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ORGANIC MASS SPECTROMETRY—V*

MASS SPECTRA OF BICYCLO[2.2.1]HEPTANE AND BICYCLO[2.2.2]OCTANE DERIVATIVES

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Abstract—Mass spectra of bicyclo[2.2.1]heptane and bicyclo[2.2.2]octane derivatives have been recorded. The elimination of $CH_2{=}CH_2$, CO, $CH_2{=}CO$, or $CH_2{=}CHOH$ by a retro-Diels–Alder reaction, whenever possible, is a very favorable process. Acetylene is not easily eliminated by the same mechanism, instead aromatization by loss of one or two hydrogen atoms becomes prominent. In the case of saturated compounds, rupture of one bond followed by hydrogen migration with formation of an ethyl radical is a more favorable process than the simple elimination of ethylene to produce a radical ion.

SEVERAL investigators have reported mass spectra of bicyclo[2.2.1]heptane (norbornane) derivatives in connection with the studies of monoterpenoids. Reed,[1] and Ryhage and Sydow[2–4] obtained mass spectra of some of bicyclic hydrocarbons, alcohols and ketones related to natural monoterpenoids, but as the compounds studied were limited and variation of their structures not systematic, general patterns of fragmentations have not been established. Meyerson *et al.*[5] discussed a detailed fragmentation of bicycloheptadiene in comparison with other C_7H_8 hydrocarbons (see below). In order to obtain general fragmentation modes of bridged bicyclic systems, mass spectra of bicyclo[2.2.1]heptane and bicyclo[2.2.2]octane derivatives have been examined.

The compounds are arranged into four groups.

Group 1. The characteristic structural features of the bicyclic ring are a double bond (or a benzene residue) and a two-carbon bridge (or C=O) such that upon electron impact a $CH_2{=}CH_2$, $CH_2{=}CO$ or $CH_2{=}CHOH$ (or C=O) group may be eliminated

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* Paper IV in this series: A. Tatematsu, T. Goto and S. Matsuura, *J. Chem. Soc. Japan* **87**, 71 (1966).

[1] R. J. Reed, *Mass Spectra of Terpenes* in F. W. McLafferty, *Mass Spectrometry of Organic Ions* Chap 10. New York (1963). Among the compounds referred, norcamphane and two methylnorbornenes are closely related to the compounds discussed in this paper. Although the author discussed fragmentations of these compounds, the spectrum of norcamphane differs from ours, and in the case of methylnorbornenes, we do not agree with the formulation of the most important fragmentation process.

[2] R. Ryhage and E. von Sydow, *Acta Chem. Scand.* **17**, 2025 (1963).

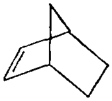
[3] E. von Sydow, *Acta Chem. Scand.* **17**, 2504 (1963).

[4] E. von Sydow, *Acta Chem. Scand.* **18**, 1099 (1964).

[5] S. Meyerson, J. D. McCollum and P. N. Rylander, *J. Amer. Chem. Soc.* **83**, 1401 (1961).

by a retro-Diels–Alder (RDA) type fragmentation to produce a residual fragment ion which appears as a base peak (except 8). For example, benzobicyclo[2.2.1]heptane (IV) shows the strongest peak at *m/e* 116, which corresponds to M-28. That the fragmentation is not a "random" process,[6] but the RDA type to eliminate the 5,6-ethylene bridge selectively is indicated by the mass spectrum of *exo,exo*-2,3-dideuteriobenzobicyclo[2.2.1]heptane (IVa); the M-28 ion in the spectrum contains

Group 1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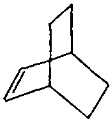
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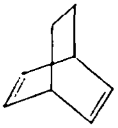
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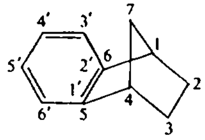

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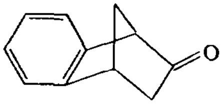

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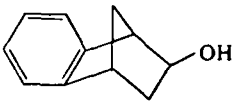

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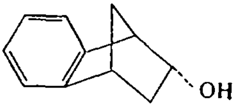

