Chem. Ber. **113**, 3416 – 3440 (1980)

Cycloadditions of Allyl Cations, 21[1)]

Synthesis and ^{1}H NMR Spectra of Bicyclo[3.2.1]octa-2,6-dienes and 3-Methylenebicyclo[3.2.1]oct-6-enes from Bicyclo[3.2.1]oct-6-en-3-ones Methylated at C-2 and C-4

H. M. R. Hoffmann * and *Heidrun Vathke* *)

Institut für Organische Chemie, Universität Hannover,
Schneiderberg 1 B, D-3000 Hannover

Received 1st February, 1980

Bicyclo[3.2.1]oct-6-en-3-ones **5** – **8**, methylated at C-2 and C-4, have been transformed into methylated bicyclo[3.2.1]octa-2,6-dienes **19** – **24** and 3-methylenebicyclo[3.2.1]oct-6-enes **16** – **18** by three routes: 1) Conversion into tertiary alcohols **9** – **11** with methylmagnesium halide and dehydration. 2) Reduction to epimeric secondary alcohols **12** – **15** with $LiAlH_4$ and also i-Bu_2AlH, followed by dehydration. 3) Methylenation with CH_2Br_2, $Zn/TiCl_4$ in THF/CH_2Cl_2. – The reduction of 2,4-methylated bicyclo[3.2.1]oct-6-en-3-ones **5** – **8** with $LiAlH_4$ and i-Bu_2AlH gives axial and equatorial alcohols; the sterically more demanding i-Bu_2AlH attacks preferentially from the *exo* side, yielding predominantly axial alcohols. Physical, spectroscopic, and chemical properties of the resulting bicyclo[3.2.1]oct-6-en-3-ols **12** – **15** have been correlated by conformational analysis. Axial alcohols form hydrogen bonds intramolecularly, giving inter al. lower melting points and shorter retention times than equatorial alcohols, a sharp OH band in the IR, and a downfield ^{1}H NMR shift of the signals of the olefinic protons 6-H, 7-H (in CCl_4 solvent). They also show marked coupling (^3J = 10 – 12 Hz) of the OH proton in solvent CCl_4. Exceptions to these trends are ascribed to flattening of the six-membered ring. The dehydration of the sterically hindered tertiary 3-methylbicyclo[3.2.1]oct-6-en-3-ols **9** – **11** with phosphoryl chloride in pyridine produces bicyclo[3.2.1]octa-2,6-dienes **19** – **21** in high yields, but requires forcing conditions (≈ 100 °C) compared to secondary alcohols (0 – 25 °C). Bicyclo[3.2.1]octa-2,6-dienes, unlike the isomeric 3-methylenebicyclo[3.2.1]oct-6-enes, form crystalline $AgNO_3$ complexes. 2,3,4,4-Tetramethylbicyclo[3.2.1]octa-2,6-diene (**21**) reacts with atmospheric oxygen at ambient temperature and – 20 °C to give 2,4,5,5-tetramethyl-3-oxatricyclo[4.2.1.$0^{2,4}$]non-7-ene (**26**).

Cycloadditionen von Allyl-Kationen, 21[1)]

Synthese und ^{1}H-NMR-Spektren von Bicyclo[3.2.1]octa-2,6-dienen und 3-Methylenbicyclo[3.2.1]oct-6-enen aus 2,4-methylierten Bicyclo[3.2.1]oct-6-en-3-onen

2,4-Methylierte Bicyclo[3.2.1]oct-6-en-3-one **5** – **8** wurden auf drei Wegen in methylierte Bicyclo[3.2.1]octa-2,6-diene **19** – **24** und 3-Methylenbicyclo[3.2.1]oct-6-ene **16** – **18** umgewandelt: 1) Reaktion mit Methylmagnesiumhalogenid zum tertiären Alkohol **9** – **11** und Dehydratation. 2) Reduktion zu den entsprechenden epimeren sekundären Alkoholen **12** – **15** mit $LiAlH_4$ und i-Bu_2AlH und anschließende Dehydratation. 3) Direkte Methylenierung mit CH_2Br_2, $Zn/TiCl_4$ in THF/CH_2Cl_2. – Die Reduktion der 2,4-methylierten Bicyclo[3.2.1]oct-6-en-3-one **5** – **8** mit

*) Now Mrs. *H. Ernst* (1.7.1980). New address: BASF Hauptlabor, D-6700 Ludwigshafen.

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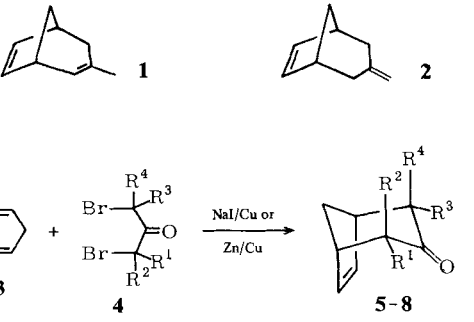
$LiAlH_4$ und i-Bu_2AlH liefert axiale und äquatoriale Alkohole; das sterisch anspruchsvollere i-Bu_2AlH greift vorzugsweise von der *exo*-Seite an unter Bildung axialer Alkohole. Physikalische, spektroskopische und chemische Eigenschaften der resultierenden Bicyclo[3.2.1]oct-6-en-3-ole **12** – **15** werden über die Konformationsanalyse korreliert. Axiale Alkohole gehen intramolekulare Wasserstoffbrücken ein und haben niedrigere Schmelzpunkte und kürzere Retentionszeiten als äquatoriale Alkohole, eine scharfe OH-Bande im IR und eine Tieffeldverschiebung der olefinischen Protonen 6-H, 7-H im ^{1}H-NMR-Spektrum. Sie zeigen außerdem eine ausgeprägte Kopplung (^3J = 10 – 12 Hz) des OH-Protons im Lösungsmittel CCl_4. Ausnahmen gegenüber diesen Trends werden einer Abflachung des sechsgliedrigen Rings zugeschrieben. Die Dehydratation der sterisch gehinderten tertiären 3-Methylbicyclo[3.2.1]oct-6-en-3-ole **9** – **11** mit Phosphoroxychlorid in Pyridin liefert Bicyclo[3.2.1]octa-2,6-diene **19** – **21** in hoher Ausbeute, aber benötigt forcierende Bedingungen (≈ 100 °C) im Vergleich zu den sekundären Alkoholen (0 – 25 °C). Anders als 3-Methylenbicyclo[3.2.1]oct-6-ene bilden die gespannten isomeren Bicyclo[3.2.1]octa-2,6-diene kristalline $AgNO_3$-Komplexe. 2,3,4,4-Tetramethylbicyclo[3.2.1]octa-2,6-dien (**21**) reagiert bei Raumtemperatur und –20 °C mit atmosphärischem Sauerstoff unter Bildung von 2,4,5,5-Tetramethyl-3-oxatricyclo[4.2.1.$0^{2,4}$]non-7-en (**26**).

