

155. Synthesis and Rearrangement of 7-Halobicyclo[3.2.0]hept-2-en-6-ols

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Synthese und Umlagerung von 7-Halo-bicyclo[3.2.0]hept-2-en-6-olen

Zusammenfassung

Die Reaktion von verschiedenen 7-halogen-substituierten Bicyclo[3.2.0]hept-2-en-6-onen mit komplexen Metallhydriden oder mit Methylmagnesiumiodid zu den entsprechenden 7-Halo-bicyclo[3.2.0]hept-2-en-6-olen verläuft unter Angriff des Nucleophils *trans* zum Halogen, um dem vicinalen Kohlenstoff-Halogen-Dipol auszuweichen. In Gegenwart von starken Basen unterliegen die Halohydrine einer Umlagerung, die je nach der durch die intramolekularen Wechselwirkungen bedingten Konformation, entweder unter Hydridverschiebung zu Bicyclo[3.2.0]hept-2-en-6-onen oder, unter Ringverengung, zu Bicyclo[3.1.0]hex-2-en-6-carbaldehyden führt.

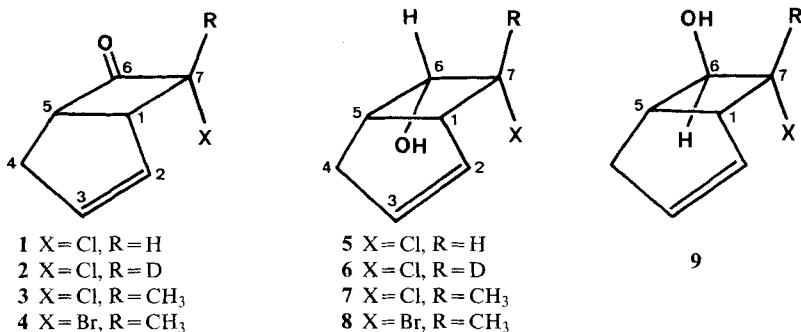
1. Introduction. – Base-catalysed rearrangements of simple 2-halocyclobutanones and -ols [1], of 7-halobicyclo[3.2.0]hept-2-en-6-ones [2] [3] and of 7,7-dichlorobicyclo[3.2.0]hept-2-en-6-ols [4] have been reported. In this paper we describe the synthesis and configurational assignment of various 7-halobicyclo[3.2.0]hept-2-en-6-ols and the rearrangements observed by treatment of these compounds with base (preliminary communication [5]).

2. Synthesis of 7-halobicyclo[3.2.0]hept-2-en-6-ols. – The required reactants, 7-*endo*-halobicyclo[3.2.0]heptenones **1**, **3**, **4** and 7-*exo*-halobicyclo[3.2.0]heptenones **10** to **12**, were prepared by cycloaddition of the appropriate haloketenes to cyclopentadiene and purified (as previously described) [3] [6] [7]. The preparation of 7-*endo*-chloro-7-*exo*-deuteriobicyclo[3.2.0]heptenone **2** is described in the experimental section.

Lithium aluminium hydride or sodium borohydride reduction of the 7-*endo*-haloketones **1** to **4** proceeded stereospecifically at room temperature to give the corresponding 7-*endo*-halobicyclo[3.2.0]hepten-6-*endo*-ols **5** to **8** respectively in

¹⁾ In part.

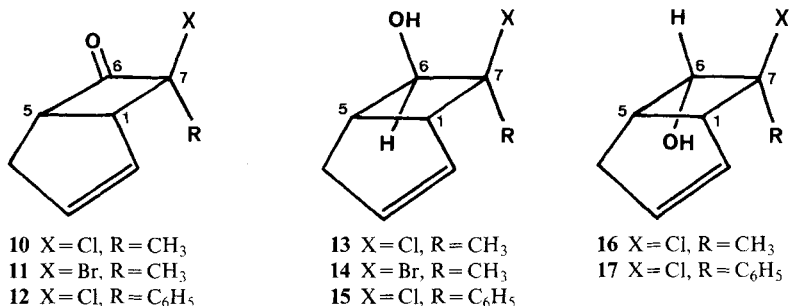
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good yields³). No evidence was obtained for the formation of even small amounts of the epimeric *exo*-alcohols **9**.

Obviously, the well known steric factor leading to the preferential attack of hydride carriers from the *exo*-face of bicyclo[3.2.0]hept-6-ones [4] [8] is reinforced by the presence of the electronegative 7-*endo*-halogen atom, the hydride carrier usually approaching the carbonyl group in α -haloketones in order to maintain a maximal distance from the carbon-halogen dipole [9].

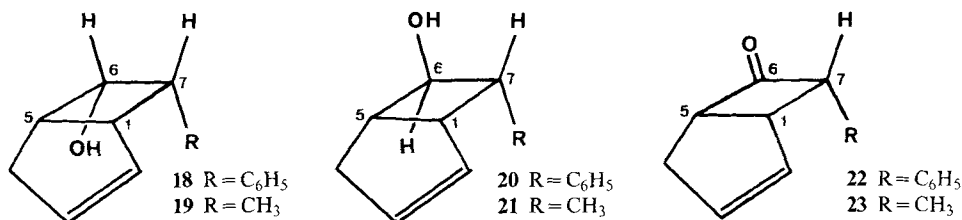
In the case of the *exo*-haloketones **10** to **12**, the two factors, steric and dipole effects, are opposed. Reduction of **10** and **11** with LiAlH₄ or NaBH₄ gave predominantly the 6-*exo*-alcohols **13** and **14** respectively, purified by bulb tube distilla-



tion or fractional crystallization. Reduction of 7-*endo*-phenyl-7-*exo*-chloroketone **12** with NaBH₄ gave a crystalline chlorohydrin with the 6-*exo*-alcohol structure **15** on the basis of the coupling constants for H-C(6) ($J = 6.0$ with H-C(5) and $J = 1.5$ Hz with H-C(1)) and the chemical shift ($\delta = 3.00$) of H-C(5) (see section 3). Reduction of **12** with LiAlH₄ gave the chloro-*exo*-alcohol **15** (but no chloro-*endo*-alcohol **17**), and 7-*endo*-phenylbicyclo[3.2.0]hept-2-en-6-*endo*-ol (**18**). This alcohol **18** was the only LiAlH₄ reduction product (75%) of 7-*endo*-phenylbicyclo[3.2.0]hept-2-en-6-one (**22**).

These results indicate that the directive power of the carbon-halogen dipole overcomes the bulk effect due to both the cyclopentene ring and the 7-*endo*-substituent so promoting *endo*-attack by simple hydride carriers.

³) Details for the preparation of the halohydrins **5** and **7** have been given [7].



The bulkier lithium tri-*t*-butoxyaluminium hydride reduced the methylchloro-ketone **10** less stereoselectively, the *exo*- and *endo*-alcohols **13** and **16** being formed in a 3:2 ratio. In this way it was possible to obtain the chloroalcohol **16**, the only *trans*-halohydrin in this series; it was separated in 91% purity by low temperature fractional crystallization from the above mixture of **13** and **16**.

When the bicyclo[3.2.0]heptenones **1**, **3** and **12** were treated under more vigorous conditions (e.g. LiAlH₄ in boiling tetrahydrofuran) the initial reduction was followed by rearrangement and further reduction (section 7).

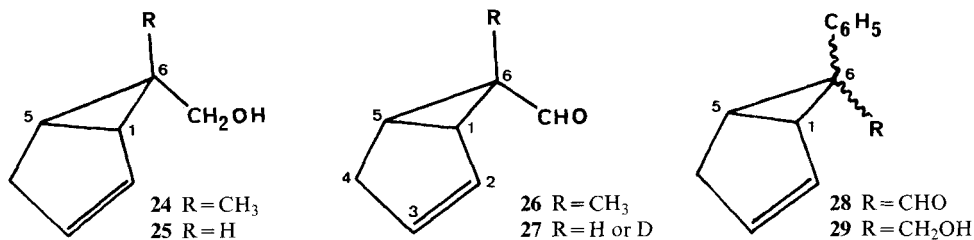
3. Configurational assignments of bicyclo[3.2.0]hept-2-en-6-ols. - The configuration of the hydroxyl group in halohydrins **5** to **8** and **13** to **16** was assigned by examination of the NMR. spectra [10]. Some criteria upon which the present configurational assignments were made [4] may be summarized as follows: a) The vicinal coupling constant between H-C(5) and H-C(6) is always greater for the 6-*endo*- than for the 6-*exo*-alcohols; but on this basis assignments are only valid if both 6-epimeric alcohols are available, e.g. **13** and **16**, **19** and **21**; b) The transannular coupling constant between H-C(1) and H-C(6) is greater for the 6-*endo*- (~2.5 Hz) than for the 6-*exo*-alcohols (~1 Hz); c) After consideration of inductive and anisotropic effects due to *cis*- or *trans*-substituents at C(7), the chemical shift of H-C(6) in an *endo*-position is at higher field than that of *exo*-H-C(6), possibly due to the anisotropic effect of the adjacent five-membered ring; d) The H-C(5) signal is at higher field in the 6-*exo*-alcohols (e.g. **13**, **20** and **21**, $\delta = 3.0$ – 2.5) than in the 6-*endo*-isomers (e.g. **16**, **18** and **19**, $\delta = 3.6$ – 3.2): $\Delta\delta$ (H-C(5))_{*endo-exo*} ≈ 0.6 .