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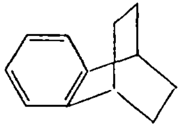
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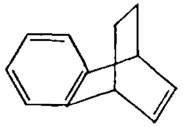
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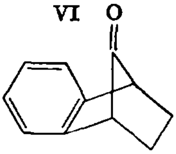

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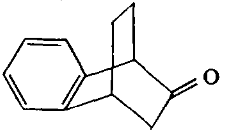

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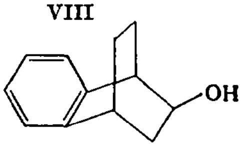

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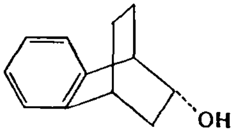

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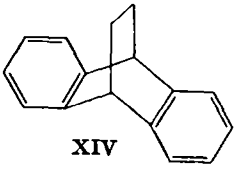
XIV

TABLE 1. PARTIAL MASS SPECTRA OF THE COMPOUNDS IN GROUP 1 (intensity is in parentheses)

Compd.	M	M-15	RDA	RDA-1	RDA-2	RDA-15
I	94(20)	79(20)	66(100)	65(7)	—	51(20)
II	108(16)	—[a]	80(100)	79(33)	—	—
III	106(0)	—	78(100)	77(11)	—	—
IV	144(39)	129(29)	116(100)	115(33)	—	—
V	158(27)	—	116(100)	115(37)	—	—
VI, VII	160(15)	—	116(100)	115(28)	—	—
VIII	158(47)	—	130(77)	129(100)	128(33)[b]	—
IX	156(3)	—	128(100)	127(11)	—	—
X	158(0)	—	130(100)	129(53)	128(23)	115(35)
XI	172(25)	—	130(100)	129(50)	128(65)[c]	115(27)
XII, XIII	174(22)	—	130(100)	129(34)	128(21)	115(18)
XIV	206(17)	—	178(100)[d]	—	—	—

[a] No indication means that the intensity of the corresponding peak is less than 6 % of the base peak.
[b] A metastable peak is observed at *m/e* 103·8 which corresponds to the process *m/e* 158 → 128.
[c] A metastable peak is observed at *m/e* 95·1, which corresponds to the process *m/e* 172 → 128.
[d] *m/e* 89 = 178/2 (21) peak is observed.

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[6] F. W. McLafferty, *Analyt. Chem.* **31**, 82 (1959).

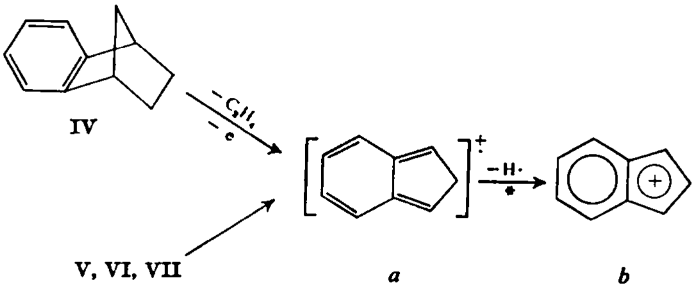
no deuterium atom (Table 2). Since the spectrum does not alter by changing the temperature of the inlet system of the mass spectrometer from 100° to 220°, the fragmentation is not due to thermal decomposition.

The ion at *m/e* 115 is produced from *m/e* 116 ion by elimination of a hydrogen atom and probably not from the molecular ion since a metastable peak is observed only for the process 116 → 115 and not for 144 → 115. Bicyclo[2.2.1]heptane (XV), which cannot undergo the RDA reaction, shows a metastable peak for the process 96 → 67. Hence elimination of ethylene from the molecular ion is possibly a one-step reaction. If it were a two-step reaction, then during the elimination of the two-carbon fragment, hydrogen migration, which is always observed with the saturated bicyclic compounds (group 2), should occur.

