replaced halide ion in a synfacial manner[1]) [15]. A difference between the two reagents which may be significant is that the extent of allylic rearrangement is appreciably higher with LAH than with TBTH.

Although the reduction of primary allylic halides with LAH nearly always proceeds without double bond migration or geometric change [16], it was forecast [18], after the first reported cases [17], that secondary allylic halides will be reduced with allylic rearrangement. *Hatch* proposed that the allylic course is determined by LAH initially complexing with the allylic halide and then delivering hydride to the terminal vinyl carbon in a cyclic process [18]. No satisfactory explanation has been put forward to account for the abrupt change in reaction course between primary and secondary halides. The difference has been attributed to the greater steric impediment supposedly encountered by the aluminohydride ion at a secondary than a primary allylic carbon atom [18]. If the present LAH reaction is simply considered as an attack by free hydride or aluminohydride ion on an allylic halide, then the process fits the general case of an S_N2' mechanism which is generally thought to prefer a synfacial course [19]. However, it could also be argued that the *endo* side of the bicyclo[3.2.1]octene skeleton, on account of the ethane bridge, is sterically more hindered than the *exo* side, and thus the synfaciality of the displacement is purely coincidental since the leaving group has the *exo* configuration.

It now appears that the stereochemistry of the S_N2' reaction may be synfacial or apofacial depending on the substrate and the nucleophile [15]. Although the few examples mostly demonstrate synfaciality [3] [10] [20], there are now well-documented exceptions [21]. *Nguyen Trong Anh* has postulated that the *timing* of the entry and departure of nucleophile and leaving group, respectively, should determine the stereochemical course of the substitution; for a synchronous exchange of groups an anti- or apofacial arrangement will be favoured and for the departure of leaving group prior to entry of nucleophile a syn or synfacial arrangement will be favoured [22]. We have similarly suggested that, in principle, two transition states are feasible, a linear (apofacial) one and a quasicyclic (synfacial) one and that the actual course

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[1]) Two related apofacial reactions are the 1,2 group transfer experienced in a carbocation on attack by nucleophile; termed a geitonodesmic process (*S. J. Cristol, F. P. Parungo, D. E. Plorde & K. Schwarzenbach*, J. Amer. chem. Soc. *87*, 2879 (1965)) and the bond switching exemplified by the *Barton-Head* rearrangement (*D. H. R. Barton & A. J. Head*, J. chem. Soc. *1956*, 932) which has been recently termed a dyotropic shift (*M. T. Reetz*, Angew. Chem. *84*, 161 (1972)). We propose the word diplotropic (Gr. *διπλόος*, twofold, double) as being more appropriate.

followed in a particular S_N2' reaction will be determined by the nature of the exchanging groups and conformational and configurational factors [15].

For the case of a cyclohexenyl derivative disposed in a halfchair conformation, the bonds undergoing rupture and formation are both quasiaxial and accordingly they afford the best chances of orbital interaction between the entering and leaving groups (Fig. 1a). It is also true that electrostatic bonding or complexation of metal hydride to the quasiaxial leaving group is particularly convenient for internal hydride transfer in the *syn*-quasiaxial arrangement (Fig. 1b).

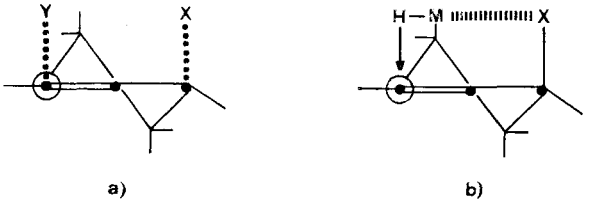

Fig. 1. *Synfacial displacement of a leaving group X a) by nucleophile Y in a cyclohexenyl derivative in a half chair conformation, and b) by complexed metal hydride (MH)*

The bicyclo[3.2.1]octenyl derivatives have been shown, despite some flattening by the ethane bridge, to possess cyclohexenyl moieties disposed as half-chairs [23]. Accordingly, we feel that the present observation of a synfacial displacement of halide by LAH in compounds **5**, **6** and **7** is due to the operation of electronic factors and is not merely the consequence of steric impediment. The concomitant formation of non-allylically rearranged product suggests that it is an allylic contact ion-pair which is undergoing nucleophilic attack rather than the covalent species [24]. Support for this idea comes from the borohydride reduction. In the semi-aqueous medium both hydride ion and water are competing for the same substrate. In the event, the weaker nucleophile, water will engender an S_N1 process and the corresponding transition state will resemble the more stable product, whence more attack at the secondary C(4) atom than C(2) is seen. On the other hand the more nucleophilic hydride ion prefers the tertiary C(2) atom.