Further evidence for the configuration of the hydroxyl group of the halohydrins **8** and **13** to **15** was obtained by dehalogenation using tri-*n*-butyltin hydride in boiling benzene, conditions not expected to affect the configuration at C(6): Both *exo*-haloalcohols **13** and **14** were converted to 7-*endo*-methylbicyclo[3.2.0]hept-2-en-6-*exo*-ol (**21**), identical by NMR. [11] to the compound prepared by Berson *et al.* [12].

Tri-*n*-butyltin hydride reduction of the *endo*-bromoalcohol **8** gave a mixture of the dehalogenated product, 7-*endo*-methylbicyclo[3.2.0]hept-2-en-6-*endo*-ol (**19**), and a rearranged product, 6-*exo*-methylbicyclo[3.1.0]hex-2-en-6-*endo*-carbinol (**24**), separated by column chromatography. The pure *endo*-alcohol **19** was identical to a sample obtained by an unambiguous method [6]. The *exo* to *endo* inversion of the methyl group at C(7) in the reaction **8** $\rightarrow$ **19** is rationalized by postulating an intermediate radical [13] which, under kinetic control, preferentially abstracts a hydrogen atom from the *exo* face⁴). The rearranged alcohol **24** was identical to

⁴) Treatment of the haloketones **3** and **4** with tri-*n*-butyltin hydride in benzene furnishes 7-*endo*-methylbicyclo[3.2.0]hept-2-en-6-one (**23**) almost exclusively [14].

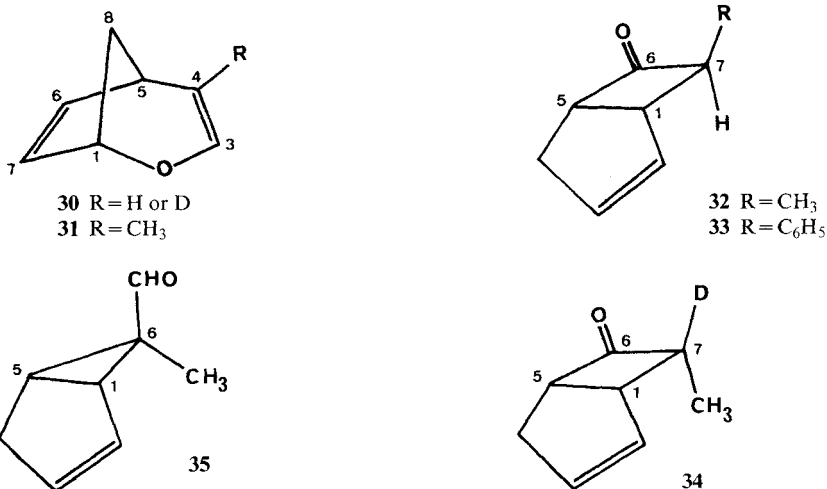
the product obtained on reduction of the *endo*-aldehyde **26** (see section 4) with LiAlH_4 . By treatment of the corresponding *endo*-chloroalcohol **7** with tri-*n*-butyltin



hydride, only the rearranged compound **24** was obtained (68%). The tri-*n*-butyltin hydride-induced rearrangements of **7** or **8** to **24** are stereospecific; there was no evidence for the formation of the 6-*exo* epimer.

Similar treatment of 7-*endo*-phenyl-7-*exo*-chlorobicyclo[3.2.0]hept-2-en-6-*exo*-ol (**15**) gave a mixture of two alcohols, inseparable by chromatography on silica gel. However, the NMR. spectrum of the mixture indicated the presence (30%) of the ring contracted alcohol **29**⁵, obtained in a pure state by vigorous LiAlH_4 treatment of the *endo*-phenyl-*exo*-chloroketone **12** (see section 7). The major component (70%) was the unrearranged, dechlorinated 6-*exo*-alcohol **20**, the structure of which was assigned mainly on the basis of the chemical shift ($\delta = 2.69$) of the H-C(5) multiplet, at higher field than that ($\delta = 3.24$) of the 6-*endo*-alcohol **18** (cf. section 2).

4. Base-catalysed rearrangement of the chlorohydrins. - The eight halohydrins (**5** to **8** and **13** to **16**) were all susceptible to base-catalysed rearrangement⁶. A summary of reaction conditions, products and yields is presented in Table 1.



⁵) The configuration at C(6) of **29** was not established (see, however, footnote 8 in section 7).

⁶) Experimental details concerning the base-catalysed rearrangement of chlorohydrins **5** and **7** have been presented [7].

Table 1. Rearrangement of 7-halobicyclo[3.2.0]hept-2-en-6-ols with base

Compound	Reaction conditions	Products	Yield %	Compound	Reaction conditions	Products	Yield %
5	a)		81	13	a)		72
6	c)		60		b)		85
	f)		87		c)		34 and 32
					d)		23 $\rightleftharpoons$ 32 (75:25)
					f)		23 $\rightleftharpoons$ 32 (66:34)
							87
7	a)		80	14	a)		83
	d)		53				
	f)		91				
				15	a)	22 $\rightleftharpoons$ 33 (60:40) R = CH ₃ , C ₆ H ₅	50
8	a)	31 $\rightleftharpoons$ 26 R = H, D, CH ₃	66	16	f)	35	96

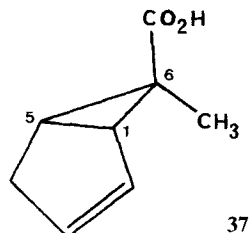
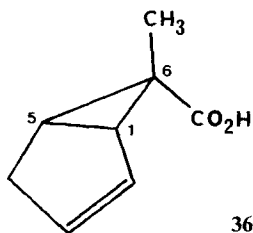
a) Stirring in 1N aqueous NaOH 2 h at RT., then extraction. b) Heating in 1N aqueous NaOH, steam distillation as formed. c) Stirring in 1N NaOD in D₂O 0.5 h at RT. d) Stirring with 1 mol of sodium methylsulfinyl carbanion in dimethylsulfoxide at 0°C. e) Stirring with sodium hydride in ether. f) Shaking 2 min with 8N aqueous KOH in methanol.

Three classes of halohydrins were available: a) the *endo*-hydroxy-*endo*-halobicyclo[3.2.0]hept-2-enes (*endo,endo*-halohydrins **5** to **8**); b) the *exo*-hydroxy-*exo*-halobicyclo[3.2.0]hept-2-enes (*exo,exo*-halohydrins **13** to **15**); c) the *endo*-hydroxy-*exo*-halobicyclo[3.2.0]hept-2-ene (*exo,endo*-halohydrin **16**).

No example of an *exo*-hydroxy-*endo*-halobicyclo[3.2.0]hept-2-ene (**9**) was available.

Compounds of each class gave different results with base: a) the four *endo,endo*-halohydrins rearranged *via* ring contraction to give the 6-*endo*-isomers of bicyclo[3.1.0]hex-2-en-6-carbaldehydes, in valence tautomeric equilibrium with the corresponding 2-oxabicyclo[3.2.1]octa-3,6-dienes; b) the three *exo,exo*-halohydrins rearranged *via* intramolecular hydride shift to give 7-epimeric mixture of 7-mono-substituted bicyclo[3.2.0]hept-2-en-6-ones; c) the *exo,endo*-halohydrin rearranged *via* ring contraction to give the 6-*exo*-isomer of a bicyclo[3.1.0]hex-2-en-6-carbaldehyde.

5. Characterization of the base-catalysed rearrangement products. – The valence tautomeric mixture $30 \rightleftharpoons 27$ was identical to the mixture prepared by *Meinwald et al.* [7] [15]. In the methyl-substituted series, the NMR. spectrum of the valence tautomeric mixture $31 \rightleftharpoons 26$ exhibited a similar spin-system to that observed for the mixture $30 \rightleftharpoons 27$. Furthermore, silver oxide converted $31 \rightleftharpoons 26$ into 6-*exo*-methylbicyclo[3.1.0]hex-2-en-6-*endo*-carboxylic acid (**36**) [3] [7]. The structure of the 6-*exo*-aldehyde **35** was ascertained from spectral data, which showed the absence of a valence tautomeric enol ether, and by silver oxide oxidation to 6-*endo*-methylbicyclo[3.1.0]hex-2-en-6-*exo*-carboxylic acid (**37**), identical with authentic material [3] [7].



The epimeric 7-methylbicycloheptenones **23** and **32** were separated by preparative gas chromatography: the major component, the *endo*-epimer **23**, was identical to the product obtained on cycloaddition of methylketene and cyclopentadiene [6] [16] and the minor component had spectral characteristics in accord with the *exo*-methyl structure **32**.

The presence of deuterium at C(7) in ketone **34** (see *Table I*) was established by comparison of its NMR. signal due to $\text{CH}_3\text{--C}(7)$ (broadened singlet at $\delta = 0.99$) with the corresponding signal in the non-deuterated ketone **23** (doublet at $\delta = 0.99$, $J = 7.5$ Hz). The ratio of epimeric 7-methylbicycloheptenones **23** (or **34**) to **32** was estimated by gas chromatography.

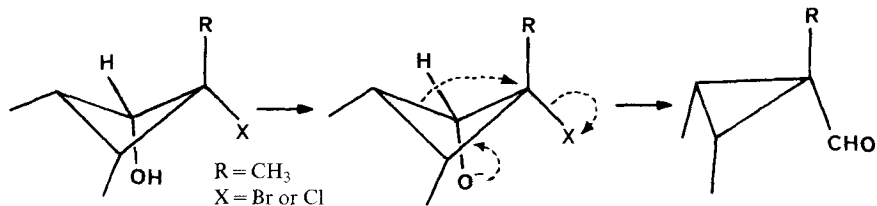
The epimeric 7-phenylbicycloheptenones **22** and **33** were identical (NMR.) with the mixture obtained from the cycloaddition of phenylketene and cyclopentadiene [6]. The ratio of epimers **22:33** obtained from **15** was estimated by integration

of the signals due to the *exo*-H-C(7) ($\delta = 4.30$) of the *endo*-phenylketone **22** and the *endo*-H-C(7) ($\delta = 3.86$) of the *exo*-phenylketone **33** in the NMR. spectrum of the product mixture in benzene.