TABLE 2. PARTIAL MASS SPECTRA OF BENZOBICYCLOHEPTENE (IV) AND ITS DIDEUTERIO DERIVATIVES (IVa AND IVb)

m/e	IV	*exo,exo-* IVa	*endo,endo-** IVb
147		3·5	16·5
146		23·5	26·5
145	4·5	11·5	8·5
144	38·5	4·0	3·0
143	2·5	1·5	2·0
132			6·0
131		6·0	19·0
130	4·0	21·0	29·5
129	28·5	16·5	16·5
128	14·0	11·5	9·0
127	4·5	6·0	3·0
118			15·0
117	10·5	14·0	61·5
116	100·0	100·0	100·0
115	33·0	28·5	26·5

* The mass spectrum indicated that the material employed here was contaminated with about 30% of trideuterio derivatives. The synthetic method induced some D exchange of aromatic ring protons (Experimental).



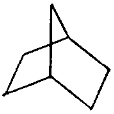
Mass spectra of 2-keto (V) and 2-hydroxy (*exo*, VI; *endo*, VII) derivatives of IV also show similar peaks at *m/e* 116 and 115, indicating that $CH_2{=}CO$ and $CH_2{=}CHOH$ molecules can also be eliminated by the RDA mechanism.

The bicyclo[2.2.2]octane series show similar fragmentation patterns, but benzobicyclo[2.2.2]octene (VIII) is an exception. Although it contains a benzene ring, its mass spectrum is similar to compounds in Group 2.

The M-15 peak in the spectrum of benzobicyclo[2.2.1]heptene (IV) might correspond to the elimination of the bridge-methylene group with a hydrogen migration. However, the spectra of *exo,exo*- and *endo,endo*-2,3-dideuterio derivatives (IVa and IVb) are very similar to each other and the most intense peak around the M-15 region appears at *m/e* 130 in both spectra, suggesting that it is not necessarily the bridge-methylene group which is eliminated as a methyl radical. Such a random rearrangement has been predicted by Biemann[7] in the case of the M-15 peak of I.

Group 2. This group contains compounds having no carbon-carbon double bond or benzene ring in the bicyclic system. The RDA fragmentation is not possible and hence simultaneous fission of two bonds to eliminate a two-carbon neutral fragment (C_2) is not a favorable process. Instead, rupture of a bond with a hydrogen transfer, followed by elimination of a two-carbon fragment (C_2 + H) as a radical becomes an important process. Metastable peaks corresponding to the processes *m/e* 96 → 67, 110 → 67, and 110 → 81 are found in the mass spectra of XV, XVI and XIX respectively, indicating the presence of one-step loss of an ethyl or a CH_3CO radical (C_2 + H) from the molecular ion.

Group 2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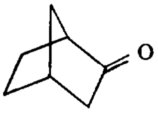
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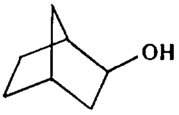
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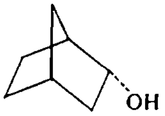
XVIII

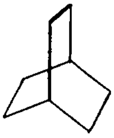
XIX

TABLE 3. PARTIAL MASS SPECTRA OF THE COMPOUNDS IN GROUP 2

Compd.	M	M-15	M-C_2[a]	M-(C_2 + H)[b]	M-(C_2 + 2H)[c]	M-18	
XV	96(33)	81(83)	68(79)	67(100)	—	—	—
XVI	110(41)	—	68(22)	67(93)	66(100)		81(19)
XVII, XVIII	112(3)	—	68(74)	67(90)	66(74)	94(100)	79(88)
XIX	110(67)	95(11)	82(56)	81(78)	80(11)	—	—

[a] Loss of a C_2-fragment without rearrangement.

[b] Loss of a C_2-fragment with transfer of a hydrogen.

[c] Loss of a C_2-fragment with transfer of two hydrogens.

Group 3. These compounds can eliminate an acetylene molecule by (formal) RDA type mechanism, but this process is not favorable as compared with loss of ethylene in the case of group 1, since the spectra show an intense parent peak and since the M-26 peak is rather weak. Instead, they show a prominent M-1 peak.

The fragmentation of bicyclo[2.2.1]heptadiene (XX) has been discussed by Meyerson *et al.*,[5] and the same mechanism seems to be applicable to benzobicyclo-[2.2.1]heptadiene (XXI). Elimination of a hydrogen atom from the molecular ion is

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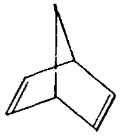
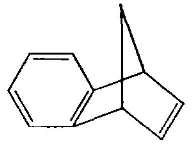
[7] K. Biemann, *Mass Spectrometry-Organic Chemical Applications* p. 138. McGraw-Hill, New York (1962).