The similarity of the macroscopic chemical behaviour of TBTH and LAH is particularly striking not only in the reduction of the allylic halogen, but also in their identical selective reduction of vinylic bromine in **27** and **28**. Traditionally these two reagents are thought to have quite different chemical natures; LAH being considered as a typical nucleophile, whereas TBTH has come to be regarded as a specific reducing agent for alkyl halides proceeding by a homolytic pathway. From the parallelism of the reductive behaviour of the two reagents it cannot be automatically concluded that a common mechanism is operating. In fact the results themselves give no direct clue to the intimate nature of the reduction process. On the other hand, the findings constitute a timely warning against the all too common assumption that uncatalysed reductions of alkyl halides by organotin hydride always occur by a free radical process [25]. Thus one is not sure whether the differences in the ratios of rearranged to unrearranged products reflect the intermediacy of a radical in the TBTH reduction or simply a difference in nucleophilicity between TBTH and LAH. Investigations are under way to decide between these alternatives.

One final point concerns the selective reduction of the vinyl bromides **27** and **28** by the two reagents. Although *cis*- and *trans*-α-bromostilbene have been reduced with an organotin hydride [26], the present example indicates that LAH will be equally effective for the selective reduction of vinyl bromides. A similar conclusion has been reached by *Brown*, who showed that the hydrogenolysis of aryl bromides could be far more conveniently achieved with LAH than with triphenyltin hydride [27].

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Experimental Part

IR. spectra were recorded, as films on NaCl plates, unless otherwise noted, on a *Perkin-Elmer* 257 spectrometer. NMR. spectra were determined at 60 MHz on a model R-12 *Perkin-Elmer* instrument using carbon tetrachloride as solvent. Chemical shifts are expressed as ppm with reference to tetramethylsilane taken as zero. UV. spectra were recorded on a model 402 *Perkin-Elmer* spectrophotometer. Gas liquid chromatography (GLC.) was carried out on model F11 (analytical) or F21 (preparative) *Perkin-Elmer* instruments. All boiling and melting points are uncorrected. Microanalyses were performed by Dr. *K. Eder*, Ecole de Chimie, Genève.

A. Addition of Dichlorocarbene to 2-Methylnorborn-2-ene (8) [7]. – A mixture of **8** (10.8 g; 0.1 mole), chloroform (12 g; 0.1 mole), 50% aqueous sodium hydroxide solution (20 ml) and triethylbenzylammonium chloride (0.4 g) was heated and stirred at 40° for 24 h [8]. The mixture was diluted with water and then extracted with ether. The ether layer was separated and washed with water three times, once with a dilute sodium hydrogen carbonate solution, again with water, and finally with a saturated sodium chloride solution. The ether solution was dried over sodium sulfate and subsequently evaporated. The residual oil was fractionally distilled *in vacuo* to afford *3-chloro-2-methylenebicyclo[3.2.1]oct-3-ene* (**9**) (1.55 g; 10%), and *exo-3,4-dichloro-2-methylbicyclo[3.2.1]oct-2-ene* (**8**) (9.7 g; 51%).

3-Chloro-2-methylenebicyclo[3.2.1]oct-3-ene (**9**). – B.p. 41–42°/0.15 Torr. UV. spectrum: λ_{max} (in cyclohexane) 242 nm ($\varepsilon = 21\,300$). IR. spectrum: max. at 3095, 3045, 1639, 1587, 890, 885 and 667 cm^{-1} characteristic of the α,β-diene and the C—Cl bond.

$C_9H_{11}Cl$ (154.64) Calc. C 69.92 H 7.17 Cl 22.93% Found C 69.80 H 7.13 Cl 23.22%

exo-*3,4-Dichloro-2-methylbicyclo[3.2.1]oct-2-ene* (**7**). – B.p. 66–67°/0.1 Torr. IR. spectrum: max. at 1647 and 658 cm^{-1} characteristic of the tetrasubstituted double bond and the chloro function.

