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THE STEREOCHEMISTRY OF BICYCLO[3.2.1]OCTANE—XVIII[1]

THE ADDITION OF MONOCHLOROCARBENE TO BICYCLO[2.2.2]OCTENE-2, 1-METHYL- AND 2-METHYLNORBORNENE-2

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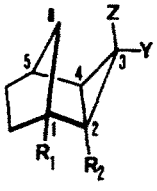
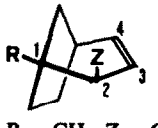
Abstract—Monochlorocarbene undergoes addition to bicyclo[2.2.2]octene-2 to give *anti*- and *syn*-3-chlorotricyclo[3.2.2.$0^{2,4}$]nonane in a ratio of 5:1. On warming the mixture, only the *syn* isomer rearranges to 2-chlorobicyclo[3.2.2]nonene-3. The addition of monochlorocarbene to 1-methylnorbornene-2 affords 1-methyl-*anti*-3-chloro-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane. 1-methyl-*exo*-4-chlorobicyclo[3.2.1]octene-2 and 1-methyl-*exo*-2-chlorobicyclo[3.2.1]octene-3 in a ratio of 3:1:1. Similar addition to 2-methylnorbornene-2 gives 2-methyl-*anti*-3-chloro-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane and 2-methylenebicyclo[3.2.1]octene-3 in a ratio of 10:1. The *exo-anti* tricyclic structures are stable to heat and aqueous silver ion. In contrast, the *exo-syn* adducts are remarkably labile and are assumed to be the precursors of the rearranged products. The factors which govern the stereochemistry of the addition and rearrangement processes are discussed.

INTRODUCTION

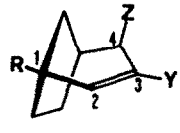
IT IS well established that dihalocarbenes add stereospecifically to simple olefins to give cyclopropanes which may, in appropriate cases, undergo rearrangement or elimination.[3] When a bridged bicyclic olefin is used, the reaction takes on an added dimension of interest. Firstly, because it can afford a useful preparative entry to the next higher homologue from an easily accessible olefin such as norbornene and secondly, because useful insights are obtained into the stereochemistry of the processes of addition and rearrangement.

The reaction of dichlorocarbene with norbornene is typical. Thus the addition occurs *exo* to give *exo*-3,4-dichlorobicyclo[3.2.1]octene-2 (II) which arises by stereospecific rearrangement of the intermediate cyclopropane adduct (I).[4]





XI: R = CH_3, Z = Cl
XIV: R = CH_3, Z = OH



I: $R_1 = R_2 = H$, Y = Z = Cl
III: $R_1 = R_2 = H$, Y = Cl, Z = H
IV: $R_1 = R_2 = H$, Y = H, Z = Cl
X: $R_1 = CH_3$, $R_2 = H$, Y = Cl, Z = H
XIII: $R_1 = CH_3$, $R_2 = H$, Y = H, Z = Cl
XVI: $R_1 = H$, $R_2 = CH_3$, Y = Cl, Z = H
XXIV: $R_1 = H$, $R_2 = CH_3$, Y = H, Z = Cl

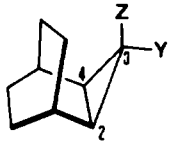
II: R = H, Y = Z = Cl
V: R = H, Y = H, Z = Cl
XII: R = CH_3, Y = H, Z = Cl
XV: R = CH_3, Y = H, Z = OH

The synthetic utility of this route has been demonstrated by the preparation of bicyclo[3.2.1]octanone-3 which can be obtained uncontaminated by its isomers and in reasonable yield from II by reductive dechlorination and by hydrolysis of the vinyl chloride so obtained.[5] When monochlorocarbene is used in place of dichlorocarbene in the reaction, *anti*-3-chloro-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane (III) and *exo*-4-chlorobicyclo[3.2.1]octene-2 (V) are found, thereby showing that it is only a *syn*-disposed chlorine atom which is capable of undergoing the act of migration in the rupture of the *exo*-tricyclo[3.2.1.$0^{2,4}$]octane skeleton (IV → V).[6]

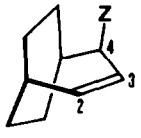
These rearrangements are special cases of the rearrangement of a cyclopropyl compound to its allylic derivative which provide an interesting substantiation of the principle of conservation of orbital symmetry.[7] In the present paper, we have extended our earlier work by examining bicyclo[2.2.2]octene-2 and the 1- and 2-methyl derivatives of norbornene. As we shall see, further information is obtained concerning the nature of the addition process and how orbital symmetry determines the stereochemistry of ring opening and elimination where it occurs.