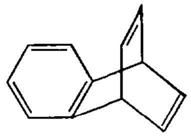
Group 3



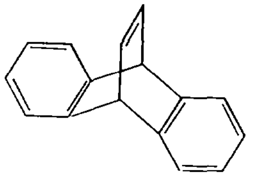
XX



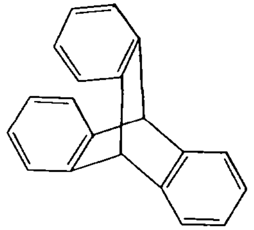
XXI



XXII



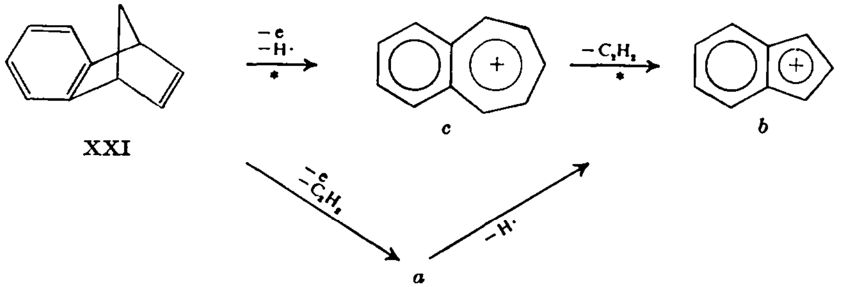
XXIII



XXIV

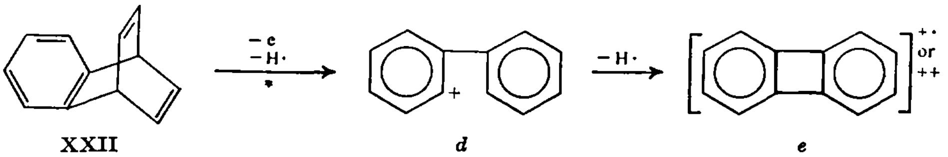
TABLE 4. PARTIAL MASS SPECTRA OF THE COMPOUNDS IN GROUP 3

Compd.	M	M-1	M-2	RDA	(M-1)-26	(M-2)/2
XX	92(50)	91(100)	—	66(51)	65(21)	—
XXI	142(91)	141(100)	—	116(17)	115(37)	—
XXII	154(66)	153(100)	152(28)	128(18)	—	76(22)
XXIII	204(100)	203(70)	202(40)	178(8)	—	101(28)
XXIV	254(100)	253(92)	252(46)	—	—	126(37)



facilitated by the formation of the stable benzotropylium ion (*c*), which then decomposes by expulsion of an acetylene molecule to form indenyl ion (*b*), while a RDA fragmentation gives an isoindene ion (*a*) to a minor extent.

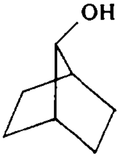
Bicyclo[2.2.2]octatriene derivatives (XXII to XXIV) give a fairly intense M-2 peak as well as a prominent M-1 peak. Fragmentation of benzobicyclo[2.2.2]octatriene (XXII), for example, may be represented as follows:



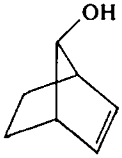
The RDA fragmentation leading to the M-26 ion is also operating but only to a minor extent, and the absence of the (M-1)-26 peak suggests that the M-1 ion is not a tropylium derivative. The doubly-charged M-2 peak appears in each of the spectra as strong as the singly-charged M-2 peak. Such a high stability of the doubly-charged ion is not unexpected since it is an even-electron ion having a polycyclic aromatic system.

Group 4. The compounds in this group have a hydroxyl group on the methylene bridge, and their mass spectra exhibit strong M-29 and M-31 peaks, which may be derived from the molecular ion by expulsion of a CHO and CH_2OH group, respectively. Deuterium labelling experiments with *anti*-7-benzobicyclo[2.2.1]heptenol (XXX; Table 6) shows that the hydrogen atom of the CHO fragment comes from Ha, whereas both Ha and Hb are involved in the CH_2OH fragment.