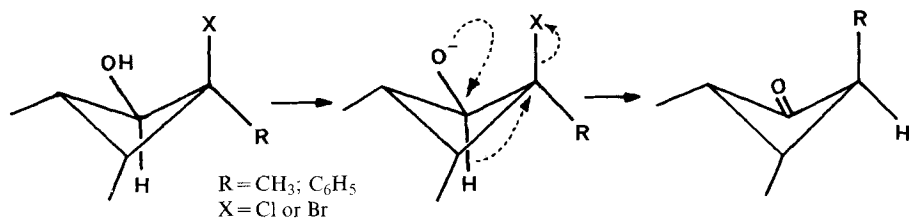
6. Mechanisms of rearrangement. - Stereoelectronic reasons lead to the following alternatives for the base-catalysed reaction of cyclobutane-halohydrins with a secondary alcohol function (see *Schemes 1* to *6*): for the *cis*-isomers, 1,2-hydride shift to cyclobutanones, for the *trans*-isomers, epoxide formation, and for both *cis*- and *trans*-isomers, ring contraction to cyclopropane-carbaldehydes. From the bicycloheptene-halohydrins discussed in this paper, ring contraction of the *exo*-halo compounds would be expected to lead to *exo*-carbaldehydes, that of the *endo*-halo compounds to *endo*-carbaldehydes.

With the three diastereomeric classes of bicycloheptene-halohydrins we observe that a) *endo,endo*-halohydrins (*cis*) prefer ring contraction (to *endo*-aldehydes, *Scheme 1*) over hydride shift (*Scheme 4*); b) *exo,exo*-isomers (*cis*) prefer hydride shift (*Scheme 2*) over ring contraction (*Scheme 5*), and c) the *exo,endo*-halohydrin prefers ring contraction (to *exo*-aldehyde, *Scheme 3*) over epoxide formation (*Scheme 6*). The transition state conformations suggested in *Schemes 1* to *6* parallel corresponding situations found in 5- and 6-membered ring systems [17].

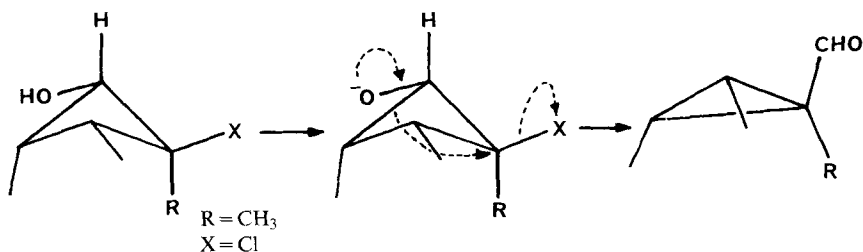
Scheme 1

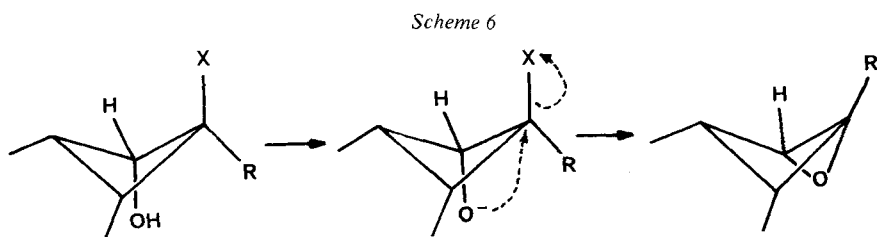
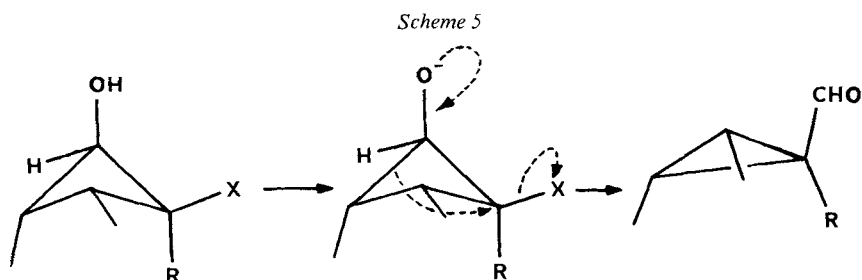
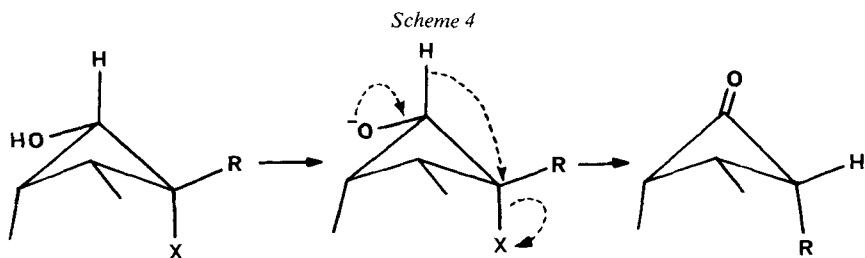


Scheme 2



Scheme 3





Two possible rationalizations are in agreement with our results. 1) If ring contraction of such systems is generally favoured over the alternative paths⁷⁾, the exception, hydride shift with the *exo,exo*-halohydrins (Scheme 2), could be due to bulk interference of the 7-*endo*-substituent and the 5-membered ring atoms in the ring contraction path (Scheme 5). 2) If ring contraction is favoured in the *trans*-halohydrins and hydride shift in the *cis*-isomers, the ring contraction with the *endo,endo*-halohydrins (Scheme 1) is an exception, which could be explained by bulk interference of solvation of the chloride ion leaving from the *endo*-side in the hydride shift path (Scheme 4).

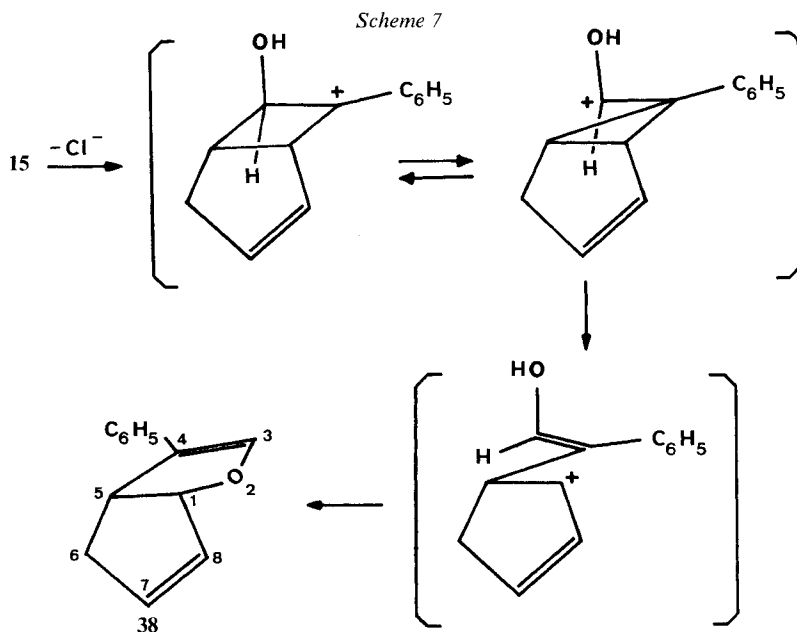
The intramolecular nature of the hydride shift in the rearrangement of chlorohydrin 13 to ketone 32 was demonstrated by performing the reaction in D₂O containing NaOD. The presence of deuterated *endo*-methylketone 34 and undeuterated *exo*-methylketone 32 in the product illustrates that a 1,2-suprafacial shift (Scheme 2) to the primary *exo*-methylketone [3] [14] is followed by base-catalysed isomerization to the *endo*-methylketone.

⁷⁾ The 6-epimeric 7,7-dichloro-6-hydroxybicyclo[3.2.0]heptane derivatives prefer ring contraction over other paths [4]. Of the two alternative modes of ring contraction, elimination of the chlorine atom *trans* to the hydroxyl group is favoured.

7. One-step conversion of 7-halobicyclo[3.2.0]hept-2-en-6-ones into bicyclo[3.1.0]hex-2-ene-6-carbinols. - 7-Halobicyclo[3.2.0]hept-2-en-6-ones were converted into bicyclo[3.1.0]hex-2-ene-6-carbinols with LiAlH_4 in boiling tetrahydrofuran, ketones **1** and **3** giving the alcohols **25** and **24** respectively in $\sim 65\%$ yield. Similar treatment of the phenylchloroketone **12** yielded a separable mixture of 20% of the dechlorinated cyclobutanol **18** and 44% of the ring contracted alcohol **29**⁸⁾; the constitution of the latter compound was ascertained from spectral data. We believe that these reactions first involve reduction of the carbonyl group in **1**, **3** and **12** to a hydroxyl group (**5**, **7** and **15**) with subsequent ring contraction under the reaction conditions to the carbaldehydes **27**, **26** and **28**, which are then further reduced to the observed alcohols **25**, **24** and **29**⁹⁾.