Although the parent 3-methylbicyclo[3.2.1]octa-2,6-diene (**1**) and the isomeric 3-methylenebicyclo[3.2.1]oct-6-ene (**2**) have been known for more than 10 years[2], homologs of **1** and **2** methylated at C-2 and C-4 have as yet attracted no interest. We here describe several routes to these bicyclics which merit interest in their own right and serve as models for a number of naturally occurring sesquiterpenes and other natural products. Our approach to this class of bicyclics is summarized in Scheme 1 and starts from bicyclo[3.2.1]oct-6-en-3-ones **5** – **8**, which are readily accessible from cyclopentadiene (**3**) and α,α'-dibromoketones (**4**) by the NaI/Cu[1,3] and Zn/Cu route[4] (Equation 1). The bicyclic ketones were transformed into the desired bicyclic dienes by three routes:

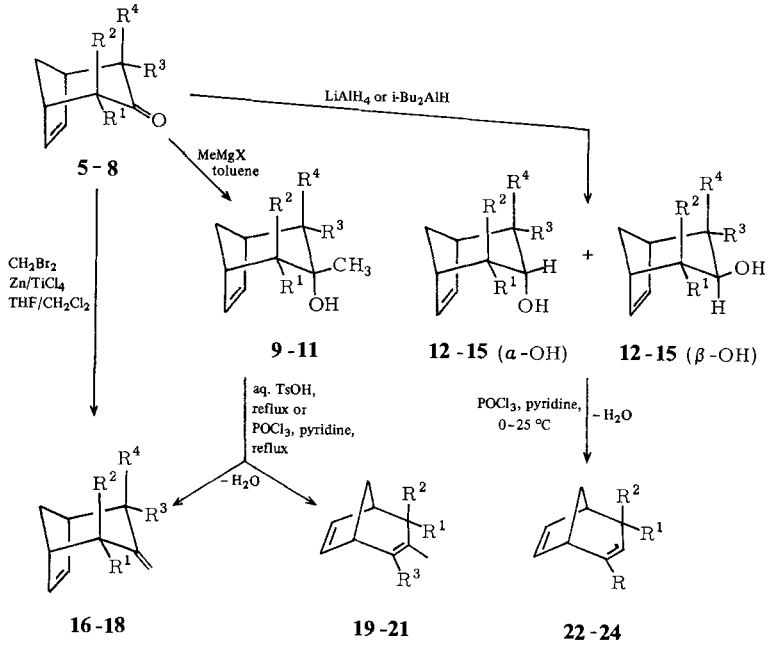


(1)

1) Conversion into tertiary alcohols **9** – **11** by reaction with methylmagnesium halide and dehydration.

2) Reduction to the corresponding epimeric secondary alcohols **12** – **15** followed by dehydration.

3) Direct methylenation to **16** – **18** using methylene bromide, zinc, and titanium tetrachloride in absolute tetrahydrofuran/methylene chloride[5].



R^1	R^2	R^3	R^4	Ketone	Tertiary Alcohol[a] (ex Ketone)	Secondary Alcohol (ex Ketone) axial α	eq β	Exocyclic Diene (ex Ketone, ex tert. ROH)	Endocyclic Diene (ex tert. ROH) R^1	R^2	R^3		Endocyclic Diene (ex sec. ROH) R^1	R^2	R
Me	Me	H	H	**5**	**9**	**12α**	**12β**	**16**	**19**	Me	Me	H	**22**	Me	Me	H
Me	H	Me	H	**6a**	**10**	**13aα**	**13aβ**	**17αα**	**20α**	Me	H	Me	**23α**	Me	H	M
H	Me	H	Me	**6b**	**10**	**13bα**	**13bβ**	**17ββ**	**20β**	H	Me	Me	**23β**	H	Me	M
Me	H	H	Me	**6c**	**10**	**13cα**	**13cβ**	**17αβ**							
Me	Me	Me	H	**7a**	**11**	**14aα**	**14aβ**	**18α**	**21**	Me	Me	Me	**24**	Me	Me	M
Me	Me	H	Me	**7b**	**11**	**14bα**	**14bβ**	**18β**							
Me	Me	Me	Me	**8**		**15α**	**15β**								

[a] Mainly α-alcohol; see text.

Scheme 1. Routes to Bicyclo[3.2.1]octa-2,6-dienes and 3-Methylenebicyclo[3.2.1]oct-6-enes

1. Tertiary Bicyclic Alcohols. 3-Methylbicyclo[3.2.1]oct-6-en-3-ols 9 – 11

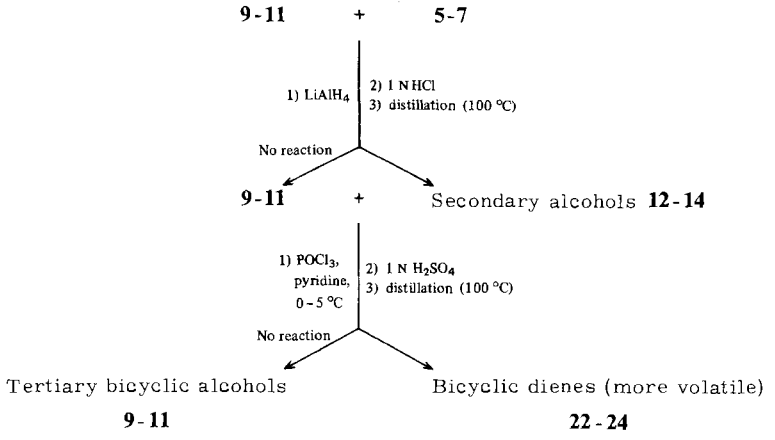
Whilst the bicyclic ketones **5** – **7**, except for the sterically accessible **6**, do not react in satisfactory yields with ethereal methylmagnesium iodide, a change of solvent to toluene or benzene improves the yield (Table 1).