Group 4



XXV



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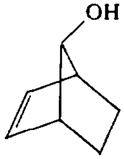
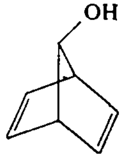
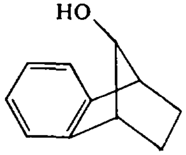


XXVII



XXVIII



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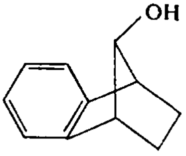

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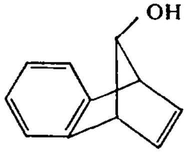
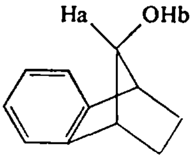


XXXI

TABLE 5. PARTIAL MASS SPECTRA OF THE COMPOUNDS IN GROUP 4

Compd.	M	M-15	M-18	M-19	M-29	M-31	M-33
XXV	112(16)	97(13)	94(100)	—	83(32)	81(61)	79(100)
XXVI, XXVII	110(48)	95(32)	92(28)	91(23)	81(68)	79(100)	77(40)
XXVIII	108(9)	107(47)[a]	—	91(26)[b]	79(100)	77(45)	—
XXIX	160(13)	—	142(13)	141(13)	131(100)	129(36)	—
XXX	160(18)	—	142(5)	141(5)	131(100)	129(37)	—
XXXI	158(18)	—	—	141(7)[b]	129(100)	127(23)	128(44)[c]

[a] M-1 peak.
[b] M-17 peak.
[c] M-30 peak.



XXX

The prominent M-1 peak (*m*/*e* 107) in the spectrum of XXVIII is possibly the hydroxytropylium ion. The *m*/*e* 91 and 141 peaks correspond to the tropylium and benzotropylium ion (*c*), respectively.

Syntheses of deuterated compounds. Treatment of benzobicyclo[2.2.1]heptadiene (XXI) with butyl sodium and deuterium oxide by the application of the procedure reported for the preparation of 2,3-dideuterionorbornene[8] afforded 2,3-dideuteriobenzobicyclo[2.2.1]heptadiene (XXIa), which was subjected to catalytic hydrogenation giving *endo*,*endo*-2,3-dideuteriobenzobicyclo[2.2.1]heptene (IVb). Catalytic reduction of XXI with deuterium afforded the *exo*,*exo*-2,3-dideuterio isomer (IVa). The structures of these deuterated compounds and the below-described alcohol XXXa were proved by examination of their NMR spectra (Experimental and Ref. 27). The stereospecific course of catalytic reduction of norbornadiene was recently reported by Arnold *et al.*[9]

TABLE 6. PARTIAL MASS SPECTRA OF *anti*-7-BENZOBICYCLOHEPTENOL (XXX) AND ITS MONODEUTERIO DERIVATIVES (XXXa AND XXXb)

m/*e*	XXX	7-Deuterio compd. (XXXa)	*O*-Deuterio compd.* (XXXb)
162		2·5	2·0
161	2·5	17·0	17·0
160	17·5	4·0	8·0
143		5·5	2·0
142	5·0	5·5	8·5
141	5·0	2·0	7·0
133		4·0	13·5
132	14·5	24·0	100·0
131	100·0	100·0	46·5
130	7·0	11·5	14·5
129	37·0	42·0	56·0
128	15·5	17·0	20·0
127	7·5	7·5	9·5
118			2·5
117	3·0	3·5	5·0
116	10·0	9·0	15·5
115	12·5	9·0	14·0

* The sample was prepared in an inlet system of the mass spectrometer by mixing XXX with D_2O and the spectrum was recorded after evaporation of the solvent under vacuum.

LAD reduction of benzobicyclo[2.2.1]hepten-7-one (X) yields 7-deuteriobenzobicyclo[2.2.1]hepten-*anti*-7-ol (XXXa) and *syn*-7-ol in a ratio of 70:30. Separation of these alcohols was carried out by elution chromatography over florisil.