Proofs of structure of products

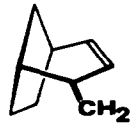
Monochlorocarbene adds to bicyclo[2.2.2]octene-2 to give one extremely stable compound, *anti*-3-chlorotricyclo[3.2.2.$0^{2,4}$]nonane (VII) and two thermally unstable compounds, the *syn* isomer (VI) and 4-chlorobicyclo[3.2.2]nonene-2 (VIII). The structure of VII is based on the tiny value for the vicinal coupling constant of the C_3 proton (^3J = 1·6 Hz) which indicates a *trans* relation to the pair of protons on C_2 and C_4.[8] Evidence for the structure of VI and VIII is circumstantial. The downfield position of the triplet observed at 3·4 ppm in the mixture of products isolated at low temperature is that expected for the less shielded position of the C_3 proton in VI. Moreover, the size of its coupling constant (^3J = 7·7 Hz) corroborates the necessary *cis* relation of the proton to its neighbours[8] The structure of VIII follows from its mild hydrolysis to 4-hydroxybicyclo[3.2.2]nonene-2 (IX), the structure of which is rigorously established by its NMR data.*



VI: Y = H, Z = Cl
VII: Y = Cl, Z = H



VIII: Z = Cl
IX: Z = OH



XVII

Similar addition to 1-methylnorbornene-2 affords one stable, easily isolable 1:1 adduct and a pair of isomeric labile products; viz. 1-methyl-*anti*-3-chloro-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane (X), 1-methyl-*exo*-2-chlorobicyclo[3.2.1]octene-3 (XI) and its allylic isomer, the *exo*-4-chloro compound XII. The *trans* disposition of protons on C_2 and C_4 to the one on C_3 follows from the magnitude of the coupling constant shown by the C_3 proton in X.[8] However, the *exo-anti* structure of X is completely defined by the shielding experienced by both the *syn* and *anti* C_8 protons.[6,10] If the

* [a] The magnitude of the coupling constants obtained by inspection corroborates the basic structure; [b] However, further analysis shows the OH group to be quasiaxial.

chemical shifts of the C_8 protons of X (Table 1) are compared with the value of 1·21 ppm observed for the corresponding protons of norbornane in carbon tetrachloride,* then the observed shieldings of +0·39 and +0·64 ppm not only indicate that the *syn* proton lies closer to the face of the cyclopropane ring than does the *anti*, but that the chlorine atom cannot be contiguous to the *syn* C_8 proton as the latter would be strongly deshielded.

No direct proof is offered for the stereochemistry of the allylic chlorine substituent in XI and XII. An *exo* disposition is assumed by analogy with the reaction of monochlorocarbene with norbornene where the structure of the rearranged 1:1 adduct, i.e. *exo*-4-chlorobicyclo[3.2.1]octene-2, was rigorously established.[1b, 6, 12] However, evidence for the 1-methylbicyclo[3.2.1]octene skeleton rests securely on the mild hydrolysis of XI and XII to their corresponding *exo*-2- and 4-hydroxides (XIV and XV) whose structures are corroborated by their NMR spectra.†

2-Methylnorbornene-2 on treatment with monochlorocarbene gives 2-methyl-*anti*-3-chloro-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane (XVI) and 2-methylenebicyclo[3.2.1]-octene-3 (XVII). The definition of the structure of XVI is made on the basis of its NMR spectral data (Table 1). The small value of the vicinal coupling constant of the C_3 proton (1·5 Hz) and the shielding experienced at C_8 (+0·32 and +0·71 ppm for the *syn* and *anti* protons) confirm the fusion of the cyclopropane ring on the *exo* side of the norbornane skeleton and the *anti* configuration of the C_3 chlorine atom.[8, 10,†] Indeed, the data for X and XVI are closely similar to that for the parent compound III (Table 1). Identification of XVII was based on its spectral data. XVII, like its 3-bromo derivative,[4f] proved very unstable as it appears to polymerize readily.