By comparison, on reduction of ketones **5**, **6**, and **7** with $LiAlH_4$ and i-Bu_2AlH the proportion of axial alcohol increases along the sequence **5** < **7** < **6** (see below). Thus, bicyclic ketone **5**, which gives the greatest proportion of equatorial alcohol **12β** with $LiAlH_4$ and i-Bu_2AlH (Table 2, below), also gives the poorest yield of tertiary alcohol **9**.

Table 1. Tertiary Alcohols (%) from Bicyclic Ketones and Methylmagnesium Iodide in Toluene

Ketone	Tertiary Alcohol	Yield (%)
5	**9**	19–26
6	**10**	75
7	**11**	41
8	–	–

The separation of the tertiary alcohols **9**–**11** from the remaining ketones **5**–**7** was accomplished by chemical means (Scheme 2); the ketones were reduced to the secondary alcohols **12**–**14** which were selectively dehydrated to the bicyclic dienes **22**–**24**. Finally, the dienes and the tertiary alcohols were separated by Kugelrohr distillation or chromatography. GC analysis of the diastereoisomeric alcohols **11** on a SE30 column showed three peaks. Hence, in addition to the expected two epimeric axial alcohols, equatorial alcohols must have been formed as well.



Scheme 2. Separation of Tertiary Bicyclic Alcohols **9**–**11** from Starting Ketones **5**–**7**

Whilst a suitable method for separating the various epimers was not found (GC, column chromatography), spectroscopic and chemical evidence points to axial alcohols as the major products. The olefinic protons 6- and 7-H (6.27–6.30 ppm) appear at even lower field than those of the secondary axial alcohols (6.04–6.24 ppm, Table 3). In solvent DMSO the signals of 6- and 7-H are shifted only slightly upfield (6.18–6.25 ppm). This is consistent with strong intramolecular hydrogen bonding of the OH protons, as is the sluggish reaction with phosphoryl chloride compared to the reaction of the secondary alcohols. Finally, the IR spectra in CCl_4 show only strong and sharp OH bands at 3590 to 3600 cm^{-1}.

2. Secondary Bicyclic Alcohols. 2,4-Methylated Bicyclo[3.2.1]oct-6-en-3-ols 12–15

The bicyclic ketones **5–8** were reduced with a 1.1 molar equivalent of $LiAlH_4$ (4.4 equivalents hydride) and 0.55 molar equivalent of $LiAlH_4$ in boiling ether and also with i-Bu_2AlH in absolute toluene at −78 °C (cf Table 2). Clearly, the sterically more demanding reducing agent i-Bu_2AlH promotes formation of axial alcohol. The equatorial alcohol **13aβ** was also prepared from ketone **6a** by reduction with sodium in ethanol. Axial and equatorial alcohols have been assigned by spectroscopic and chemical evidence. Thus, the equatorial alcohol **13aβ** is dehydrated to endocyclic diene **23α** at 0 °C ($POCl_3$, pyridine), whereas the sterically less accessible, axial epimer **13aα** reacts at room temperature. Models show that axial alcohols can form intramolecular hydrogen bonds with the olefinic double bond and hence assume a spherical and compact structure compared with the equatorial epimers. As a consequence, axial alcohols are eluted earlier than equatorial epimers on chromatography with silica gel and also have shorter GC retention times (CWAX 20 M).

Chromatography:	GC retention times:
12α < 12β	**12α < 12β**
13aα < 13cα < 13aβ	**13aα < 13cα < 13bα < 13aβ < 13cβ < 13bβ**
14aα < 14bα < 14bβ < 14aβ	**14aα < 14aβ < 14bα < 14bβ**

Table 2. Reduction of Bicyclo[3.2.1]oct-6-en-3-ones **5–8** to Bicyclo[3.2.1]oct-6-en-3-ols **12–15**

Ketone	Alcohol		Reducing Agent (molar equivalents)		Ratio α:β (axial:equatorial)
5	**12α**	**12β**	$LiAlH_4$	(1.1)	0.67
			$LiAlH_4$	(0.55)	0.83
			i-Bu_2AlH		3.6
6a[a]	**13aα**	**13aβ**	$LiAlH_4$	(1.1)	1.3
6b	**13bα**	**13bβ**	$LiAlH_4$	(0.55)	2.2
6c	**13cα**	**13cβ**	i-Bu_2AlH		5
7a[a]	**14aα**	**14aβ**	$LiAlH_4$	(1.1)	1.1
7b	**14bα**	**14bβ**	$LiAlH_4$	(0.55)	1.5
			i-Bu_2AlH		10
8	**15α**	**15β**	$LiAlH_4$	(0.55)	0.25

[a] Reduction of **6** and **7** with $LiAlH_4$ gives 6 and 4 diastereoisomeric alcohols, respectively. GC (CWAX 20 M) did not show any difference in the three α:β ratios **13aα:13aβ**, **13bα:13bβ**, **13cα:13cβ** and in the two α:β ratios **14aα:14aβ**, **14bα:14bβ**.

Hydrogen bonding also affects melting points. As far as they were isolated in pure form equatorial alcohols were solids at room temperature. The symmetrical axial alcohol **13aα** and axial alcohol **13cα** were colorless oils at 0 °C. Axial alcohol **14aα** is a solid at 0 °C, but oily at room temperature, and **12α** is a solid at room temperature. Apparently, increasing substitution on the β face of the molecule flattens the six-

membered chair by syndiaxial repulsion and in so doing weakens the intramolecular hydrogen bond. After distillation of the epimeric **13a α** and **13a β** the residue consisted of equatorial **13a β**; both alcohols have the same GC retention time on a 4 m SE 30 column. Whilst **13a β** crystallizes as colorless needles (m.p. 95–96°C), **13a α** is a colorless oil.

The IR-spectra (CCl_4) of the axial alcohols show a single sharp and strong band at 3600 cm^{-1} which is not affected by dilution, whereas equatorial alcohols have inter al. a weak and broad band at 3400–3500 cm^{-1} which disappears on dilution. However, perhaps the most convincing diagnostic is ^1H NMR spectroscopy (Tables 3–9).