$C_9H_{12}Cl_2$ (191.10) Calc. C 56.55 H 6.33 Cl 37.12% Found C 57.61 H 6.69 Cl 34.01%

A small amount of adduct formed from traces of 2-methylenenorbornene present as impurity was also isolated[2]). It proved impossible to secure a better elemental analysis of **7**, owing to its tendency to lose a molecule of hydrogen chloride on heating.

Treatment of exo-*3,4-dichloro-2-methylbicyclo[3.2.1]oct-2-ene* (**7**) *with aqueous silver nitrate.* – To a solution of **7** (2.0 g; 10.6 mmoles) on 50% aqueous acetone (5 ml), a solution of silver nitrate (2.0 g) in water (3 ml) was added. The mixture was heated under reflux for 2 h. Silver chloride was separated by filtration and the filtrate was worked up in the usual fashion. The solvent was removed and the remaining oil was distilled *in vacuo*. Two fractions were obtained. The first (41–42°/0.15 Torr; 0.79 g; 51%) was identified as *3-chloro-2-methylenebicyclo[3.2.1]oct-3-ene* (**9**); the high boiling fraction (72–73°/0.15 Torr; 0.59 g; 34%) proved to be *3-chloro*-exo-*4-hydroxy-2-methylbicyclo[3.2.1]oct-2-ene* (**16**). – This fraction crystallised on standing, and was further purified by sublimation: m.p. 66–67°.

[2]) The origin of this olefin is the base catalysed isomerisation of **8**. The same adduct was obtained as the main product in the addition of dichlorocarbene to 2-methylenenorbornane.

3-Chloro-exo-*4-hydroxy-2-methylbicyclo[3.2.1]oct-2-ene* (**16**). – M.p. 66–67°. IR. spectrum (in Nujol): max. at 3260, 1647, 1020 and 722 cm^{-1} indicative of the hydroxy and chloro groups and an endocyclic, tetrasubstituted double bond.

$C_9H_{13}ClO$ (172.70) Calc. C 62.60 H 7.59 Cl 20.53% Found C 62.61 H 7.59 Cl 20.65%

Hydrolysis of exo-*3,4-dichloro-2-methylbicyclo[3.2.1]oct-2-ene* (**7**). – *exo*-3,4-Dichloro-2-methylbicyclo[3.2.1]oct-2-ene (**7**) (500 mg; 2.8 mmoles) in 65% aqueous acetone (23 ml) was stirred at room temperature for 3 h. The solution was diluted with water and worked up the usual way to afford a mixture of *3-chloro-2-hydroxy-2-methylbicyclo[3.2.1]oct-3-ene* (**18**) and exo-*3-chloro-4-hydroxy-2-methylbicyclo[3.2.1]oct-2-ene* (**16**) in the ratio 1:3 (408 mg; 85%). Separation was effected by GLC. using a column (4.5 m, 8.0 mm) packed with 20% Carbowax 20M on Chromosorb W (80/100 mesh; acid washed and silanized), nitrogen as carrier gas (200 ml/min) and temperatures of 200° (injection) and 180° (column). The retention times were 30 min. for **16** and 25 min. for **18**.

3-Chloro-2-hydroxy-2-methylbicyclo[3.2.1]oct-3-ene (**18**) was further purified by sublimation (50°/0.01 mm): m.p. 50–51°. IR. spectrum: max. at 3350, 3020, 1629, 842 and 740 cm^{-1} characteristic of the hydroxy and chloro groups and an endocyclic, trisubstituted double bond. Mass spectrum: M^+: 172.

Dehydrochlorination of exo-*3,4-dichloro-2-methylbicyclo[3.2.1]oct-2-ene* (**7**). – A solution of **7** (2.5 g; 13 mmoles) in dry pyridine (10 ml) was stirred and heated at 110° for 2 h. After dilution with water, the solution was worked up in the usual way. The ether was distilled off and the product was fractionated through a *Vigreux* column to yield *3-chloro-2-methylenebicyclo[3.2.1]oct-3-ene* (**9**) (1.05 g; 6.8 mmoles; 52%).