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EXPERIMENTAL

Materials. Bicyclo[2.2.1] heptane derivatives, I, XV, XVI and XX were commercial products redistilled before use. Other bicyclic hydrocarbons, II[10], III[11], IV[12], VIII[13,14], IX[13,15], XIV[16], XIX[11], XXI,[12] XXII,[13,17] XXIII,[16] XXIV,[18] ketones, V,[19] X,[19,20] XI[13] and alcohols, VI, VII,[19] XII, XIII,[13] XVII, XVIII,[21] XXV,[22] XXVI,[23] XXVII,[24] XXVIII,[24–26] XXIX,[20] XXX,[19,20] XXXI,[19,26] were prepared by known methods.

exo, exo-2,3-*Dideuteriobenzobicyclo*[2.2.1]*heptene* (IVa). Catalytic reduction of XXI was carried out over PtO$_2$ with the absorption of D in AcOEt. The usual work-up procedure followed by distillation gave an oil, b.p. 96–98° (25 mm). The NMR spectrum of this product in CCl$_4$[27] showed 4 aromatic protons around τ 3 (A$_2$B$_2$ multiplet), two bridgehead protons at τ 6·70 (multiplet), one C$_7$-*syn*-proton at τ 8·27 (doublets of quartet), one C$_7$-*anti*-proton at τ 8·52 (multiplet), and two C$_2$,C$_3$-*endo*-protons centered at τ 8·86 (broad singlet). Mass spectrum of this compound indicates the presence of d$_3$-, d$_2$-, and d$_1$-compound in the ratio of 3:65:32.

2,3-*Dideuteriobenzobicyclo*[2.2.1]*heptadiene* (XXIa). A n-butylsodium reagent was prepared by the slow addition of 31·8 g (0·34 mole) n-butyl chloride into a stirred suspension of 40 g (0·70 mole) Na dispersion (40% in paraffin) in 200 ml n-pentane. To this reagent 24·0 g (0·17 mole) of XXI was slowly added with stirring and refluxed for 8 hr, when evolution of H$_2$ gas was observed. To this reaction mixture was carefully added 13·0 g D$_2$O under ice-cooling and N$_2$ atmosphere. Then the mixture was refluxed for 30 min, diluted with water and extracted with ether. The residual oil obtained by evaporation of the ether was distilled under red. press. yielding 17 g of partially deuterated XXI. This procedure was repeated twice to complete deuteration. The deuterated product thus obtained had b.p. 92–93° (22 mm). The positions of deuteration were confirmed by analysis of its NMR spectrum. The NMR spectrum measured in CCl$_4$[27] showed two bridgehead protons at τ 6·18 (triplet), two bridge-methylene protons around τ 7·75 (ABX$_2$ multiplet), and aromatic protons around τ 3 (A$_2$B$_2$ multiplet, ca. 3·7 protons), but (almost) no vinyl protons, which are observed in the NMR spectrum of XXI at τ 3·28 as a triplet, indicating that the protons at the 2,3-positions were replaced by D. Mass spectrum of the deuterated product indicates the presence of d$_3$-, d$_2$-, and d$_1$-compound in the ratio of 30:50:20. That in the d$_3$-compound one of the protons on the benzene ring is replaced by D is evident from the NMR spectrum. Hence, in the product about 90% of 2- and 3-protons are replaced by D, while about 7·5% of each of 4 benzene protons is exchanged by D.

endo,endo-2,3-*Dideuteriobenzobicyclo*[2.2.1]*heptene* (IVb). The procedure used for the preparation of IVa was applied to XXIa using H$_2$ gas. The product showed in its NMR spectrum (in CCl$_4$)[27] aromatic protons around τ 3 (A$_2$B$_2$ multiplet, ca. 3·7 protons), two bridgehead protons at τ 6·70 (multiplet), one C$_7$-*syn* proton at τ 8·27 (multiplet), one C$_7$-*anti* proton at τ 8·52 (multiplet), and two

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C_5,C_6-*exo* protons centered at τ 8·15 (broad singlet). Mass spectrum of the product indicates the presence of d_3-, d_2-, and d_1-compounds in the ratio of 30:53:17 as expected from the starting material XXIa.