Owing to intramolecular hydrogen bonding the olefinic protons 6- and 7-H of the axial alcohols appear at lower field than those of the equatorial epimers (solvent CCl_4; Table 3). Further, the OH protons of the axial alcohols **13a α**, **13b α**, **14a α** (δ = 1.42–1.57, solvent CCl_4) tend to appear as doublets with ^3J = 10–12 Hz (slow proton exchange, see Table 5). A solvent change to DMSO reduces or removes intra-

Tab. 3. Chemical Shifts of Olefinic Protons 6- and 7-H of Bicyclo[3.2.1]oct-6-en-3α(β)-ols in CCl_4 and DMSO

Axial Alcohols			Equatorial Alcohols			
	α-Series			β-Series		$N^{a)}$
	δ(CCl_4)	δ(DMSO)		δ(CCl_4)	δ(DMSO)	
12 α	6.21	6.04	**12 β**	5.89	5.88	1
13a α	6.21	6.08	**13a β**	5.91	5.95	0
13b α	6.04	6.03	**13b β**			2
13c α	6.20		**13c β**			1
14a α	6.24	6.09	**14a β**	5.94	5.97	1
14b α	6.11		**14b β**	5.92		2
15 α	6.13	6.09	**15 β**	5.96	6.02	2

[a)] Number of β-methyl groups.

molecular hydrogen bonding with a concomitant upfield shift of 6- and 7-H signals for the α-alcohols (Table 3). Intramolecular hydrogen bonding is also impeded by flattening of the cyclohexane chair in the presence of syndiaxial β-methyl groups (see also melting points of axial alcohols, above). Once again, the signals of olefinic protons 6- and 7-H shift upfield, as can be seen most clearly for the axial alcohols **13a α**, **13c α** and **13b α**:

Alcohol	**13a α**	**13c α**	**13b α**
Number of β-methyl groups	0	1	2
6- and 7-H chemical shift (ppm, CCl_4)	6.21	6.20	6.04

The signal of the protons 6-, 7-H in symmetric alcohols is sharper than that of unsymmetric alcohols which show line broadening. In solvent DMSO the OH proton of axial and equatorial secondary alcohols appears as a doublet; consistently, the signal of the axial alcohols is upfield from that of the equatorial epimer (Table 4). The 3α-

Tab. 4. Chemical Shifts and Coupling Constants ^3J of OH Protons in Solvent DMSO

α-Series	δ(DMSO)	J(Hz)	β-Series	δ(DMSO)	J(Hz)
12α	3.52	7.2	**12β**	4.11	6.2
13aα	2.96	9.4	**13aβ**	4.27	7.2
13bα	4.13	4.8	**13bβ**	4.36	6.5
14aα	3.10	[a]	**14aβ**	4.14	5.3

[a] The signals for 3β-H and the OH proton coincide.

protons of the equatorial alcohols appear at higher field (2.62 – 3.44 ppm) than the 3β-protons of the corresponding axial epimers (3.03 – 3.83 ppm) with the exception of the pairs **12α** and **12β** as well as **14bα** and **14bβ** (Table 5, solvent CCl_4); note that the epimeric **14b** alcohols in particular are expected to assume a flattened six-membered chair conformation. Thus with increasing number of β-methyl groups the 3α-proton tends to be shifted downfield; again, flattening of the cyclohexane moiety is considered to reduce anisotropic shielding by the olefinic double bond.

Tab. 5. Chemical Shifts and Coupling Constants of 3β(α)-Protons in Bicyclo[3.2.1]oct-6-en-3-ols[a]

α-Series	3β-H	$^3J_{\beta,\beta}$	J_{OH}	$^3J_{\beta,\alpha}$	β-Series	3α-H	$^3J_{\alpha,\beta}$	$^3J_{\alpha,\alpha}$
12α	3.23				**12β**	3.33 dd	10.5	6.5
13aα	3.51 t	5			**13aβ**	2.62 t	8.5	
	3.51 dt	5	12					
13bα	3.83 t			7.1	**13bβ**	2.99 t		5.3
13cα	3.23 dd	5	10	11	**13cβ**			
14aα	3.10 d	5			**14aβ**	2.82 d	9	
	3.10 dd	5	11.5					
14bα	3.03				**14bβ**	3.44 d		7
15α	3.30 s				**15β**	3.03 s		

[a] 90 MHz ^{1}H NMR, solvent CCl_4.

In some spectra of the axial alcohols **13aα**, **13cα** and **14aα** the 3β-proton was coupled with the OH proton (which in this case appears as a slightly broadened doublet), in other spectra no coupling occurred. In solvent DMSO coupling of the OH proton with 3-H was visible (Table 4).

The signals of the 3β-protons of the axial alcohols **13aα**, **13cα**, **14aα** and **14bα** are broadened (W coupling with bridgehead protons) compared with the 3α-protons of the equatorial epimers. Because of syndiaxial repulsion of the β-methyl groups the "axial" alcohol **13bα** shows no line broadening.

The β-methyl protons are deshielded compared to the α-methyl protons. The α-methyl as well as the β-methyl protons of the axial alcohols appear downfield (α: 0.94 – 1.00; β: 1.03 – 1.14) from the corresponding signals of the equatorial alcohols (α: 0.90 – 0.93; β: 0.91 – 1.11, Table 6). The coupling constants ^3J of the β-methyl

Tab. 6. Chemical Shifts and Coupling Constants ^3J of Methyl Protons[a] (CCl_4 Solvent)

Axial Alcohol	α-Me	β-Me	Equatorial Alcohol	α-Me	β-Me
12α	0.97 s	1.03 s	**12β**	0.90 s	0.91 s
13aα	1.00 d (7)	–	**13aβ**	0.94 d (6.8)	–
13cα	0.94 d (7.2)	1.08 d (7.5)	**13cβ**		1.11 d (7.2)
14aα	0.97 s	1.03 s	**14aβ**	0.89 s	0.93 s
	0.96 d (7)	–		0.93 d (7)	–
14bα		1.05 s	**14bβ**	0.88 s	0.99 s
		1.14 d (7.2)		–	1.04 d (7.5)
15α		1.13 s	**15β**	0.89 s	1.00 s

[a] Coupling constant ^3J in brackets. The greater ^3J coupling of axial methyl protons is probably general. See also ref.[3]. As far as the methyl protons appear as singlets, the upfield signal is assigned to the α-methyl protons, the downfield signal to the β-methyl protons.