TABLE 1. NMR AND IR SPECTRAL DATA OF *anti*-3-CHLORO-*exo*-TRICYCLO-[3.2.1.$0^{2,4}$]OCTANE (III) AND ITS 1- AND 2-METHYL DERIVATIVES (X AND XVI)

III[a]	X[b]	XVI[b]	Assignment
t 2·84 ppm (^3J = 1·5 Hz)	t 2·93 ppm (^3J = 1·2 Hz)	d 3·00 ppm (^3J = 1·5 Hz)	C_3
m 2·41	m 2·39	m 2·19	C_5
	—	m 1·97	C_1
m 1·08	m 0·68	d 0·60	C_2 and/or C_4
d 0·91 ($^2J \sim$ 10·5 Hz)	d 0·82 ($^2J \sim$ 10·5 Hz)	d 0·89 ($^2J \sim$ 11·0 Hz)	C_8 *syn*
d 0·66 ($^2J \sim$ 10·5 Hz)	d 0·57 ($^2J \sim$ 10·5 Hz)	d 0·50 ($^2J \sim$ 11·0 Hz)	C_8 *anti*
—	s 1·36	s 1·26	methyl
IR max 782 cm^{-1}	776 m^{-1}	782 cm^{-1}	C-Cl stretching

[a] In CCl_4.
[b] In $CDCl_3$.

* The comparison is still valid since the solvent shift should be trivial.[11]
† See footnote *b* on page 2090.

DISCUSSION

The addition process

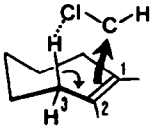
On examining the product ratios it is seen that in all cases addition occurs in the *syn* and *anti* senses and always on the *exo* side of the norbornenes. Table 2 records the *syn/anti* ratios and includes those for norbornene and cycloheptene by way of comparison.

TABLE 2. STEREOSELECTIVITY OF THE ADDITION OF MONOCHLOROCARBENE TO VARIOUS OLEFINS

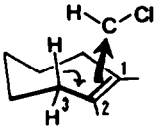
	Syn/Anti ratio
Norbornene-2	1 to 6
Bicyclo[2.2.2]octene-2	1 to 5
1-Methylnorbornene-2	1 to 1·5
2-Methylnorbornene-2	1 to 9·8
Cycloheptene	1 to 0·33

The occurence of *exo* cyclopropanation is explicable in terms of the conventional notion of the lack of encumbrance on the *exo* face of the double bond as well as the *exo* directionality of reagent approach favored by the operation of torsional interactions in the transition state.[13] Of course, the importance of torsional interactions will depend largely on whether attack occurs simultaneously at C_2 and C_3 or in a less symmetrical manner (*v. infra*) and also on the compactness of the transition state. The high exothermicity of the addition process suggests that the transition state resembles reactants rather products.[4c] Thus, the change in hybridization of the olefinic carbon atoms may not have progressed far which in turn means that the corresponding alterations in the torsional interactions at the bridgeheads could be slight. Under such circumstances, it appears that steric effects could be influential in deciding product composition. Indeed, this expectation is supported by the sensitive variation of the orientation of the addend with respect to substitution which is found.

The *syn/anti* ratios for the bicyclic olefins are remarkable as they are the opposite of those usually found for the commoner olefins belonging to the C_h and C_{2v} point groups which are typified by the entry for cycloheptene (Table 2). The *syn*-stereoselectivity generally observed by chlorocarbene has been ascribed to the electrostatic attraction resulting from hyperconjugation which outweighs the steric repulsion entailed for the *syn* addition mode.[14] Thus as electron density is fed from the C_1—C_2 π bond of cycloheptene, for example, to the electrophilic carbene species, hyperconjugative release creates partial positive charge at C_3 which favors the *syn* over the *anti* disposed chlorine atom (XVIII *vs* XIX).

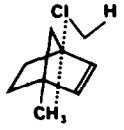


XVIII

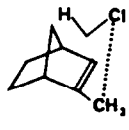


XIX

Bridging such a monocyclic olefin will render the geometry required for this hyperconjugative effect unattainable. This is, of course, the situation found in bicyclo[2.2.2]octene-2 and norbornene. Accordingly, dispersion forces should be left to decide the orientation ratio. Dispersion forces may favor either the *syn* or *anti* addition modes inasmuch as they can be repulsive or attractive depending on the dimensions of the transition states in question. Evidently, in the bridged bicyclic olefins the closeness of the ethylene and methylene bridges to the incoming carbene tips the balance in favor of *anti* addition. Norbornene gives mainly the *anti* adduct, somewhat more so than does bicyclo[2.2.2]octene-2. However, substitution by methyl on norbornene brings about a dramatic change in the *syn-anti* ratio. Substitution at C_1 has plainly increased *syn* addition. The only reasonable explanation for this result is that *attractive* dispersive forces between the methyl group and the chlorine atom of the attacking species favor *syn* over *anti* addition (XX). On the other hand, when the methyl group is substituted on C_2, then its attractive effect compels a marked preference for the *anti* addition mode (XXI).