Addition of hydrogen chloride to 3-chloro-2-methylenebicyclo[3.2.1]oct-e-ene (**9**). – Dry hydrogen chloride was passed into a solution of **9** in carbon tetrachloride at –10°. After the disappearance of the diene, the NMR spectrum of the solution was examined. Three products were detected: *2,3-dichloro-2-methylbicyclo[3.2.1]oct-3-ene* (**21**), exo-*3,4-dichloro-2-methylbicyclo-oct-2-ene* (**7**) and endo-*3,4-dichloro-2-methylbicyclo[3.2.1]oct-2-ene* (**22**) in the ratio 1:3:1, respectively. After three hours at room temperature the NMR. spectrum indicated that **21** had converted completely to **7**.

Passage of dry hydrogen chloride into a solution of **9** in chloroform at 45° gave only two compounds, namely **7** and **22** (4:1).

B. Reduction of *exo*-3,4-dichloro-2-methylbicyclo [3.2.1] oct-2-ene (7) with lithium aluminium hydride (LAH). – A solution of **7** (4.0 g; 21 mmoles) in anhydrous ether (10 ml) was added dropwise to a suspension of LAH (1.5 g; 39 mmoles) in anhydrous ether (35 ml). The mixture was stirred and heated under reflux for 18 h. The excess of reagent was destroyed by dropwise addition of a small quantity of water. The resulting solution was filtered and dried over magnesium sulfate. The ether was removed and the product was distilled under reduced pressure (53–54°/0.45 Torr; 3.0 g; 19.1 mmoles; 91%). IR. revealed the presence of two compounds (C=C: 1667 and 1632 cm^{-1}). Separation was effected using a column (4.5 m/8.0 mm) packed with 20% Apiezon L on Chromosorb W (80/100 mesh; acid washed and silanized), nitrogen as carrier gas (120 ml/min) and temperatures of 170° (injection) and 135° (column).

The major component (4:1) had the longer retention time (30.5 min) and was *3-chloro*-endo-*2-methylbicyclo[3.2.1]oct-3-ene* (**23**). – IR. spectrum: max. at 3040, 1632, 842 and 679 cm^{-1} characteristic of the tribustituted double bond and the C—Cl bond.

$C_9H_{13}Cl$ (156.65) Calc. C 69.01 H 8.37 Cl 22.66% Found C 69.05 H 8.61 Cl 22.44%

The minor component (retention time of 26.5 min) was *3-chloro-2-methylbicyclo[3.2.1]oct-2-ene* (**24**). – IR. spectrum: max. at 1667 and 720 cm^{-1} due to the tetrasubstituted double bond and C—Cl bond.

$C_9H_{13}Cl$ (156.65) Calc. C 69.01 H 8.37 Cl 22.66% Found C 69.10 H 8.50 Cl 22.51%

Both compounds were stable under the separation conditions.

Reduction of the mixture of **7** *and* **22** *with LAH.* – The reaction was carried out in exactly the same way as for pure **7** (see below). From the mixture of **7** and **22** (4:1; 3.5 g; 18.4 mmoles), **24** and **23** were obtained in a ratio of 3:7 (2.38 g; 15.2 mmoles; 84% yield).

Reduction of exo-*3,4-dichloro-2-methylbicyclo[3.2.1]oct-2-ene* (**7**) *with tri*-n-*butyltin hydride* (*TBTH*) [28]. – A mixture of **7** (5.0 g; 26 mmoles) and TBTH (9.0 g; 31 mmoles) was stirred and

heated at 80° for 18 h under nitrogen. After dilution with anhydrous ether (100 ml), ammonia was passed through the mixture until precipitation of the white quarternary ammonium salt of TBT-chloride was complete. After filtration and evaporation of the solvent, the residual oil was purified by column chromatography (basic alumina, Merck activity grade I, petroleum ether as eluant) followed by distillation *in vacuo* to yield a mixture (56%) of **23** and **24** in the ratio 1:4.