Tab. 7. Chemical Shifts of Bridgehead Protons (CCl_4 Solvent)

Axial Alcohols				Equatorial Alcohols			
12α	2.14		2.54	**12β**	2.20		2.54
13aα		2.32		**13aβ**		2.40	
13cα	2.23		2.41				
14aα	2.13		2.26	**14aβ**	2.21		2.32
				14bβ	2.19		2.44
				15β		2.17	

protons are greater by 0.2 to 0.5 Hz than ^3J of the α-methyl protons, in analogy to bicyclo[3.2.1]oct-6-en-3-ones and 3-methylenebicyclo[3.2.1]oct-6-enes (see below and lit[3]).

The methano bridge proton *anti* to the olefinic C6–C7 double bond, i. e. H_{anti}, is generally easy to locate (doublet, ^2J = 9–10.5 Hz, torsion angle with bridgehead protons 90°). Interestingly, an increasing number of β-methyl groups moves the H_{anti} signal downfield (van der Waals deshielding). A similar trend was previously reported for bicyclo[3.2.1]oct-6-en-3-ones with β-bromine substituents at C-2 and C-4, especially 2β,4β-dibromobicyclo[3.2.1]oct-6-en-3-one (δH_{syn} = 2.14, δH_{anti} = 3.02)[6]. As far as

Tab. 8. Chemical Shifts of Methano Bridge Protons H_{syn} and H_{anti} in Bicyclo[3.2.1]oct-6-en-3-ols (CCl_4 Solvent)

	H_{anti}	H_{syn}		H_{anti}	H_{syn}
13aα	1.58	2.12[a]	**13aβ**	1.47	1.90
14aα	1.95[a]	1.79[a]	**14aβ**	1.84[a]	1.62[a]
			14bβ	1.99	1.48[a]
			15β	2.01	1.67

[a] Tentative assignment.

it can be assigned the methano bridge proton *syn* to the C6 – C7 double bond, i. e. H_{syn}, appears as a doublet of triplets or multiplet (Table 8).

Tab. 9. Chemical Shifts of 2- and 4-H in Axial and Equatorial Bicyclo[3.2.1]oct-6-en-3-ols **12 – 14** (CCl_4 Solvent)

Alcohol	β-H	α-H
12α	1.55 – 2.09[a]	
13aα	1.90	
13cα	1.78 – 2.01[b]	
14aα	1.95 – 2.20[c]	
12β	1.03 – 1.33	1.56 – 1.87[b]
13aβ	1.28	
14aβ	1.17 – 1.62	
14bβ		1.80 – 2.03[c]

[a] Signals due to 4H in this region. [b] Signals due to 3H in this region. [c] Tentative assignments.

3. Preparation of Bicyclo[3.2.1]octa-2,6-dienes 19 – 24 and 3-Methylene-bicyclo[3.2.1]oct-6-enes 16 – 18 from Bicyclo[3.2.1]oct-6-en-3-ones 5 – 7

3.1. Dehydration of Tertiary Bicyclic Alcohols 9 – 11

Dehydration of the tertiary bicyclic alcohols **9 – 11**, which were used as diastereoisomeric mixtures, gives the bicyclic endocyclic dienes **19 – 21** and the exocyclic dienes **16 – 18** in high yields (Scheme 1). Attempts to dehydrate at room temperature by the two-phase method (aqueous *p*-toluenesulfonic acid/light petroleum, nitrogen atmosphere) gave low conversions [**10**: (**20** + **17**) = 28:1, **11**: (**21** + **18**) = 3.2:1], but on refluxing with aqueous *p*-toluenesulfonic acid **10** and **11** were dehydrated completely (Table 10). Similarly, phosphoryl chloride and pyridine did not react with the tertiary alcohols up to 60 °C, but on refluxing. Consistently, the more ionizing set of conditions produces more Saytzeff olefin **20** and **21**, respectively (Table 10).

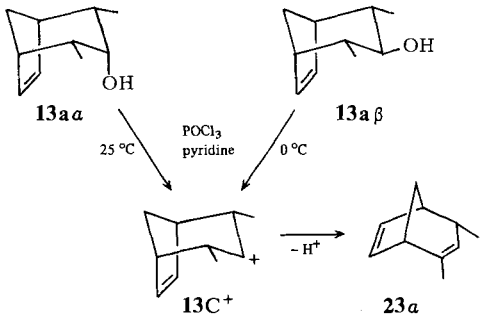
Table 10. Dehydration of Tertiary Alcohols

Alcohol	Experimental Conditions	Product Ratio (Saytzeff: Hofmann Olefin)
10	aq. TsOH, 2h reflux	**20**:**17** = 13:1
	$POCl_3$, pyridine, 2h reflux	= 3.6:1
11	aq. TsOH, 2h reflux	**21**:**18** = 6.3:1
	$POCl_3$, pyridine, 2h reflux	= 1.4:1

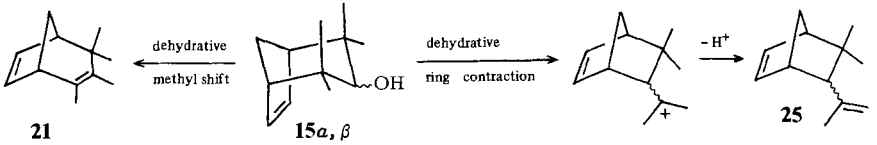
The tertiary alcohols **9** and **11** also lose water on distillation *above* 100 °C with formation of the corresponding endocyclic and exocyclic dienes (see also Scheme 2). Rearranged products were not detected.

3.2. Dehydration of Secondary Bicyclic Alcohols 12 – 15

In contrast to the sterically hindered tertiary alcohols which are dehydrated with phosphoryl chloride/pyridine at 100°C, the secondary equatorial **13aβ** reacts at 0°C, the less accessible axial epimer **13aα** at room temperature (see also Scheme 1). No rearrangements were observed between 0 and 25°C. As both epimeric alcohols **13aα** and **13aβ** give the same bicyclic diene **23α**, an E1-like elimination via the secondary cation **13C**$^+$ seems likely. The differences in reactivity of the other epimeric pairs are less marked; the axial alcohol **14aα** reacts more slowly than **14aβ** at 5°C.