XX



XXI

So far the carbene transfer process has not been unequivocally specified. It could involve the free carbene or dichloromethyllithium in the addition step. Nevertheless the foregoing description remains valid since the spatial symmetry requirements lead in each case to two diastereomeric *exo* transition states.[15] For bent chlorocarbene[16] undergoing addition to norbornene in a lop-sided approach, a *syn* or *anti* orientation of the addend is possible.[17a]* On the other hand, if dichloromethyllithium is the attacking species, the distinction between the two addition modes still exists as the chlorine atoms are enantiotopic.[15]

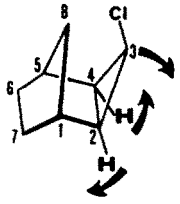
The rearrangement process

The salient features of the addition, as illustrated by the reaction of 1-methylnorbornene, are that the major product, the *exo-anti*-3-chlorocyclopropane adduct (X) is resolutely stable and that no *endo* products are observed. Consequently, the minor products, the *exo*-2-chloro- and *exo*-4-chloro-1-methylbicyclo[3.2.1]octenes (XI and XII) arise from the rearrangement of their presumed common precursor, 1-methyl-*syn*-3-chloro-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane (XIII). This is a perfectly reasonable presumption in view of the observable rearrangement of *syn*-3-chlorotricyclo-[3.2.2.$0^{2,4}$]nonane (VI → VIII). Therefore, the key to rearrangement of the cyclopropane adduct lies in the configuration of the cyclopropyl chlorine substituent which determines uniquely whether the cyclopropane ring will open or not.

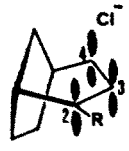
In a general way, the stereochemistry of cyclopropyl-allyl transformation has been explicitly treated from the point of view of orbital symmetry for the hypothetical

* For the possible intermediacy of linear monochlorocarbene, the stereochemistry of addition will be slightly modified in that approach is expected to be symmetrical to the double bond.[17b]

cases of the cations and anions.[7,18] For the transformation of the cyclopropyl cation, the symmetry of the highest occupied orbital of the derived allyl cation dictates that a disrotatory rupture of the appropriate C—C sigma bond take place.[18a] In principle, *two* disrotatory modes may be distinguished. However, for structures such as *exo*-tricyclo[3.2.1.$0^{2,4}$]octane (XXII) only one mode is allowed as the other is not mechanically achievable. The only way the C_2—C_4 bond can break in XXII is by the movement of C_3 towards the *endo* side with an accompanying moving apart of the protons on C_2 and C_4. This mechanical movement is expected to be aided by the relief of the strain associated with the regular boat conformation of the skeleton attached to the ethane bridge (C_6 and C_7). Similar considerations apply to the tricyclo[3.2.2.$0^{2,4}$]nonane skeleton, although the tendency to rearrangement should be smaller as the inherent strain is less than in XXII. However, despite the latent driving force accruing from the release of strain, rearrangement only occurs when the leaving group at C_3 has the *syn* configuration. A conclusion which may be drawn is that only a *syn*-disposed chlorine atom can ionize and that when it does, the positive charge so created at C_3 is immediately dispersed to C_2 and C_4 by disrotatory rupture of the bond that joins them on execution of the geometrically allowed skeletal motion.* Therefore on the principle of least motion,[20] a cyclohexenyl cation closely paired to a chloride ion is generated (e.g. XXIII) which then collapses by re-attachment of chlorine to the *exo* side of C_2 or C_4.