Reduction of exo-*3,4-dichloro-2-methylbicyclo[3.2.1]oct-2-ene* (**7**) *with sodium borohydride.* – To a stirred solution of sodium borohydride (3.4 g; 90 mmoles) in 80% aqueous diglyme (50 ml) **7** (2.0 g; 13.5 mmoles) was added. The mixture was then heated at 50° for 24 h under nitrogen. After cooling and dilution with water the mixture was worked up and the residual oil was purified by column chromatography (silica gel *Merck*, 70/325 mesh) to yield a mixture (1.33 g) of *3-chloro*-endo-*2-methylbicyclo[3.2.1]oct-2-ene* (**24**), *3-chloro-2-hydroxy-2-methylbicyclo[3.2.1]oct-3-ene* (**18**), *3-chloro*-exo-*4-hydroxy-2-methylbicyclo[3.2.1]oct-2-ene* (**16**) and *3-chloro-2-methylenebicyclo[3.2.1]oct-3-ene* (**9**) in a percentage ratio of 28, 14, 16, 32 and 10, respectively.

Reduction of exo-*3,4-dichloro-2-phenylbicyclo[3.2.1]oct-2-ene* (**6**). – Compound **6** (2.53 g; 0.01 mole) in dry ethyl ether (5 ml) was added dropwise to a suspension of LAH (0.8 g) in dry ethyl ether (20 ml). The mixture was then stirred and heated under reflux for 18 h. Excess LAH was decomposed by careful addition of water and the ethereal solution was dried over anhydrous sodium sulfate. Subsequent evaporation of the ether gave **25** and **26** (1.6 g; 0.0077 mole) 73% in the ratio of 45:55 as determined by both NMR. and GLC. Separation to the two isomers was effected by preparative GLC., using a column (4.5 m/8.0 mm) packed with 20% Apiezon L on Chromosorb W (80/100 mesh; acid washed and silanized), nitrogen as carrier gas (80 ml/min) and temperatures of 240° (injection) and 215° (column). The retention times were 68 min for **26** and 73 min for **25**.

3-Chloro-endo-*2-phenylbicyclo[3.2.1]oct-3-ene* (**25**). – UV. spectrum: λ_{max} (in hexane) 214 nm ($\varepsilon = 12200$). Mass spectrum: M^+: 218.

3-Chloro-2-phenylbicyclo[3.2.1]oct-2-ene (**26**). – NMR. spectrum: phenyl (5H) 7.33 ppm; methylene (10H) 2.40–3.90 ppm. UV. spectrum: λ_{max} (in hexane) 212 nm ($\varepsilon = 7800$) and 245 nm ($\varepsilon = 6550$). Mass spectrum: M^+: 218.

Treatment of 6 with TBTH. – a) Compound **6** (2.53 g; 0.01 mole) was stirred and heated with TBTH (3.5 g) without solvent at 80° under nitrogen for 18 h. Column chromatography over basic alumina (using petroleum ether as eluant) of the resulting reaction mixture gave **25** and **26** (1.7 g; 0.0082 mole, 82% yield) in the ratio 1:6.

b) Compound **6** (1.0 g; 0.004 mole) and TBTH (1.4 g) were dissolved in ether (10 ml) and the mixture was refluxed under nitrogen for 18 h. After evaporation of the ether, the mixture was chromatographed over basic alumina to give **25** and **26** (0.6 g; 0.0027 mole, 69% yield) in the ratio 1:6.

Stability of the mixture of **25** *and* **26** *in the presence of LAH.* – Both mixtures of **25** and **26** obtained from the LAH reduction (ratio 45:55) and from the TBTH reduction (ratio 1:6) were treated separately with LAH in refluxing ether for 24 h. In both cases, the starting mixtures were entirely recovered and analytical GLC. did not show any change in the ratios.