7-Deuteriobenzobicyclo[2.2.1]*hepten-anti-7-ol* (XXXa). The procedure was essentially the same as used for the preparation of XXIX and XXX.[20] To a solution of 250 mg (1·5 mmoles) LAD in 15 ml anhydrous ether, 240 mg (1·4 mmoles) of X was added with stirring. The reaction mixture was stirred for 3 hr at room temp and after the usual work-up gave a mixture of two epimeric alcohols (XXIXa and XXXa) in a ratio of 30:70 which was determined by gas chromatographic analysis. Separation of these alcohols was performed by elution chromatography on florisil using a mixed solvent of pet. ether and ether. The *syn*-alcohol XXIXa, m.p. 117° (Found: C, 82·03; H + D, 8·15. $C_{11}H_{11}DO$ requires: C, 82·01; H + D, 8·12%) was eluted before the *anti* XXXa, m.p. 105° (Found: C, 82·28; H + D, 8·35%). The purity of these alcohols was checked by gas chromatography, in which retention time of XXIXa was shorter than that of XXXa. The orientation of hydroxyl groups was established by comparison of the IR band; the *syn*-alcohol XXIXa showed clearly an internal interaction between the hydroxyl group and the π-electrons of the benzene ring, whereas the *anti* XXXa did not. For the detailed assignment of NMR bands of these alcohols, see Ref. 27.

Spectra. Unless otherwise stated, the spectra were recorded using a Hitachi RMU-6C mass spectrometer equipped with an all-glass inlet system heated at 220°. The compounds, IV, V, VIII, XVI, XVII, XXII and XXVIII were also examined at 100°, but the spectra were not altered appreciably. The ionization energy was 80 ev and the ionization current 80 μa. Peaks whose intensity is stronger than 5% of the base peak, and observed metastable peaks (m^*) are shown below (the peaks shown in the Figures are omitted). The numbers in parentheses are intensity relative to the base peak (=100).

(I): 77(14), 51(20), 44(20), 41(20), 40(35), 39(55); m^* 75·0 ($79^+ \rightarrow 77^+$).
(II): 77(10), 67(7), 41(7); m^* 78·0 ($80^+ \rightarrow 79^+$).
(III): 52(16), 51(15), 50(13), 39(10); m^* 76·0 ($78^+ \rightarrow 77^+$).
(IV): 128(14), 95(19), 75(9), 63(9), 51(9), 50(7), 39(7); m^* 115·3 ($144^+ \rightarrow 129^+$), 114·0 ($116^+ \rightarrow 115^+$).
(V): 130(7), 129(19), 128(11), 127(6), 64(6), 63(7), 51(7); m^* 85·1 ($158^+ \rightarrow 116^+$), 114·0 ($116^+ \rightarrow 115^+$), 68·9 ($115^+ \rightarrow 89^+$).
(VI)(VII): 129(6), 128(5); m^* 84·0 ($160^+ \rightarrow 116^+$), 140·0 ($142^+ \rightarrow 141^+$), 114·0 ($116^+ \rightarrow 115^+$).
(VIII): 127(13), 115(23), 77(8), 51(7); m^* 105·0 ($158^+ \rightarrow 129^+$), 103·8 ($158^+ \rightarrow 128^+$).
(IX): 141(1), 102(6), 51(6); m^* 105·0 ($156^+ \rightarrow 128^+$), 126·0 ($128^+ \rightarrow 127^+$), 81·2 ($128^+ \rightarrow 102^+$).
(X): 127(10), 64(16), 63(9), 51(15); m^* 128·0 ($130^+ \rightarrow 129^+$), 101·6 ($130^+ \rightarrow 115^+$).
(XI): 127(10), 116(10), 63(8), 51(8), 39(8); m^* 95·1 ($172^+ \rightarrow 128^+$), 101·7 ($130^+ \rightarrow 115^+$).
(XII)(XIII): 127(7); m^* 139·8 ($174^+ \rightarrow 156^+$), 97·0 ($174^+ \rightarrow 130^+$), 128·0 ($130^+ \rightarrow 129^+$), 101·6 ($130^+ \rightarrow 115^+$).
(XIV): 176(8), 89(21), 88(7), 76(12); m^* 154·0 ($206^+ \rightarrow 178^+$), 129·5 ($178^+ \rightarrow 152^+$).
(XV): 95(8), 66(17), 65(8), 55(25), 54(42), 53(17), 41(21), 39(35); m^* 68·3 ($96^+ \rightarrow 81^+$), 46·7 ($96^+ \rightarrow 67^+$), 66·0 ($68^+ \rightarrow 67^+$).
(XVI): 95(6), 79(7), 55(10), 54(38), 53(12), 41(42), 39(31); m^* 77·0 ($110^+ \rightarrow 92^+$), 39·6 ($110^+ \rightarrow 66^+$).
(XVII)(XVIII): 97(7), 93(7), 83(21), 81(16), 77(8), 71(8), 70(17), 69(12), 65(7), 57(40), 56(14), 55(30), 54(8), 53(21), 43(19), 41(51), 39(40); m^* 66·3 ($94^+ \rightarrow 79^+$).
(XIX): 79(11), 77(10), 69(22), 68(33), 67(100), 66(10), 65(11), 56(10), 55(24), 54(56), 53(11), 44(10), 41(33), 39(22); m^* 61·1 ($110^+ \rightarrow 82^+$), 59·5 ($110^+ \rightarrow 81^+$), 54·8 ($82^+ \rightarrow 67^+$).
(XX): 63(10), 51(12), 50(8), 44(8), 40(12), 39(47); m^* 90·0 ($92^+ \rightarrow 91^+$), 46·4 ($91^+ \rightarrow 65^+$).
(XXI): 140(7), 139(8), 89(8), 71(8), 70(9), 65(8), 63(16), 62(7), 51(9), 50(7), 39(13); m^* 140·0 ($142^+ \rightarrow 141^+$), 93·8 ($141^+ \rightarrow 115^+$), 68·9 ($115^+ \rightarrow 89^+$).
(XXII): 151(7), 127(6), 77(8), 75(6), 64(9), 63(10), 51(9); m^* 152·0 ($154^+ \rightarrow 153^+$), 81·0 ($128^+ \rightarrow 102^+$).
(XXIII): 178(8), 176(6), 102(8), 100(7), 89(11), 88(11), 76(9); m^* 202·0 ($204^+ \rightarrow 203^+$).
(XXIV): 250(12), 127(12), 125(15), 113(18), 112(7), 44(18).