Unlike the tertiary bicyclic alcohols which are partially dehydrated at room temperature under acidic two-phase conditions (see above), the secondary alcohols, having a smaller ionization, are stable at reflux for at least one hour under these E1-S_N1 like conditions (see also increasing proportion of Saytzeff olefin in acidic, ionizing conditions, Table 10). The secondary alcohols **15α** and **15β** are dehydrated by phosphoryl chloride/pyridine at 116°C, yielding two olefins in a 1:1 ratio (GC, SE 30). One product is 2,3,4,4-tetramethylbicyclo[3.2.1]octa-2,6-diene (**21**). The other olefin **25** shows 2 methyl singlets at 1.00 and 1.02 ppm, 1 methyl signal at 1.76, 2 olefinic protons at 4.55 and 4.66, 2 at 6.14 as well as 2 aliphatic protons at 2.33 and 2.70 ppm (bridgehead protons?). Presumably, **25** is the product of dehydrative ring contraction*).



*) *Note added on revision (21.3.1980):* 3-*exo*-Isopropenyl-2,2-dimethylbicyclo[2.2.1]hept-5-ene has now been prepared independently by $CH_2Br_2/Zn/TiCl_4$ induced methylenation of 3-*exo*-acetyl-2,2-dimethylbicyclo[2.2.1]hept-5-ene (*G. Buchbauer* et al., Monatsh. Chem. **107**, 387 (1976)) and found to be identical with hydrocarbon **25**. The ring contraction of a bicyclo[3.2.1]oct-6-ene to a norbornene derivative appears to be novel and is being studied further.

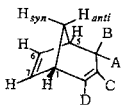
3.3. ^{1}H NMR Data of Bicyclo[3.2.1]octa-2,6-dienes 19 – 24

Owing to anisotropic shielding by the cyclopentenoid double bond the *endo*, A-methyl protons resonate at higher field (0.84 – 0.89 ppm) than the *exo*, B-methyl protons (1.09 – 1.13 ppm). The present and a previous investigation show that *exo*-methyl protons in bicyclo[3.2.1]oct-6-en-3-ones[3], 3-methylenebicyclo[3.2.1]oct-6-enes (Table 12) and secondary bicyclo[3.2.1]oct-6-en-3-ols (Table 6) all have a larger ^3J coupling (by 0.2 to 0.5 Hz) than the methyl protons in the respective *endo*-epimers. In contrast, for the two bicyclic dienes **20β** and **23β** which contain a cyclohexenoid six-membered ring, the *exo*-methyl protons have a smaller coupling constant (^3J = 6.9 and 7.3 Hz, respectively) than the *endo*-α-methyl protons of the epimeric dienes **20α** and **23α**, respectively (^3J = 7.1 and 7.5 Hz).

In all bicyclo[3.2.1]octa-2,6-dienes[2] which we have prepared, the signal of 7-H appears downfield from 6-H just as the D-methyl protons appear downfield from the C-methyl protons. If the chemical shift difference δ7-H – δ6-H is affected by through space coupling (homoconjugation) of the C6 – C7 and the C2 – C3 double bonds[7], it is plausible that δ7-H – δ6-H is smaller for **20β** (0.50 ppm) than for **20α** (0.65 ppm) and smaller for **23β** (0.43 ppm) than for **23α** (0.73 ppm). Models show that

Table 11. ^{1}H NMR Data of Bicyclo[3.2.1]octa-2,6-dienes **19** – **24**[a] (90 MHz, Solvent CCl_4)

19-24



	A	B	C	D	A	B	C	D	6-H	7-H	H_{syn}	H_{anti}	1-H[b]	5-H[b]
19	Me	Me	Me	H	0.86 s	1.13 s	1.47	5.58	5.68	6.32	1.76 – 1.97		2.51	2.41
20α	Me	H	Me	Me	0.89 d (7.1)	2.36	1.46	1.65	5.64	6.29	1.96	1.76	2.37	2.61
20β	H	Me	Me	Me		1.13 d (6.9)			5.68	6.18				2.37
21	Me	Me	Me	Me	0.87 s	1.13 s	1.46	1.65	5.79	6.34	1.76 – 2.00		2.35	
22	Me	Me	H	H	0.86 s	1.12 s	4.89[c]	5.98	5.67	6.21	1.88 – 1.92		2.55	2.38
23α	Me	H	H	Me	0.85 d (7.5)	2.33	4.66	1.69	5.59	6.32	2.04	1.82	2.37	2.69
23β	H	Me	H	Me		1.09 d (7.3)			5.74	6.17				
24	Me	Me	H	Me	0.84 s	1.09 s	4.58	1.65	5.61	6.23	1.86 – 1.96		2.37	

[a] **20β** and **23β** were accompanied by their respective epimers **20α** and **23α**, because ketone **6b** could not be prepared diastereoisomerically pure (see $AgNO_3$ separation, below). – [b] The chemical shifts given for the multiplets of the bridgehead protons 1- and 5-H refer to the irradiation frequency for optimal decoupling of 7- and 6-H. When the signals for 1- and 5-H are resolved, the bisallylic bridgehead proton 1-H resonates at lower field than 5-H in **19** and **22**, but the reverse holds for dienes **20α** and **23α**. – [c] Protons C and D couple with ^3J = 9.5 Hz, in accord with the range found for vicinal olefinic coupling in cyclohexenes (^3J = 8.8 – 10.5 Hz). Diene **22** is a key compound, because 1-H, H_C, H_D, 5-, 6-, and 7-H can be easily assigned by decoupling experiments.

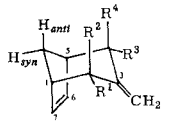
the two double bonds can homoconjugate more effectively in the α-series, and less so in the β-series where the β-methyl group and H_{anti} repel each other and flatten the cyclohexene moiety.

The methano bridge protons H_{syn} and H_{anti} generally resonate at 1.76 – 2.04 ppm. In **20α** and **23α** H_{syn} appears as a doublet of triplets (2.00 ppm). H_{anti} appears at higher field (1.79 ppm) as an AB-type doublet (^2J = 10 Hz, no coupling with 1- and 5-H). However, the signal due to H_{anti} appears to be sensitive to steric crowding, being shifted downfield by β-methyl groups and bromine atoms (see above).