Reduction of 2-phenyl-3,4-dibromobicyclo[3.2.1]oct-2-ene (**5**) *with LAH.* – *exo*-2-phenyl-3,4-dibromobicyclo[3.2.1]oct-2-ene (**5**) (7.0 g; 10.2 mmoles) in anhydrous ether (25 ml) was added dropwise over 20 min to a stirred solution of LAH (1.4 g; 18.4 mmoles) in anhydrous ether, and then heated under reflux for 18 h. The reaction mixture was then cooled and a saturated aqueous sodium sulfate solution (3 ml) was carefully added. Solids were removed by filtration and washed well with ether. The combined ethereal extracts were washed with water, dried over magnesium sulfate, and examined by GLC. (Apiezon L, 20% on Chromosorb W; 80/100 mesh acid washed and silanized; 2 m × 2 mm; column temperature 180°). Four compounds (**27**, **28**, **29**, **30**) were present in a ratio of 87.7, 8.7, 3.0 and 0.6%. The major component was isolated by crystallisation and the others identified with samples prepared separately (see below).

endo-*2-Phenyl-3-bromobicyclo[3.2.1]oct-3-ene* (**27**). – The ethereal solution was evaporated and the resultant oily solid (3.8 g; 71%) was chromatographed over basic alumina (80 g, *Merck* activity grade I) using light petrol (b.p. 40–60°) as eluant. The solvent was removed and the residue recrystallized from pentane to give endo-*2-phenyl-3-bromobicyclo[3.2.1]oct-3-ene* (**27**) as small

colourless crystals, m.p. 81–82°. Crystallization of the oily residue from pentane furnished a further batch of **27** (0.8 g).

$C_{14}H_{15}Br$ Calc. C 63.9 H 5.7 Br 30.4% Found C 63.63 H 5.82 Br 30.81%

UV. spectrum: λ_{max} (in cyclohexane) 226 nm (ε = 13480). Mass spectrum: M^+: 262 and 264 in the ratio 1:1.

The residual oil was collected (250 mg) and was shown by NMR. to contain a small amount (~10%) of **27**.

endo-*2-Phenylbicyclo[3.2.1]oct-3-ene* (**29**). – Compound **27** (1.0 g) in ether (25 ml) was added to an ethereal suspension of LAH (1.0 g) and the mixture heated under reflux for 24 h. The mixture was worked up and purified by column chromatography over basic alumina and subsequently by thick layer chromatography (silica gel F_{254}). *endo*-2-Phenylbicyclo[3.2.1]oct-3-ene (**29**) was obtained (170 mg).

UV. spectrum: λ_{max} (in cyclohexane) 223 nm (ε = 9800). Mass spectrum: M^+: 184.

Reduction of 2-phenyl-3,4-dibromobicyclo[3.2.1]oct-2-ene (**5**) *with TBTH.* – A solution of **5** (3.42 g, 1.0 mmole) and TBTH (3.20 g, 1.1 mmole) in ether (50 ml) under nitrogen was stirred and heated under reflux for 18 h. Ether was evaporated and the residual oil was passed twice over a column of basic alumina using light petroleum (60–80°) as eluant to remove tin bromide. The solvent was evaporated and GLC. revealed the presence of **27** and *2-phenyl-3-bromobicyclo-[3.2.1]oct-2-ene* (**28**) in the ratio of 1:9 (1.6 g; 63%). Subsequent column chromatography over basic alumina using light petroleum (b.p. 40–60°) as eluant gave **28** in 96% purity contaminated with 4% of **27**.

$C_{14}H_{15}Br$ Calc. C 63.9 H 5.7 Br 30.4% Found C 63.78 H 5.85 Br 30.64%

UV. spectrum: λ_{max} (in cyclohexane) 220 nm (ε = 8150) and 243 nm (ε = 7700). Mass spectrum: M^+: 262 and 264 in the ratio 1:1.

2-Phenylbicyclo[3.2.1]oct-2-ene (**30**). An ethereal solution of the above mixture of **28** and **27** (0.50 g) was added dropwise to a stirred solution of LAH (500 mg) in ether at room temperature. The mixture was then heated under reflux for 24 h and worked up in the usual way. Analysis of the product by GLC. showed it to be essentially *2-phenylbicyclo[3.2.1]oct-2-ene* (**30**), with a small amount (5%) of endo-*2-phenylbicyclo[3.2.1]oct-3-ene* (**29**).

NMR. spectrum: Two characteristic peaks: 3.37 ppm (5 H, phenyl) and 5.79 ppm (1 H, vinyl). UV. spectrum: λ_{max} (in cyclohexane) 221 nm (ε = 6100) and 251 nm (ε = 7900). Mass spectrum: M^+: 184 (parent peak at 57).