(XXV): 93(8), 84(13), 77(11), 71(16), 70(63), 69(15), 68(58), 67(29), 66(24), 57(70), 56(18), 55(38), 54(17), 53(21), 51(8), 43(21), 42(10), 41(48), 39(42); m^* 78·8 ($112^+ \rightarrow 94^+$), 66·3 ($94^+ \rightarrow 79^+$).

(XXVI)(XXVII): 109(12), 82(20), 78(20), 68(12), 67(32), 66(20), 65(12), 55(35), 54(22), 53(27), 51(17), 44(15), 43(10), 41(32), 39(40); m^* 90·0 ($92^+ \rightarrow 91^+$), 77·0 ($81^+ \rightarrow 79^+$ or $110^+ \rightarrow 92^+$).

(XXVIII): 78(17), 65(7), 53(10), 52(8), 51(18), 50(10), 39(28); m^* 106·0 ($108^+ \rightarrow 107^+$), 57·8 ($108^+ \rightarrow 79^+$), 58·2 ($107^+ \rightarrow 79^+$), 56·3 ($105^+ \rightarrow 77^+$), 46·4 ($91^+ \rightarrow 65^+$), 75·0 ($79^+ \rightarrow 77^+$).

(XXIX): 128(19), 116(9), 115(16), 40(12); m^* 107·0 ($160^+ \rightarrow 131^+$), 140·0 ($142^+ \rightarrow 141^+$), 80·8 ($131^+ \rightarrow 103^+$), 63·2 ($131^+ \rightarrow 91^+$).

(XXX): 128(15), 116(10), 115(13), 91(9), 77(7), 51(7); m^* 107·0 ($160^+ \rightarrow 131^+$), 140·0 ($142^+ \rightarrow 141^+$), 80·8 ($131^+ \rightarrow 103^+$), 63·2 ($131^+ \rightarrow 91^+$).

(XXXI): 115(7), 102(6), 77(8), 62(8), 51(11); m^* 105·7 ($158^+ \rightarrow 129^+$).

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