3.4. Preparation of 3-Methylenebicyclo[3.2.1]oct-6-enes 16 – 18

The bicyclic dienes **16**, **17**, and **18**, which have an *exo*-methylene bond and are difficult to prepare via the Wittig reaction[8], were obtained under more electrophilic conditions, i. e. from the ketones **5** – **7** with methylene bromide, zinc, and titanium tetrachloride in absolute tetrahydrofuran/methylene chloride[5]. As methylenation of the bicyclic ketones was not complete, unreacted ketone was reduced with $LiAlH_4$ to the secondary alcohols and separated by chromatography on silica gel (see also reaction of ketones with Grignard reagent and Scheme 2).

Table 12. ^1H NMR Data of 3-Methylenebicyclo[3.2.1]oct-6-enes **16** – **18** (90 MHz, CCl_4)



Olefin	**16**	**17αα**	**17ββ**	**17αβ**	**18α**
R^1 Me	1.04 s	0.99 d (6.8)	–	0.97 d (6.8)	1.04 s
R^2 Me	1.13 s	–	1.13 d (7)	–	1.15 s
R^3 Me	–	R^1	–	–	1.00 d (6.8)
R^4 Me	–	–	R^2	1.19 d (7.3)	–
$=CH_2$	4.54 4.65 (1.9)[a]	4.67 (1.9)[a]			4.64 4.77 (2)[a]
7-H	5.79[b]	5.82			5.82[b]
6-H	5.93[b]				5.94[b]
5-H	2.09[c]				2.11[c]
1-H	2.51[c]	2.10 – 2.50			2.34[c]
4-H					
2-H	–				
H_{syn}		1.98[d]			1.71[d]
H_{anti}		1.61[d]			1.98[d]

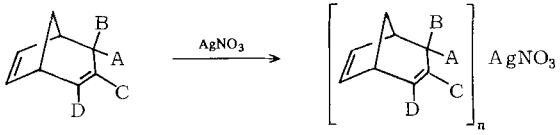
[a] ^2J coupling constant (Hz). – [b] These protons appear as an ABX pattern, being coupled with each other (^3J = 5.8 Hz) and with bridgehead protons 1-H and 5-H (^3J = 2.8 Hz). – [c] These protons are assigned on the assumption that due to steric compression by two methyl groups 1-H appears at lower field than 5-H. – [d] In **17αα** H_{syn} and H_{anti} appear in a sequence opposite to that in **18α**. In this respect **17αα** resembles the endocyclic dienes **20α** and **23α** in that H_{anti} (1.61 ppm, AB-type doublet) appears at higher field than H_{syn} (1.98 ppm, doublet of triplet pattern). In fact, the whole family of bicyclics derived from **6a** (**6a**, **10a**, **13aα**, **13aβ**, **17αα**, **20α**, **23α**, see Scheme 1) shows H_{anti} at higher field than H_{syn}.

^{1}H NMR Spectra (Table 12). The α-methyl protons in **16** – **18** appear at higher field (0.97 – 1.04 ppm) than the β-methyl protons (1.13 – 1.19 ppm), as in all other bicyclo[3.2.1]oct-6-enes which we have obtained. Anisotropic shielding of the *endo*-methyl protons by the C6 – C7 double bond accounts for this fact. β-Methyl protons on a tertiary carbon have a greater coupling constant ^3J than the epimeric α-protons, in analogy to bicyclo[3.2.1]oct-6-en-3-ones and secondary bicyclo[3.2.1]oct-6-en-3-ols (see above).

4. Reactions of Bicyclo[3.2.1]octa-2,6-dienes 20 – 24

4.1. Silver Nitrate Complexes

20 – **24**, perhaps by virtue of homoconjugation of the two double bonds and ring strain, react with $AgNO_3$ to form colorless, crystalline complexes **20-A** – **24-A**. Complexes **20α-A**, **20β-A**, and **21-A** of the dienes **20α**, **20β** and **21**, respectively, analyse for 2 mol of diene per mol $AgNO_3$ (C,H analysis). All other complexes which melt in the temperature range 114 – 118 °C, analyse for 1.5 to 2 mol of diene, with the exception of complex **22-A** which decomposes at 153 °C and contains 1 mol of diene per mol $AgNO_3$. Parallel to the decrease in diene content a decrease in complex stability is observed, e. g. on treatment with ether or pentane. Thus, **22-A**, **23α-A**, **23β-A**, and **24-A** (C = H) are cleaved almost completely on addition of absolute ether or pentane: usefully on further addition of water the dienes are recovered in more than 90% yield.



20-24 **20-A—24-A**

Diene	A	B	C	D	Complex	n
20α	Me	H	Me	Me	**20α-A**	2
20β	H	Me	Me	Me	**20β-A**	2
21	Me	Me	Me	Me	**21-A**	2
22	Me	Me	H	H	**22-A**	1
23α	Me	H	H	Me	**23α-A**	1.5-2
23β	H	Me	H	Me	**23β-A**	1.5-2
24	Me	Me	H	Me	**24-A**	1.5-2

The differing stoichiometry and stability of these complexes seems consistent with a preferred coordination of two olefinic units with one silver ion. Dienes **20α**, **20β**, and **21** are presumably monodentate ligands and coordinate via the C6 – C7 double bond (n = 2). Diene **22** is the only bicyclic, which has a second *unhindered* double bond and is bidentate, forming a 1:1 complex with silver ion (n = 1).

On refluxing the freshly precipitated $AgNO_3$ adducts **20α-A**, **20β-A**, and **21-A** (C = Me) in absolute ether or pentane for 15 minutes, ca. 1 mol equivalent diene **20α**,

20β, and **21** is set free. The remaining molar equivalent can be recovered by shaking with water and ether or pentane. Aged samples (1 – 2 months) of **20α-A**, **20β-A**, and **21-A** can no longer be decomposed in this fashion, but must be worked up with aqueous ammonia.

The precipitation of $AgNO_3$ complexes has proved useful for

a) Purifying bicyclo[3.2.1]octa-2,6-dienes without recourse to chromatography

b) Separating bicyclo[3.2.1]octa-2,6-dienes from their methylene isomers which are not complexed by $AgNO_3$

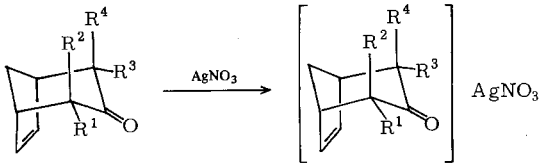
c) Stabilizing the rather sensitive endocyclic dienes which can be stored for months in this fashion

d) Generating bicyclo[3.2.1]octa-2,6-dienes as required, the complexes being cleaved easily and in high yield.