NMR.-Data. – The chief spectral features of the compounds **7**, **9**, **16**, **18**, **21**, **22**, **23**, **24**, **25**, **27** and **29** are listed in the Tables I and II. All spectra were obtained at 60 MHz and analyzed by spin decoupling using the frequency sweep method. The coupling constants were obtained from the expanded spectra (5 ppm, 100 or 50 Hz). Chemical shifts are expressed in ppm from internal TMS taken as zero. Coupling constants are in Hz and the form of the signals is designated as *s* = singlet, *d* = doublet, *t* = triplet, and *m* = multiplet.

The *endo* configuration of the methyl group in **23** and the phenyl group in **27** were rigorously established by double irradiation experiments. For **23** the magnitude of the long range coupling between the vinyl proton and the allylic hydrogen was found to be 2.0 Hz. This value is consistent with *exo* stereochemistry of the allylic proton, accordingly the geminal methyl group has the *endo* configuration [30].

Similarly for **27**, the vinyl-allylic coupling was found to be 1.5 Hz. This value, taken together with the value of 4.5 Hz found for the vicinal coupling between the C(1) and C(2) protons confirm the *endo* configuration of the C(2) phenyl group [30].

The allylic hydrogen in *endo*-3,4-dichloro-2-methylbicyclo[3.2.1]oct-2-ene (**22**) showed as multiplet (^3J = 4.9 Hz) at 4.95 ppm. The magnitude of the coupling constant and the chemical shift of this signal suggest the *endo* configuration of the chlorine [30]. In the NMR. spectrum of the mixture of **8**, **22** and **21** obtained at −10°, additional signals appeared: sharp singlet at 1.76 ppm and a doublet at 6.09 ppm (^3J = 7.5 Hz, further finely split). This data strongly suggests that this product is 2,3-dichloro-2-methylbicyclo[3.2.1]oct-3-ene (**21**), with undefined stereochemistry at C(2).

Table I. *NMR. data of the 2-methylbicyclo[3.2.1]octene derivatives*

Compound	C(1)	C(4)	C(5)	C(2) subst.
7	2.49	4.17 *m* ($J = 2.8$) ($^5J = 1.3$)	2.69 *m*	1.84 *d* ($^5J = 1.3$)
9	3.04 *d* of *m* ($J = 4.5$)	6.21 *d* ($^3J = 7.3$)	2.65 *m*	5.05 *s* and 4.82 *t* ($J = 1.2$)
16	2.44 *m*	3.67 *m* ($^3J = 2.7$) ($^5J = 1.2$)	2.55 *m*	1.81 *d* ($^5J = 1.2$)
18		6.00 *d* ($^3J = 7.3$)	2.60 *m*	1.35 *s*
21		6.09 *d* of *d* ($^3J = 7.5$) ($^4J = 1.3$)	2.70 *m*	1.76 *s*
22		4.95 *m* ($^3J = 4.9$)	2.65 *m*	1.84 *s*
23	2.50 *m*	5.91 *d* of *d* ($^3J = 6.7$) ($^4J = 2.0$)	2.40 *m*	1.10 *d* ($^3J = 7.2$)
24		2.40 *m*		1.78 *d* ($^5J = 1.7$)

Table II. *NMR. data of the 2-phenylbicyclo[3.2.1]octene derivatives*

Compound	C(1)	C(2)	C(3)	C(4)	C(5)	C(2) subst.
25	2.52 *m*	4.03 *d* of *m* ($^3J = 4.6$)		6.31 *d* of *d* ($^3J = 6.7$) ($^4J = 1.5$)	2.52 *m*	7.27 *m*
27	2.46 *m*	4.10 *d* of *m* ($^3J = 4.5$) ($^4J = 1.5$)		6.54 *d* of *d* ($^3J = 7.0$) ($^4J = 1.5$)	2.46 *m*	7.25 *m*
29	2.40 *m*	3.86 *d* of *m* ($^3J = 5.0 \pm 1$)	5.50 *d* of *d* of *d* ($^3J = 9.5$) ($^3J = 2.2$) ($^4J = 1.7$)	6.06 *d* of *d* of *d* of *d* ($^3J = 9.4$) ($^3J = 6.6$) ($^4J = 2.5$) ($^4J = 1.2$)	2.40 *m*	7.16 *m*

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