8. Acid-catalysed rearrangement of 7-endo-phenyl-7-exo-chlorobicyclo[3.2.0]hept-2-en-6-exo-ol (15**).** - The unsubstituted and alkylchlorohydrins **5**, **7**, **8**, **13** and **14** are stable to dilute acid and aqueous silver nitrate at RT. In contrast, 7-endo-phenyl-7-exo-chlorobicyclo[3.2.0]hept-2-en-6-exo-ol (**15**) readily rearranges, with loss of HCl, to the cyclic enol ether **38** when treated with 4N HCl, or aqueous silver nitrate, or when the alcohol **15** is chromatographed on silica gel in benzene.

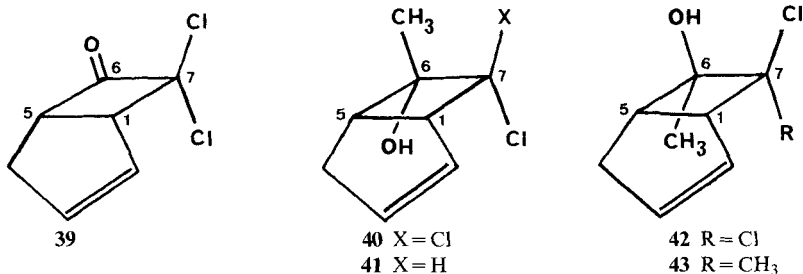
A possible course of this rearrangement is shown in *Scheme 7*. Acid-catalysed conversion of bicyclo[3.1.0]hex-2-ene-carbaldehydes into 2-oxabicyclo[3.3.0]octa-3,7-dienes, which correspond to the last two steps of *Scheme 7*, are known [18].



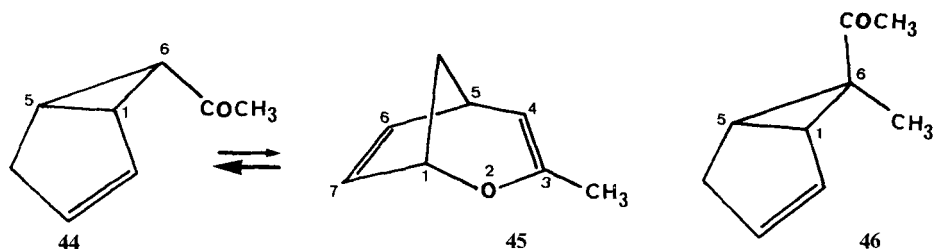
⁸⁾ From the configuration of **12** it would be expected that **29** carries the 6-phenyl group in *endo* position.

⁹⁾ This pathway from **12** to **29** is in contrast with the observed hydride shift under aqueous base conditions of the product **15** from the mild LiAlH_4 reduction of **12**. There is no reason to assume that the more drastic hydride reduction conditions produced the *endo*-alcohol **17**.

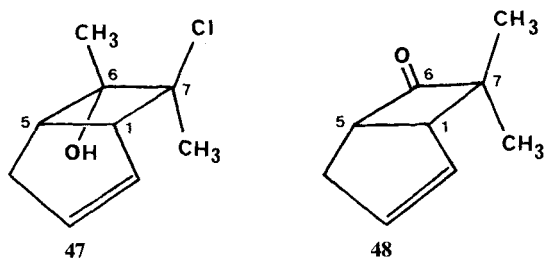
9. Reaction of 7-halobicyclo[3.2.0]heptenones with methylmagnesium iodide and rearrangements of the methylhalohydrin products. - The reaction of 7,7-dichlorobicyclo[3.2.0]hept-2-en-6-one **39** with methylmagnesium iodide to give a mixture of the two methylchlorohydrins **40** and **42** in a ratio of 67:33 and the rearrangements of the separated isomers have been discussed [4].



The same *Grignard* reaction with the ketone **1** gave the halohydrin **41** as the sole product. Treatment with base converted **41** to the valence tautomeric mixture of the *endo*-acetyl derivative **44** and the enol ether **45** (92:8, NMR. in CDCl₃). Reaction of 7-*endo*-methyl-7-*exo*-chlorobicyclo[3.2.0]hept-2-en-6-one (**10**) with methylmagne-

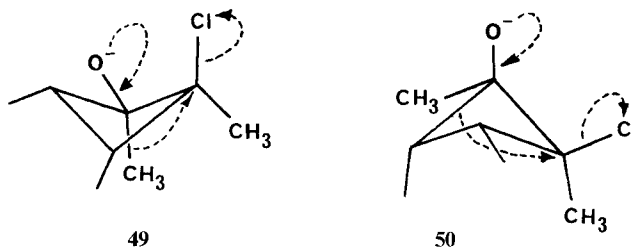


sium iodide at RT. yielded a ketone, while at lower temperatures starting material was recovered. From spectral data the ketone was assigned the rearranged structure **46**. Both the *exo*-alcohol **43** (cf. Scheme 5) and the *endo*-alcohol **47** (cf. Scheme 3) could be intermediates in the formation of 6-*endo*-methyl-6-*exo*-acetylbicyclo[3.1.0]hex-2-ene (**46**). Methylmagnesium iodide, however, probably does not experience severe steric restriction in approaching the *endo*-face of the carbonyl group [4] and, since *Grignard* reagents are influenced by vicinal dipoles in the same



way (see above) as hydride reducing agents [20], it seems likely that the intermediate alcohol is the *cis*-halohydrin **43** with an *exo*-hydroxyl group.

Careful chromatography of the methyl *Grignard* product from **10** failed to reveal any dimethylketone **48**, which would have resulted from the shift of the methyl group analogous to the hydride shifts described above. The reluctance of the chlorohydrin **43** to undergo a methyl shift is probably due to the unfavourable interactions in a transition state which has the methyl group and the chlorine atom in



trans-diaxial positions. The interference of the methyl group at C(6) with the 5-membered ring atoms in conformation **49** is presumably greater than a similar interaction involving the methyl group at C(7) in transition state **50**, which leads to ring contraction.

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Experimental Part

General. – The purity of all compounds was checked by gas liquid chromatography (GC.), thin layer chromatography (TLC.) and/or by their NMR. spectra. **Melting points** were determined in a Büchi apparatus (system *Dr. Tottoli*) and are uncorrected. All compounds not described as impure gave correct elemental analyses for carbon and hydrogen, and, when determined, for chlorine or bromine (Mr. H. Frohofer and his staff in Zürich and Mr. J. Stewart and his staff in Leeds).

NMR. spectra: NMR. spectra were recorded on a Varian A-60 or HA-100 spectrometer by Dr. T. Winkler and Mr. P. Ziegler of the NMR. laboratory Zurich University and on an A-60 in Leeds by Mrs. C. Ingle. They are reported on the δ -scale in ppm units (multiplicity, coupling constants in Hertz, number of protons H. (assignment); tetramethylsilane was used as internal standard ($\delta=0$). Peak shapes are denoted by the following symbols: *s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet, *m* = multiplet.

GC.: GC.-A: analytical, 1520-B (*Aerograph*), flame ionisation detector, oven temp. 63°, column 3 ft. $\times$ 1/8 in., 5% silicone QF-1 on chromosorb W-AW/DMCS 100/120 mesh, 25 ml/min N₂. – GC.-B: analytical, 1520-B (*Aerograph*), flame ionisation detector, oven temp. 100°, column 5 ft. $\times$ 1/8 in., 5% emulphor O on chromosorb W-AW/DMCS 100/120 mesh, 25 ml/min N₂. – GC.-C: preparative, 1520-B (*Aerograph*), thermal conductivity detector, oven temp. 180°, column 20 ft. $\times$ 3/8 in., 20% emulphor O on chromosorb W 60/80 mesh, 200 ml/min He. – GC.-D: the same as GC.-B but oven temp. 120°.

1. Preparation of 7-*exo*-deuterio-7-endo-chlorobicyclo[3.2.0]hept-2-en-6-one (2). – To a solution of 70.8 g (0.4 mol) 7,7-dichlorobicyclo[3.2.0]hept-2-en-6-one (**39**) in 250 ml CH₃COOD was added with stirring and cooling 26.2 g (0.4 mol) of Zn powder in small portions over a period of 30 min. The cold mixture was diluted with 1 l water and extracted with ether. The ethereal extract, after washing 4 times with water and once with saturated NaHCO₃ solution, was dried over Na₂SO₄ and concentrated. The residue was distilled at 12 Torr through a 10 cm Vigreux column to obtain 46.9 g (82%) 7-*exo*-deuterio-7-endo-chlorobicyclo[3.2.0]hept-2-en-6-one (**2**) as a colourless oil, b.p. 97–99°/12 Torr. – IR. (CCl₄):

1800s, C=O; 3060w; 2950m; 2910m; 2845m; 2195w, C-D. - The NMR. spectrum was identical with that of the 7-*exo*-protio-7-*endo*-chloro-derivative **1** [6] with the exception that the signal at 5.09 ppm (H-C(7)) was missing and the signal at 3.95-3.67 ppm (H-C(1) and H-C(5)) was simpler.

2. Preparation of substituted bicyclo[3.2.0]hept-2-en-6-ols. - *Method A.* To a stirred ice-cooled suspension of complex metal hydride in dry ether was added a solution of a 7-substituted bicyclo[3.2.0]hept-2-en-6-one in ether. The resulting suspension was stirred at RT. for 90 min. Water was added carefully, then 10% hydrochloric acid. The ether layer was separated and the aqueous phase extracted 3 times with ether. The combined ether fractions were dried (Na₂SO₄) and evaporated. The residue was distilled under reduced pressure to give the corresponding bicyclo[3.2.0]hept-2-en-6-ol.