XXII



XXIII: R = H
XXV: R = CH_3

However, the fact that these rearrangements occur extremely readily in non-ionizing media, suggest that the rearrangement could also be a fully concerted process which by-passes the ionic intermediate. Unfortunately, the present results do not permit a distinction between these possibilities.† The same considerations apply when rearrangement is accompanied by elimination. Reaction of chlorocarbene with 2-methylnorbornene-2 gives 2-methyl-*anti*-3-chloro-*exo*-tricyclo[3.2.1.$0^{2,4}$]-octane (XVI) as the chief product. Although the loss of a molecule of hydrogen chloride is formally possible, it does not happen, as XVI is unable for reasons of orbital symmetry to ionize or to rearrange to the ionizable allylic derivative. On the other hand, the minor product, 2-methylenebicyclo[3.2.1]octene-3 (XVII) derives from its undoubted precursor, 2-methyl-*syn*-3-chloro-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane (XXIV) either by losing hydrogen chloride directly in one step (XXIV → XVII) or by shedding a proton from the cation obtained on ionic rearrangement (XXIV → XXV → XVII).

* In the solvolysis of cyclopropyl derivatives ample evidence exists that ionization proceeds in step with ring opening.[19]

† Of course, similar considerations apply to other recently reported cases of the transposition of both the *exo*- and *endo*-tricyclo[3.2.1.$0^{2,4}$]octane skeleton.[22]

EXPERIMENTAL

B.ps are uncorrected. IR spectra were recorded as films on a Perkin–Elmer Model 137-B Infracord spectrometer (NaCl prism, calibrated with a film of polystyrene). NMR spectra were taken on Varian Associates Model A-60-A and HR-100 instruments in $CDCl_3$ as solvent. Chemical shifts are expressed as ppm using TMS as internal standard (TMS = 0). Coupling constants are in c/s (Hz) and the form of the signals is expressed as s = singlet; d = doublet; t = triplet; and m = multiplet. Microanalyses were performed by Dr. G. Robertson, Jr., Florham Park, N.J., U.S.A.

General procedure for the addition of monochlorocarbene to bridged bicyclic olefins. The procedure used was essentially that of Closs and Closs.[21] The olefin was mixed with CH_2Cl_2. After flushing the entire apparatus with dry N_2, MeLi soln in ether (free from LiBr, Foote Mineral Company, Exton, Pa.) was added dropwise with stirring to the olefin soln. As the addition proceeded, gentle boiling under reflux (using a condenser cooled with a mixture of solid CO_2 and acetone) occurred along with the formation of a ppt of LiCl. After the addition was complete, the reaction mixture was allowed to cool to 25° after which it was poured onto its own volume of water and crushed ice. The layers were separated and the water layer was extracted with ether. The organic layers were combined and dried over $MgSO_4$. The ether and excess olefin were removed by distillation and finally the resultant oil was fractionally distilled at a convenient press.*

A. *Addition of monochlorocarbene to bicyclo*[2.2.2]*octene*-2. Freshly sublimed bicyclo[2.2.2]octene-2 (25 g; 0·23M) in anhyd ethyl ether was allowed to react with a mixture of CH_2Cl_2 (15·3 g; 0·18M) and MeLi (1·7M soln; 105 ml; 0·18M). Ether and unreacted starting material were removed by a combination of distillation and sublimation. Distillation *in vacuo* of the residue afforded a colorless oil (b.p. 59–61°/2 mm; 1·54 g; 5·5% yield). The NMR spectrum showed a multiplet centred at 5·91, a multiplet at 4·85 and a narrow triplet at 3·07 ppm indicative of vinyl protons, an allylic proton and a deshielded cyclopropyl proton respectively. The ratio of the intensities of the last two signals was habitually 5 to 1 in several experiments. When solvent and unreacted olefin were removed at temps below 60°, then an additional signal, a wide triplet at 3·40 ppm (^3J = 7·7 Hz), was distinctly visible in the NMR spectrum of the resulting oil. On gently heating the sample, the signal at 3·40 ppm progressively diminished as the signal at 4·85 ppm increased in intensity.

Thus reaction has afforded *syn* and *anti*-3-chlorotricyclo[3.2.2.0^{2,4}]nonane (VI and VII) and VIII. Separation of the chlorides was prevented by the facile conversion of VI to VIII and the decomposition of the latter. Accordingly, the mixture of VII and VIII was treated with $AgNO_3$ aq.