Method B. The 7-substituted bicyclo[3.2.0]hept-2-en-6-one was added dropwise with stirring over 5 min to an excess of NaBH₄ in aqueous methanol (70%) at 0°. Reduction was usually complete within 5 min. (TLC.): the mixture was poured into water and then extracted with dichloromethane and worked up as usual. The bicyclo[3.2.0]hept-2-en-6-ols were purified by bulb tube distillation or fractional crystallization.

2.1. 7-endo-Chlorobicyclo[3.2.0]hept-2-en-6-endo-ol (5). - *Method A.* With LiAlH₄ [7]. *Method B.* The chloroketone **1** (5 g) with NaBH₄ (0.75 g) gave the *endo*-alcohol **5** (4.9 g, 96%), m.p. 16.5-17°, b.p. 90° (air-bath)/15 Torr, identical with the product obtained by method A; *p*-bromobenzoate of **5**, m.p. 79-80°.

2.2. 7-*exo*-Deuterio-7-endo-chlorobicyclo[3.2.0]hept-2-en-6-endo-ol (6). - *Method A.* From 28.7 g (0.2 mol) 7-*exo*-deuterio-7-endo-chlorobicyclo[3.2.0]hept-2-en-6-one (**2**) with 3.8 g (0.1 mol) LiAlH₄ in 200 ml ether, after distillation through a 10 cm Vigreux column: **6**, 25.2 g (86%) was obtained as a colourless oil, b.p. 56°/0.5 Torr. - IR. (CCl₄): 3550m OH; 3050w; 2960m; 2920m; 2835w; 2215w, C-D. - The NMR. spectrum was identical with that of protium analog **5** except that the signal at 4.74 (H-C(7)) was missing and the signals at 4.34 (H-C(6)) and at 3.65 (H-C(1)) were simplified.

2.3. 7-endo-Chloro-7-*exo*-methylbicyclo[3.2.0]hept-2-en-6-endo-ol (7). - *Method A.* With LiAlH₄ [7]. *Method B.* The 7-endo-chloro-7-methylketone **3** (1.0 g) with NaBH₄ (0.18 g) also gave the 6-*endo*-alcohol **7** (0.95 g) identical with the product obtained by method A; *p*-bromobenzoate of **7**, m.p. 91-92°.

2.4. 7-endo-Bromo-7-*exo*-methylbicyclo[3.2.0]hept-2-en-6-endo-ol (8). - *Method A.* 2.6 g (13 mmol) 7-endo-bromo-7-*exo*-methylbicyclo[3.2.0]hept-2-en-6-one (**4**) [6] [23] [24] and 0.9 g (22.6 mmol) LiAlH₄ in 80 ml ether yielded, after bulb tube distillation at 100-110°/0.8 Torr, 2.2 g (86%) **8**. - NMR. (100 MHz in CCl₄): 5.90 and 5.60 (2m, 2H, H-C(2), H-C(3)); 3.78 (*d* × *d*, *J* = 6.4 and 3.5, 1H, H-C(6)); 3.5-2.8 (m, 2H, H-C(1), H-C(5)); 2.75 (*m*, 1H, *endo*-H-C(4)); 2.23 (*m*, 1H, *exo*-H-C(4)); 2.01 (*s*, 3H, CH₃-C(7)); 1.91 (*s*, 1H, OH).

2.5. 7-*exo*-Chloro-7-endo-methylbicyclo[3.2.0]hept-2-en-6-*exo*-ol (13). - *Method A:* 25.3 g (162 mmol) 7-*exo*-chloro-7-endo-methylbicyclo[3.2.0]hept-2-en-6-one (**10**) [6] [22] [23] and 3.06 g (80 mmol) LiAlH₄ in 300 ml ether yielded 17.8 g (70%) **13**, m.p. 44-45° (pentane, -20°). *Method B:* 7-*exo*-Chloro-7-methylketone **10** (7.5 g) with NaBH₄ (1.3 g) gave a mixture of 6-*exo*- (**13**) and 6-*endo*- (**16**) alcohols, 78:22 (NMR.). Crystallization from pentane at -50° gave the 6-*exo*-alcohol **13** as cubes, m.p. 43-44.5° (97% pure). The mother liquor of this crystallization was retained (see 2.9). - IR. (CCl₄): 3560, OH. - NMR. (100 MHz in CCl₄): 5.79 (*m*, 2H, H-C(2), H-C(3)); 3.58 (*d* × *d*, *J* = 6.0 and 1.8, 1H, H-C(6)); 3.36 (*m*, 1H, H-C(1)); 2.83 (*m*, 1H, H-C(5)); 2.45 (*m*, 2H, H₂-C(4)); 1.54 (*s*, 3H, CH₃-C(7)). *p*-Bromobenzoate of **13**, m.p. 75-75.5°.

2.6. 7-*exo*-Bromo-7-endo-methylbicyclo[3.2.0]hept-2-en-6-*exo*-ol (14). - *Method A:* 2.0 g (9.9 mmol) 7-*exo*-bromo-7-endo-methylbicyclo[3.2.0]hept-2-en-6-one (**11**) [6] [23] [24] and 0.6 g (15.1 mmol) LiAlH₄ in 40 ml ether gave a colourless oil, b.p. 100-105°/0.07 Torr, 1.5 g (74%) **14**. - NMR. (100 MHz in CCl₄): 5.82 (*m*, 2H, H-C(2), H-C(3)); 3.48 (*m*, 2H, H-C(1), OH); 3.31 (*d* × *d*, *J* = 6.2 and 2.0, 1H, H-C(6)); 2.87 (*m*, 1H, H-C(5)); 2.7-2.2 (*m*, 2H, H₂-C(4)); 1.74 (*s*, 3H, CH₃-C(7)).

2.7. 7-*exo*-Chloro-7-endo-phenylbicyclo[3.2.0]hept-2-en-6-*exo*-ol (15). - **2.7.1. Method A.** From 2.0 g (9.2 mmol) 7-*exo*-chloro-7-endo-phenylbicyclo[3.2.0]hept-2-en-6-one (**12**) [6] [25] and 0.5 g (13 mmol) LiAlH₄ in 40 ml ether, 1.5 g of crude product was obtained, containing (NMR.) the chloro-*exo*-alcohol **15** and the dechlorinated *endo*-alcohol **18** (ca. 7:3) with some other impurities. Purer samples of **15** were obtained according to procedures 2.7.2 and 2.7.3. For **18**, see 2.8.

2.7.2 Method B. A solution of 6.56 g (30 mmol) 7-*exo*-chloro-7-endo-phenylbicyclo[3.2.0]hept-2-en-6-one (**12**) [6] [25] was stirred with 0.35 g (16 mmol) LiBH₄ in 50 ml ether at 0° for 20 min and then treated with water only, followed by a work-up as described in the general procedure to give 7.23 g of undistilled dried **15**. Distillation caused loss of HCl. The crude sample ("crude **15**") contained at least 70% of the chloro-*exo*-alcohol **15** and max. 10% (if any) of the 6-epimeric chloro-*endo*-alcohol **17**

(NMR.). - NMR. (60 MHz in CDCl_3): 7.25 (*m*, 5H, ArH); 5.9-5.3 (*m*, 2H, H-C(2), H-C(3)); 4.30 (*dxd*, *J* = 6.0 and 1.5, 1H, H-C(6)); 3.78 (*m*, 1H, H-C(1)); 3.00 (*m*, 1H, H-C(5)); 2.7-2.3 (*m*, 2H, H₂-C(4)).

2.7.3. *Method C*. The phenylchloroketone **12** (1.0 g) in methanol (150 ml) was added to NaBH_4 (0.5 g) and Na_2CO_3 (0.5 g) in water at 0°. Reduction was complete only after 1.5 h. The crude, unstable chloro-*exo*-alcohol **15** crystallized from pentane at -50° with considerable loss, m.p. 59-61°; *p*-bromobenzoate, of **15**, m.p. 106-107°.

2.8. 7-*endo*-Phenylbicyclo[3.2.0]hept-2-en-6-*endo*-ol (**18**). - *Method A*: 2.66 g (15.6 mmol) 7-*endo*-phenylbicyclo[3.2.0]hept-2-en-6-one (**22**) [6] [14] and 1.5 g (39.5 mmol) LiAlH_4 in 50 ml ether gave, after distillation (bulb tube) at 155°/0.1 Torr, 2.0 g (75%) **18** as a viscous oil. - NMR. (100 MHz in CCl_4): 7.25 (*m*, 5H, ArH); 5.95 (*m*, 2H, H-C(2), H-C(3)); 4.70 (*dxdxd*, *J* = 3.0 and 6.7 and 7.3, 1H, H-C(6)); 4.11 (*dxd*, *J* = 7.5 and 7.3, 1H, H-C(7)); 3.75 (*m*, 1H, H-C(1)); 3.24 (*m*, 1H, H-C(5)); 2.8-2.2 (*m*, 2H, H₂-C(4)).

2.9. 7-*exo*-Chloro-7-*endo*-methylbicyclo[3.2.0]hept-2-en-6-*endo*-ol (**16**). - *Method A*. From 5.5 g (35 mmol) 7-*exo*-chloro-7-*endo*-methylbicyclo[3.2.0]hept-2-en-6-one (**10**) [6] [22] [23] and 18.0 g (70.6 mmol) lithium tri-*t*-butoxyaluminium hydride in 150 ml ether, after distillation (bulb tube) at 100°/11 Torr, 4.3 g (78%) of a mixture containing **13** and **16** (3:2, NMR.) was obtained. The *exo*-alcohol **13** was identified by comparison (NMR.) with a pure sample of **13** (2.5). The remaining signals in the mixture were assigned to the *endo*-alcohol **16** (see below). *Method B*. The pentane mother liquors from the crystallization of the 6-*exo*-alcohol **13**, after the NaBH_4 reduction of **10** (2.5) were kept at -50° for 7 weeks, when the 6-*endo*-alcohol **16** crystallized in long needles. After decantation and washing with cold pentane the *endo*-alcohol **16** was 91% pure (NMR.). It was an unstable oil at RT. and was stored at -20°. - NMR. (60 MHz in CDCl_3): 5.93 and 5.72 (2*m*, 2H, H-C(2), H-C(3)); 4.53 (*m*, 1H, H-C(6)); 3.4 (*m*, 2H, H-C(5), H-C(1)); 2.48 (*m*, 2H, H₂-C(4)); 2.98 (*s*, 1H, OH); 1.38 (*s*, 3H, CH₃-C(7)). *p*-Bromobenzoate of **16**, m.p. 89-90°.

3. Tri-*n*-butyltin hydride treatment of 7-halobicyclo[3.2.0]hept-2-en-6-ols. - A solution of 1 mol equivalent 7-halobicyclo[3.2.0]hept-2-en-6-ol and 1.05 mol equivalent tri-*n*-butyltin hydride in 50 ml benzene was refluxed for 48 h. The solvent was evaporated and the residue distilled at reduced pressure in a bulb tube, leaving as a residue the higher boiling tri-*n*-butyltin hydride and tri-*n*-butyltin chloride.

3.1. *Treatment of 7-endo-chloro-7-exo-methylbicyclo[3.2.0]hept-2-en-6-endo-ol (7)* (1.3 g, 8.2 mmol) with 2.5 g (8.6 mmol) tri-*n*-butyltin hydride gave 0.7 g (68%) 6-*exo*-methylbicyclo[3.1.0]hex-2-en-6-*endo*-carbinol (**24**) as a colourless oil, b.p. 80-90°/11 Torr, which solidified at low temperatures. The IR. and NMR. spectra were identical to those described under 5.2.

3.2. *Treatment of 7-endo-bromo-7-exo-methylbicyclo[3.2.0]hept-2-en-6-endo-ol (8)* (1.3 g, 6.4 mmol) with 2.0 g (6.7 mmol) tri-*n*-butyltin hydride gave a mixture that was chromatographed on silica gel in ethyl acetate/benzene 1:9 to yield 0.2 g (25%) 7-*endo*-methylbicyclo[3.2.0]hept-2-en-6-*endo*-ol (**19**), b.p. 90-100°/11 Torr, and 0.3 g (38%) 6-*exo*-methylbicyclo[3.1.0]hex-2-en-6-*endo*-carbinol (**24**), b.p. 85-95°/11 Torr. The two oily products were identified by comparison of their NMR. spectra with those of authentic samples (see [6] and 5.2).

3.3. *Treatment of 7-exo-chloro-7-endo-methylbicyclo[3.2.0]hept-2-en-6-exo-ol (13)* (1.5 g, 9.5 mmol) with 2.9 g (10 mmol) tri-*n*-butyltin hydride gave 1.0 g (85%) 7-*endo*-methylbicyclo[3.2.0]hept-2-en-6-*exo*-ol (**21**) [11], b.p. 100-110°/11 Torr. - IR. (CCl_4): 3600-3300, OH. - NMR. (100 MHz in CCl_4): 5.71 (*s*, 2H, H-C(2), H-C(3)); 3.35 (*dxd*, *J* = ~5 and ~5, 1H, H-C(6)); 3.11 (*dxdxm*, *J* = ~9 and ~6, 1H, H-C(1)); 2.50 (*dxdxm*, *J* = ~6 and ~5, 1H, H-C(5)); 2.7-2.2 (*m*, 3H, H₂-C(4), H-C(7)); 0.97 (*s*, 3H, CH₃-C(7)).

3.4. *Treatment of 7-exo-bromo-7-endo-methylbicyclo[3.2.0]hept-2-en-6-exo-ol (14)* (0.6 g, 2.95 mmol) with 0.9 g (3.1 mmol) tri-*n*-butyltin hydride gave 0.3 g (82%) 7-*endo*-methylbicyclo[3.2.0]hept-2-en-6-*exo*-ol (**21**), b.p. 100-110°/11 Torr; IR. and NMR. spectra identical with those described (3.3).

3.5. *Treatment of 7-exo-chloro-7-endo-phenylbicyclo[3.2.0]hept-2-en-6-exo-ol (15)*. - 2.5 g (11.4 mmol) of crude **15** (60-70% pure, see 2.7.2) and 3.5 g (12 mmol) tri-*n*-butyltin hydride gave a crude product chromatographed on silica gel in benzene/ethyl acetate 95:5. Tri-*n*-butyltin hydride was eluted first. From later fractions a mixture (1.2 g, 7:3) of 7-*endo*-phenylbicyclo[3.2.0]hept-2-en-6-*exo*-ol (**20**) and 6-phenylbicyclo[3.1.0]hex-2-en-6-*endo*-carbinol (**29**) was obtained. The latter compound was identified by comparison of the NMR. spectrum of the mixture with that of pure **29** obtained by vigorous LiAlH_4 reduction of **12** (see 5.3). The remaining signals in the spectrum were assigned to 7-*endo*-phenylbicyclo[3.2.0]hept-2-en-6-*exo*-ol (**20**). - NMR. (100 MHz in CDCl_3): 5.71 and 5.55 (2*m*, 2H, H-C(3), H-C(2)); 4.12 (*m*, 1H, H-C(6));

3.47 (*m*, 2H, H-C(1), OH); 2.69 (*m*, 1H, H-C(5)); 2.6-2.2 (*m*, 2H, H₂-C(4)). The alcohol **20** could not be obtained pure.

4. Rearrangements of 7-halobicyclo[3.2.0]hept-2-en-6-ols by base. - 4.1. *With aqueous sodium hydroxide.* The 7-halobicyclo[3.2.0]hept-2-en-6-ol (1 mol equivalent) was stirred with 1N NaOH solution (1.2-2 mol equivalents) at RT. for 60-120 min. The organic material was extracted into ether and the combined ether extracts were dried (Na₂SO₄) and concentrated. The residue was distilled under reduced pressure.

4.1.1. *Treatment of 7-endo-chlorobicyclo[3.2.0]hept-2-en-6-endo-ol (5) and its 7-deuterio derivative 6.* For treatment of **5** see [7]. From 2.00 g (13.7 mmol) of 7-*exo*-deuterio-7-endo-chlorobicyclo[3.2.0]hept-2-en-6-endo-ol (**6**) and 35 ml 1N NaOH, 1.10 g (73%) of a colourless oil, b.p. 80-90°/40 Torr, was obtained as a 7:3 valence tautomeric mixture of 6-*exo*-deuteriobicyclo[3.1.0]hex-2-ene-6-endo-carbaldehyde (**27**, R=D) and 4-*deuterio*-2-oxabicyclo[3.2.1]octa-3,6-diene (**30**, R=D). The NMR. spectrum was identical with the mixture of the corresponding 6- and 4-protio derivatives (**27** and **30**) [15] except that the signals at 1.59 (H-C(6)) of **27**, and at 4.93 (H-C(4)) of **30** were missing, and that the CHO signal at 9.07 of **27** and the H-C(3) signal at 5.73 of **30** had lost a coupling of 6 and 7 Hz, respectively.

4.1.2. *Treatment of 7-endo-chloro-7-exo-methylbicyclo[3.2.0]hept-2-en-6-endo-ol (7).* [7].

4.1.3. *Treatment of 7-endo-bromo-7-exo-methylbicyclo[3.2.0]hept-2-en-6-endo-ol (8)* (0.25 g, 1.24 mmol) with 2.5 ml 1N NaOH gave, after 60 min, 0.1 g (66%) of a mixture of 6-*exo*-methylbicyclo[3.1.0]hex-2-ene-6-endo-carbaldehyde and its valence tautomer 4-methyl-2-oxabicyclo[3.2.1]octa-3,6-diene (**26** ⇌ **31**, 4:1), b.p. 80-90°/20 Torr (bulb tube). NMR. spectrum identical with that described [7].

4.1.4. *Treatment of 7-*exo*-chloro-7-endo-methylbicyclo[3.2.0]hept-2-en-6-*exo*-ol (13).* - 4.1.4.1. *With cold aqueous NaOH.* - 3.17 g (20 mmol) **13** and 30 ml 1N NaOH gave after 70 min 1.76 g (72%) of a mixture (GC.-B) consisting of 7-*exo*- (**32**) and 7-endo-methylbicyclo[3.2.0]hept-2-en-6-one (**23**) (1:2), b.p. 80-90°/11 Torr (bulb tube). The products were identified by comparison with pure samples (GC.-B and NMR.) (see 4.1.4.2).