B. To a soln of the mixture of VII and VIII (1·46 g) in 50% aqueous acetone (45 ml), a soln of $AgNO_3$ (0·75 g) in water (7·5 ml) was added. The reaction mixture was heated under reflux for 3 hr and then diluted with water and extracted with ether. Work-up in the usual manner (*v. supra*) gave a yellowish oil (1·29 g). Separation of the two components was carried out by preparative TLC on silica gel (on a 10 × 10 inch plate), using a soln of 10% EtOAc in cyclohexane as eluent. From 500 mg of mixture, 431 mg of VII as an oil and 48 mg of IX as a solid (m.p. 113–116° (sublimes)) were obtained.

anti-3-*Chlorotricyclo*[3.2.2.0^{2,4}]nonane (VII). The NMR spectrum showed signals at 3·07 (^3J = 1·6 Hz, intensity 1H due to the proton on C_3), 1·98 (unresolved m; 2H; C_1 and C_5), 1·51 (unresolved m; 4H; C_6C_7) and 1·30 ppm (unresolved m; 6H; C_2, C_4, C_8 and C_9). (Found: C, 69·26; H, 8·39; Cl, 22·50. Calcd. for $C_9H_{13}Cl$ (156·65): C, 69·00; H, 8·36; Cl, 22·64%).

2-*Hydroxybicyclo*[3.2.2]*nonene*-3 (IX). The IR spectrum showed max at 3300, 1650, 1011 and 862 cm^{-1}; The NMR spectrum showed signals at 6·04 (d of d of d; $^3J_{large}$ = 10·6; $^3J_{medium}$ = 8·2; $^4J_{small}$ = 1·3 Hz; intensity 1H due to C_4 proton), 5·5 (d of d of d of d; $^3J_{large}$ = 10·6; $^3J_{medium}$ = 3·3; $^4J_{small}$ = 1·8; $^4J_{small}$ = 0·8 Hz; 1H; C_3 proton) and 4·35 ppm (t of d of d; $^3J_{medium}$ = 3·3; $^4J_{small}$ = 1·3 and $^4J_{small}$ = 0·8 Hz; 1H; C_2 proton). (Found: C, 78·01; H, 10·14. Calcd. for $C_9H_{14}O$ (138·20): C, 78·21; H, 10·21%).

C. *Addition of monochlorocarbene to* 1-*methylnorbornene*-2. Freshly distilled 1-methylnorbornene-2 (108 g; 1M) was allowed to react with CH_2Cl_2 (63·75 g; 0·75M) and MeLi (1·62M soln; 480 ml; 0·75M). Distillation afforded a colorless oil (b.p. 56–59°/4·5 mm; 13·33 g; 6·7%). The NMR spectrum showed multiplets at 5·79 and 4·25 ppm indicative of vinylic and allylic protons and a narrow triplet at 2·93 ppm due to a deshielded cyclopropyl proton. The ratio of intensities of the last two signals was 1·5 to 1 in several experiments. It was not possible to separate this mixture of XI, XII and X due to the facile thermal decomposition of XI and XII.† Accordingly, treatment with aqueous silver nitrate was carried out.

* We thank R. T. Medary for carrying out the control experiment with cycloheptene.

† Similar difficulties were encountered when norbornene was used (Ref. 6).

D. To a soln of the mixture of X, XI and XII (5 g) in 50% aqueous acetone (50 ml), a soln of $AgNO_3$ (5 g) in water (10 ml) was added. The mixture was heated under reflux for 1 hr. The ppt was removed by filtration and the filtrate was worked-up in the usual way. A yellowish oil was obtained (4·02 g). This oil was chromatographed over silica gel (80 g). Petroleum ether eluted X (2·63 g) as an oil. Elution with 18 and 20% ethyl ether in pet ether yielded XIV (0·5 g) m.p. 44·5–46° and XV (0·51 g, an oil) respectively.

1-*Methyl*-anti-3-*chloro*-exo-*tricyclo*[3.2.1.$0^{2,4}$]*octane* (X). For IR and NMR data see Table 1. (Found: C, 69·08; H, 8·33; Cl, 22·79. Calcd. for $C_9H_{13}Cl$ (156·65): C, 69·00; H, 8·36; Cl, 22·64%).