4.1.4.2. *With hot aqueous NaOH.* A solution of 3.40 g (21.4 mmol) **13** in 3 ml ethanol was added during 10 min to 30 ml boiling 1N aqueous NaOH. The reaction product was distilled as formed by passing steam through the mixture. The distillate was extracted 3 times with ether. The combined ether extracts were dried (Na₂SO₄), evaporated and distilled, b.p. 80-90°/11 Torr (bulb tube), to give 2.23 g (85%) of a mixture containing (GC.-B) 45% **32** and 55% **23** separated by preparative GC.-C. The first compound eluted (45%) was 7-*exo*-methylbicyclo[3.2.0]hept-2-en-6-one (**32**). - NMR. (100 MHz in CCl₄): 5.83 and 5.73 (*m*, 2H, H-C(2), H-C(3)); 3.84 (*m*, 1H, H-C(5)); 2.99 (*m*, 1H, H-C(1)); 2.9-2.2 (*m*, 3H, H-C(7), H₂-C(4)); 1.24 (*d*, *J* = 8.0, 3H, CH₃-C(7)). The last component eluted (55%), 7-endo-methylbicyclo[3.2.0]hept-2-en-6-one (**23**), was identical (NMR.) with an authentic sample [6] [16].

4.1.4.3. *With NaOD in D₂O.* 1.00 g (6.3 mmol) **13** and 10 ml 1N NaOD in D₂O gave, after 30 min (intentionally incomplete reaction), 0.5 g of a mixture which contained (by comparison of the CH₃-signals in the NMR. spectrum with those of authentic samples) 30% starting material (**13**, δ = 1.50, *s*), 40% of the non-deuterated *exo*-isomer, 7-*exo*-methyl-7-endo-protio- (**32**, δ = 1.23, *d*, *J* = 8) and 30% of the deuterated *endo*-isomer, 7-endo-methyl-7-*exo*-deuteriobicyclo[3.2.0]hept-2-en-6-one (**34**, δ = 0.99, *s*).

4.1.5. *Treatment of 7-*exo*-bromo-7-endo-methylbicyclo[3.2.0]hept-2-en-6-*exo*-ol (14)* (0.3 g, 1.5 mmol) with 1 ml 1N NaOH yielded, after 60 min, 0.15 g (83%) of a mixture (3:7) of 7-*exo*- (**32**) and 7-endo-methylbicyclo[3.2.0]hept-2-en-6-one (**23**) b.p. 80-90°/11 Torr (bulb tube). The products were identified by comparison of the NMR. spectrum of the mixture with those of pure samples (see 4.1.4.2).

4.1.6. *Treatment of 7-*exo*-chloro-7-endo-phenylbicyclo[3.2.0]hept-2-en-6-*exo*-ol (15).* A mixture of 2.60 g (~10 mmol) of crude **15** (containing 60-70% of **15**, see 2.7.2) and 20 ml 1N NaOH afforded, after 30 min, 0.98 g (~50%) of a yellow oil, b.p. 110°/0.1 Torr (bulb tube), which consisted of 7-*exo*-phenyl- (**33**) and 7-endo-phenylbicyclo[3.2.0]hept-2-en-6-one (**22**) (*ca.* 4:6). The two products were identified by comparison of the NMR. spectrum of the mixture with spectra of the pure epimers [14] [6].

4.2. *Treatment with conc. KOH solution.* - The chloroalcohol was added to a solution of KOH (5 g) in water (15 ml) and the mixture was mechanically shaken for 2 min. Extraction with dichloromethane yielded the crude rearrangement product purified by bulb tube distillation.

4.2.1. *Treatment of 7-endo-chlorobicyclo[3.2.0]hept-2-en-6-endo-ol (5)* (300 mg) gave 195 mg (87%) of the valence tautomeric mixture (**27** ⇌ **30**) (*cf.* 4.1.1).

4.2.2. *Treatment of 7-endo-chloro-7-exo-methylbicyclo[3.2.0]hept-2-en-6-endo-ol (7)* (200 mg) gave 150 mg (91%) of the valence tautomers (**26** ⇌ **31**) as a colourless oil (*cf.* [7]).

4.2.3. *Treatment of 7-exo-chloro-7-endo-methylbicyclo[3.2.0]hept-2-en-6-exo-ol (13)* (100 mg) gave 71 mg (87%) of the equilibrium mixture of 7-*exo*- and 7-*endo*-methylbicyclo[3.2.0]hept-2-en-6-ones (**32** and **23**).

4.2.4. *Treatment of 7-exo-chloro-7-endo-methylbicyclo[3.2.0]hept-2-en-6-endo-ol (16)* (91% pure, 110 mg) gave 79 mg (96%) 6-*endo*-methylbicyclo[3.1.0]hex-2-en-6-*exo*-carbaldehyde (**35**). – IR. (CCl₄): 2730, 1707, CHO. – NMR. (60 MHz in CDCl₃): 8.97 (s, 1H, CHO); 5.83–5.56 (m, 2H, H–C(2), H–C(3)); 2.69–1.90 (m, 4H, H–C(1), H–C(5) and H₂–C(4)); 0.98 (s, 3H, CH₃–C(6)). Semicarbazone, m.p. 190–193° (preheated block). Signals due to the products **23** and **32** from the rearrangement of the 9% of 6-*exo*-alcohol **13**, present as impurity in the starting material, were noted in the IR. (1770 cm^{–1}) and in the NMR. spectra.

4.2.5. *Treatment of 7-exo-chloro-7-endo-methylbicyclo[3.2.0]hept-2-en-6-exo-ol (13)* with NaOD–D₂O. – The chloroalcohol **13** (500 mg) was shaken mechanically with NaOD–D₂O (1.9 g Na in 10 ml D₂O) for 1 min. Extraction with dichloromethane gave a mixture of unchanged chloroalcohol **13**, 1.59 (s, CH₃–C(7)), and of the two rearranged cyclobutanones, 7-*exo*-methyl-7-*endo*-protonbicycloheptenone **32**, 1.25 (d, CH₃–C(7)), and 7-*endo*-methyl-7-*exo*-deuterioketone **34**, 0.98 (s, CH₃–C(7)). The ratio of **13**:**32**:**34** was 69:8:23.

4.3. *With sodium methylsulfinyl carbanion in dimethylsulfoxide (DMSO)*. – To a stirred ice-cooled solution of 1 mol equivalent of the 7-chlorobicyclo[3.2.0]hept-2-en-6-ol in DMSO was added dropwise a 0.4 or 2.3 molar solution of 1.1 mol equivalent of sodium methylsulfinyl carbanion in DMSO [26]. The reaction mixture was stirred for 60 min at RT., diluted with ether and washed 5 times with water. The ether layer was dried (Na₂SO₄), concentrated and the residue distilled (bulb tube) under reduced pressure.

4.3.1. *Treatment of 7-endo-chloro-7-exo-methylbicyclo[3.2.0]hept-2-en-6-endo-ol (7)* (1.00 g, 6.3 mmol) in 10 ml DMSO in this way with 6.9 mmol sodium methylsulfinyl carbanion in 17 ml DMSO yielded 0.40 g (53%) of a mixture of 6-*exo*-methylbicyclo[3.1.0]hex-2-ene-6-*endo*-carbaldehyde and its valence tautomer 4-methyl-2-oxabicyclo[3.2.1]octa-3,6-diene (**26** ⇌ **31**, 4:1) b.p. 80–100°/20 Torr. The NMR. spectrum was identical with that described [7].

4.3.2. *Treatment of 7-exo-chloro-7-endo-methylbicyclo[3.2.0]hept-2-en-6-exo-ol (13)* (1.00 g, 6.3 mmol) in 10 ml DMSO with a solution of 17 ml DMSO containing 6.9 mmol sodium methylsulfinyl carbanion yielded 0.50 g (66%) of a mixture (GC.-B, 1:3) of 7-*exo*- and 7-*endo*-methylbicyclo[3.2.0]hept-2-en-6-ones (**32** and **23**), b.p. 100°/15 Torr.

4.4. *Treatment of 7-endo-chlorobicyclo[3.2.0]hept-2-en-6-endo-ol (5)* with sodium hydride in ether. To a stirred and cooled (–10°) suspension of 1.25 g (52 mmol) NaH in 20 ml ether was added during 30 min a solution of 7.23 g (50 mmol) 7-*endo*-chlorobicyclo[3.2.0]hept-2-en-6-*endo*-ol (**5**) in 20 ml ether. After standing for 120 min at RT., the mixture was filtered and the filtrate concentrated. Distillation (bulb tube) at 80–90°/40 Torr gave 3.26 g (60%) of a mixture of bicyclo[3.1.0]hex-2-ene-6-*endo*-carbaldehyde and its valence tautomer 2-oxabicyclo[3.2.1]octa-3,6-diene (**27** ⇌ **30**, 7:3), identical (NMR.) with that reported [7] [15].

5. **Reductive rearrangement of 7-endo-halobicyclo[3.2.0]hept-2-en-6-ones with lithium aluminium hydride.** – 5.1. *Bicyclo[3.1.0]hex-2-en-6-endo-carbinol (25)*. To a stirred and ice-cooled suspension of 2.50 g (66 mmol) LiAlH₄ in 50 ml tetrahydrofuran (THF) was added dropwise a solution of 7.23 g (50 mmol) 7-*endo*-chlorobicyclo[3.2.0]hept-2-en-6-one (**1**) [3] [6] [7] [21] in 20 ml THF. After refluxing for 44 h, water was added carefully, then 10% hydrochloric acid. The reaction mixture was extracted 5 times with ether; the ether extracts were dried (Na₂SO₄), evaporated, and the residue distilled, b.p. 80–90°/11 Torr (bulb tube), 3.75 g (68%), >95% pure (GC.-D), bicyclo[3.1.0]hex-2-ene-6-*endo*-carbinol (**25**), identical (NMR.) with an authentic sample [18].

5.2. *6-*exo*-Methylbicyclo[3.1.0]hex-2-ene-6-endo-carbinol (24)*. 2.00 g (16.6 mmol) 7-*endo*-chloro-7-*exo*-methylbicyclo[3.2.0]hept-2-en-6-one (**3**) [6] [22] [23] reacted with 0.60 g (15.8 mmol) LiAlH₄ in 25 ml THF as in 5.1 to yield 1.02 g (65%) solid 6-*exo*-methylbicyclo[3.1.0]hex-2-en-6-*endo*-carbinol (**24**). Recrystallization from pentane at –20° gave an analytical sample, m.p. 31.5–32.5°. – IR. (CCl₄): 3620 and 3410, OH. – NMR. (100 MHz in CCl₄): 5.65 and 5.51 (2m, 2H, H–C(2), H–C(3)); 3.3 (s, 1H, OH); 3.25 (s, 2H, CH₂–C(6)); 2.47 (d × d, J = 18.2 and 7.5, 1H, *exo*-H–C(4)); 2.11 (d × m, J = 18.2, 1H, *endo*-H–C(4)); 1.74 (d × m, J = ~6, 1H, H–C(1)); 1.37 (d × d × d, J = 7.5, 6 and ~2, 1H, H–C(5)); 1.09 (s, 3H, CH₃–C(6)).

5.3. *6-Phenylbicyclo[3.1.0]hex-2-en-6-carbinol (29)*. A suspension of 2.0 g (9.2 mmol) 7-*exo*-chloro-7-*endo*-phenylbicyclo[3.2.0]hept-2-en-6-one (**12**) [6] [25] and 0.5 g (13 mmol) LiAlH₄ in 80 ml ether was

refluxed for 6 h. Water and dilute H_2SO_4 were added and the reaction mixture was extracted twice with ether; the ether extracts were dried (Na_2SO_4) and evaporated. The residue was chromatographed on silica gel in ethyl acetate/benzene 5:95 to give 0.35 g (20%) 7-*endo*-phenylbicyclo[3.2.0]hept-2-en-6-*endo*-ol (**18**) (NMR. see 2.8) and 0.75 g (44%) 6-phenylbicyclo[3.1.0]hex-2-en-6-carbinol (**29**), b.p. $142^\circ/0.07$ Torr. – NMR. of **29** (100 MHz in CCl_4): 7.45–7.00 (*m*, 5H, ArH); 5.80 and 5.61 (2*m*, 2H, H–C(2), H–C(3)); 3.43 (*s*, 2H, CH_2 –C(6)); 2.96 (*s*, 1H, OH); 2.60–1.67 (*m*, 4H, H–C(1), H_2 –C(4), H–C(5)).

6. Lithium aluminium hydride reduction of the valence tautomeric mixture of 6-*exo*-methylbicyclo[3.1.0]hex-2-en-6-*endo*-carbaldehyde and 4-methyl-2-oxabicyclo[3.2.1]octa-3,6-diene (26** $\rightleftharpoons$ **31**).** To a stirred suspension of 0.5 g (13.2 mmol) LiAlH_4 in 50 ml ether was added dropwise a solution of 1.0 g (8.2 mmol) valence tautomeric mixture (**26** $\rightleftharpoons$ **31**). After stirring for 4 h at RT., water was added carefully, then 10% hydrochloric acid. The ether layer was separated and the aqueous phase was extracted 3 times with ether. The combined ether fractions were dried (Na_2SO_4) and evaporated. Bulb tube distillation of the residue gave 0.65 g (63%) 6-*exo*-methylbicyclo[3.1.0]hex-2-en-6-*endo*-carbinol (**24**), b.p. $105^\circ/11$ Torr, NMR. and IR. spectra identical to those described (5.2).

7. Acid-catalysed rearrangement of 7-*exo*-chloro-7-*endo*-phenylbicyclo[3.2.0]hept-2-en-6-*exo*-ol (15**). – 7.1. With 4*N* aqueous hydrochloric acid.** 0.8 g (3.6 mmol) crude **15** (60–70% of **15**, see 2.7.2) was stirred with 38 ml 4*N* aqueous HCl for 1 h at RT. The suspension was extracted with ether and the combined ether extracts evaporated. The residue was distilled to give 0.3 g (45%) 4-phenyl-2-oxabicyclo[3.3.0]octa-3,7-diene (**38**), b.p. 125 – $130^\circ/0.25$ Torr (bulb tube). – NMR. (100 MHz in CCl_4): 7.07 (*m*, 5H, ArH); 6.57 (*d*, $J=1.8$, 1H, H–C(3)); 5.90–5.40 (*m*, 3H, H–C(1), H–C(7), H–C(8)); 3.8 (*m*, 1H, H–C(5)); 2.7–2.4 (*m*, 2H, H_2 –C(6)).

7.2. With aqueous silver nitrate. 1.0 g (4.5 mmol) of crude **15** (from 2.7.2) was stirred with 2.5 g AgNO_3 in 40 ml water for 1 h at RT. The suspension was filtered and the filtrate extracted with ether. The combined ether extracts were dried, evaporated and the residue distilled, b.p. 125 – $130^\circ/0.25$ Torr (bulb tube) to give 0.25 g (30%) 4-phenyl-2-oxabicyclo[3.3.0]octa-3,7-diene (**38**), NMR. spectrum identical with that described (7.1).

7.3. With silica gel. – 4.0 g (18 mmol) of crude **15** (from 2.7.2) was passed through a silica gel column with hexane/benzene 1:2. The top one-third of the column was observed to darken slowly while 1.6 g (48%) 4-phenyl-2-oxabicyclo[3.3.0]octa-3,7-diene (**38**) was eluted; NMR. spectrum identical to that described (7.1).

8. Reaction of methylmagnesium iodide with 7-halobicyclo[3.2.0]hept-2-en-6-ones. – 8.1. Treatment of 7-*endo*-chlorobicyclo[3.2.0]hept-2-en-6-one (1**).** – An ethereal solution of CH_3MgI (1.54*M*, 56 ml) was added over 2 min to the monochloroketone **1** (12 g) in ether at 0° . After one further min the mixture was poured into saturated NH_4Cl solution. The ether layer was washed with brine and the residue from the ethereal solution distilled to yield 7-*endo*-chloro-6-*exo*-methylbicyclo[3.2.0]hept-2-en-6-*endo*-ol (**41**) (oil, 9.35 g), b.p. 51 – $53^\circ/0.5$ Torr. For analysis, traces of the ketone **11** were removed by chromatography on silica gel in benzene. – IR. (CCl_4): 3545 OH. – NMR. (60 MHz in CDCl_3): 5.87 (*m*, 2H, H–C(2), H–C(3)); 4.43 (*d*, $J=7$, 1H, H–C(7)); 3.55 (*m*, 1H, H–C(5)); 2.80 (*m*, 1H, H–C(1)); 2.52 (*m*, 2H, H_2 –C(4)); 1.25 (*s*, 3H, CH_3 –C(6)); 2.05 (*s*, 1H, OH).

8.2. Treatment of 7-*exo*-chloro-7-*endo*-methylbicyclo[3.2.0]hept-2-en-6-one (10**).** A solution of CH_3MgI (11 mmol) in ether (50 ml) was added over 5 min to a solution of the *exo*-chloro-*endo*-methylketone **10** (1.56 g, 10 mmol) in dry ether (50 ml). The solution was stirred for 30 min and poured into iced 10% sulfuric acid. Ether extraction yielded an oil which was chromatographed in benzene to give first 0.78 g (50%) of **10**, then 0.45 g (66% based on reacted ketone) of 6-*exo*-acetyl-6-*endo*-methylbicyclo[3.1.0]hex-2-ene (**46**), b.p. $120^\circ/11$ Torr (bulb tube). – IR. (CCl_4): 1690 C=O. – NMR. (100 MHz in CCl_4): 5.67 (*m*, 2H, H–C(2), H–C(3)); 2.7–2.0 (*m*, 4H, H–C(1), H_2 –C(4), H–C(5)); 2.12 (*s*, 3H, COCH_3); 1.01 (*s*, 3H, CH_3 –C(6)).

9. Treatment of 7-*endo*-chloro-6-*exo*-methylbicyclo[3.2.0]hept-2-en-6-*endo*-ol (41**) with base.** – The *endo*-alcohol **41** (9.0 g) was mechanically shaken with a strong aqueous solution of KOH (150 g in 150 ml H_2O) for 30 min. The mixture was poured into brine and extracted with dichloromethane (3×100 ml). The organic extracts were washed with brine and dried. Concentration and distillation gave 6.1 g (88%) of the valence tautomeric mixture of 6-*endo*-acetyl-bicyclo[3.1.0]hex-2-ene and 3-methyl-2-oxabicyclo[3.2.1]octa-3,6-diene (**44** $\rightleftharpoons$ **45**), b.p. 94 – $97^\circ/23$ Torr. – IR. (CCl_4): 1700 C=O. –

NMR. (60 MHz in CDCl_3): 6.33 (*m*, H–C(6), H–C(7) of **45**); 5.57 (*m*, H–C(2), H–C(3) of **44**); 4.75 (*m*, H–C(4) of **45**); 2.03 (*s*, CH_3CO of **44**); 1.53 (*d*, $\text{CH}_3\text{–C}(3)$ of **45**). From the relative intensities of the methyl signals at 2.03 and 1.53, the mixture contained $92 \pm 3\%$ of ketone **44**. – MS.: M^+ 122.07319 (theory 122.07316).

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