1-*Methyl*-exo-2-*hydroxybicyclo*[3.2.1]*octene*-3 (XIV). The IR spectra showed characteristic max at 3345, 3012, 1645, 1009, 762 and 742 cm^{-1}. The NMR spectrum showed signals at 6·08 (d of d of d, $^3J_{large}$ = 9·4, $^3J_{medium}$ = 6·6 and $^4J_{small}$ = 0·8 Hz; intensity 1H due to the C_4 proton), 5·53 (d of d, $^3J_{large}$ = 9·4, $^3J_{medium}$ = 4·0 Hz, 1H, C_3 proton), 3·50 (d, ^3J = 4·0 Hz, 1H, C_2 proton), 2·50 (broad m, 1H, C_5 proton) and 1·17 ppm (s, 3H, Me group). (Found: C, 78·00; H, 10·20. Calcd. for $C_9H_{14}O$ (138·20): C, 78·21; H, 10·21%).

1-*Methyl*-exo-2-*hydroxybicyclo*[3.2.1]*octene*-2 (XV). The IR spectra showed characteristic max at 3322, 3003, 1642, 1026 and 765 cm^{-1}. The NMR spectrum showed signals at 5·79 (d of d, $^3J_{large}$ = 9·5, $^4J_{small}$ = 1·4 Hz, intensity 1H, due to the C_2 proton), 5·45 (d of d of d, $^3J_{large}$ = 9·5, $^3J_{medium}$ = 3·7 and $^4J_{small}$ = 1·6 Hz, 1H, C_3 proton), 3·73 (poorly resolved d of d; $^3J_{medium} \sim 3·6$ and $\sim 2·8$ Hz, 1H, C_4 proton), 2·29 (broad m, 1H, C_5 proton) and 1·16 ppm (s, 3H, Me group). Found: C, 78·61; H, 10·29. Calcd. for $C_9H_{14}O$ (138·20): C, 78·21; H, 10·21%).

E. *Interaction of monochlorocarbene and 2-methylnorbornene.* Freshly distilled 2-methylnorbornene (108 g; 1M) was allowed to react with CH_2Cl_2 (63·75 g; 0·75M) and MeLi (1·62M soln: 480 ml; 0·75M). The bulk of the ether and unreacted olefin was removed under vacuum through a column packed with hollow glass beads. The temp of the distillation flask was kept at 35–40°. The residue, still containing some ether and 2-methylnorbornene, was distilled under reduced press with a solid CO_2–acetone trap installed between the pump and the distillation apparatus. A colorless oil was obtained (b.p. 55·61°/4 mm; 14·60 g). There was a very small (ca. 0·2 g) residue after distillation. The NMR spectrum of the distillate indicated the presence of two compounds (a vinylic resonance centred at 6·02 ppm; an allylic resonance at 4·61 ppm; and a cyclopropyl resonance at 3·10 ppm). From the solid CO_2–acetone trap, 12·0 g of a mixture of ether, 2-methylnorbornene and XVII were recovered. Estimations obtained from the integration of the appropriate NMR signals put the *syn/anti* adduct ratio at 1 to 9·8. All attempts at separation of XVII by distillation, VPC or column chromatography were unsuccessful. By heating the mixture at 35° under vacuum (2 mm) a colorless oil was collected in the solid CO_2–acetone trap. The NMR spectrum showed that it consisted of XVII contaminated by about 15% of XVI. The latter compound was purified by filtration over silica gel.

2-*Methyl*-anti-3-*chloro*-exo-*tricyclo*[3.2.1.$0^{2,4}$]*octane* (XVI). For IR and NMR data see Table 1. (Found: C, 69·27; H, 8·34; Cl, 22·49. Calcd. for $C_9H_{13}Cl$ (156·65): C, 69·00; H, 8·36; Cl, 22·64%).

2-*Methylenebicyclo*[3.2.1]*octene*-3 (XVII). The IR spectrum showed max at 1639, 1605 and 878 cm^{-1} characteristic of an α,β-diene possessing an exocyclic methylene group. The NMR spectrum showed a multiplet centred at 6·02 ppm (2H, due to the C_3 and C_4 protons) and signals centered at 4·66, and 4·56 ppm consisting of apparent doublets 2 Hz wide (2H, due to the geminal exocyclic methylene protons). XVII was too unstable for a satisfactory elemental analysis.*

F. *Stability test for tricyclic compounds* VII, X *and* XVI. All three compounds were stable under the following experimental conditions: heating to 120° for 1 hr and heating under reflux in a soln of 50% aqueous acetone for 24 hr in the presence of Ag cation.

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* Compare the similar properties of 2-methylene-3-bromobicyclo[3,2,1]octene-3 (Ref. 4[f]).

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