Once liberated, bicyclo[3.2.1]octa-2,6-dienes should not be stored for prolonged periods as they react with atmospheric oxygen, even at −20°C (see below).

4.2. Silver Nitrate Complexes of Bicyclo[3.2.1]oct-6-en-3-ones

Bicyclo[3.2.1]oct-6-en-3-ones, which were prepared via the NaI/Cu method[1,3] (**6a,b** and **7a,b**) and via the Zn/Cu method[4] (**5** and **8**), form crystalline $AgNO_3$ complexes, with the exception of ketone **6b**. These complexes have differing stabilities as judged by C,H analyses and decomposition with ether. Thus, the freshly precipitated complexes



5,6,7 **5-A, 6-A, 7-A**

	R^1	R^2	R^3	R^4
5-A	Me	Me	H	H
6a-A	Me	H	Me	H
6c-A	Me	H	H	Me
7a-A	Me	Me	Me	H
7b-A	Me	Me	H	Me

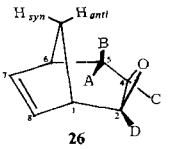
7a-A and **7b-A** are decomposed almost completely on adding absolute ether or pentane, yielding **7a** and **7b** (86%) after Kugelrohr distillation. In contrast, **6a-A** and **6c – A** lose traces of ketone (< 1%), only. Generally, the silver nitrate complexes are useful for separating and purifying the bicyclic ketones; for example, ketone **6a** was separated from a mixture of **6a** + **6b**[3].

4.3. Epoxidation

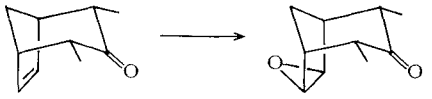
Two-phase epoxidation of 2,3,4,4-tetramethylbicyclo[3.2.1]octa-2,6-diene (**21**) with *m*-chloroperbenzoic acid gave some benzoate and epoxide **26** as the major product which was purified by distillation and also column chromatography. Epoxidation is very easy, being complete after 1 hour at room temperature. In contrast, bicyclic ketone **6a** which lacks the two (presumably homoconjugated) double bonds of **21**, reacts much less readily, requiring 2 hours' refluxing for complete conversion into the epoxide **27**.

Table 13. Coupling constants for epoxide **26**

H_{anti}, d: ^2J = 10.5 Hz
H_{syn}, m: ^2J = 10.5 Hz, $J_{syn,1}$ = 4.7 Hz, $J_{syn,6}$ = 5.3 Hz
1-H, dd: $J_{1,8}$ = 3 Hz, $J_{syn,1}$ = 4.7 Hz
6-H, dd: $J_{6,7}$ = 3 Hz, $J_{syn,6}$ = 5.3 Hz
7-H, 8-H, dd: $J_{6,7}$ = $J_{1,8}$ = 3 Hz, $J_{7,8}$ = 6 Hz (ABX type)



26



6a **27**

The structure of epoxide **26** was assigned by ^{1}H NMR spectroscopy using shift reagent Eu(fod)$_3$ which strongly shifts the easily discernible doublet due to H_{anti} (no coupling with bridgehead protons because of torsion angle of 90°), but has little effect on the olefinic protons 7-, 8-H. As the signals due to H_{anti} and H_{syn} move apart, the AB-type doublet due to H_{anti} changes to an AX doublet. The behaviour of the H_{anti} signal is understandable if the molecule has a proximate, *exo*-epoxide oxygen which interacts with H_{anti} directly through space or indirectly through contact with the shift reagent. As the signals of the various protons no longer overlap on addition of shift reagent, all coupling constants can be determined. Additional resolution was gained by recording the spectrum in $CDCl_3$ rather than CCl_4 solvent. Of the two signals due to the bridgehead protons, one moves more than the other on addition of Eu(fod)$_3$ and is assigned to 1-H. Double resonance experiments allow the assignment of 8-H (6.17 ppm, $J_{1,8}$ = 3 Hz) and thence 7-H (5.94 ppm, $J_{6,7}$ = 3 Hz) (see numbering of **26**). Of the four singlets due to the methyl protons, the upfield signal at 0.88 ppm can be assigned to the *endo*-methyl group A (anisotropic shielding of double bond).

26 also forms a well defined silver nitrate complex $C_{12}H_{18}O \cdot AgNO_3$ in high yield.

4.4. Reaction with Oxygen

Bicyclo[3.2.1]octa-2,6-dienes decompose on storage at −20°C after a few weeks, becoming viscous or forming a colorless precipitate. Specifically, 2,3,4,4-tetramethylbicyclo[3.2.1]octa-2,6-diene (**21**) was allowed to stand at 0°C and investigated periodically by ^{1}H NMR. After 18 months solvent-free **21** had disappeared completely to form polymers and epoxide **26**. Alternatively a solution of **21** in CCl_4 was stirred at room temperature in the dark. After 1 week the ratio diene **21**: epoxide **26** was 4.5:1.

Conclusions. The present investigation has yielded information on a series of novel bicyclic dienes and alcohols. Although 3-methylenebicyclo[3.2.1]oct-6-enes and bicyclo[3.2.1]octa-2,6-dienes are oily and oxygen sensitive, they can be identified, isolated and handled. The tendency of the more strained bicyclo[3.2.1]octa-2,6-dienes to form crystalline $AgNO_3$ complexes has been especially helpful. Routes other than those described here are also viable for preparing these bicyclics, as we shall show in a

future paper. The conversion of the strained bicyclic diene **21** into epoxide **26** by atmospheric oxygen is a new reaction of this class of unsaturated hydrocarbons[9)*)].

We thank Drs. *O. R. Lalko* and *D. I. Rawson* for experimental contributions and the *Deutsche Forschungsgemeinschaft* as well as the *Fonds der Chemie* for financial support.

Experimental Part

Preparation of 2,4-Methylated Bicyclo[3.2.1]oct-6-en-3-ones

2,2-Dimethylbicyclo[3.2.1]oct-6-en-3-one (**5**) and *2,2,4,4-tetramethylbicyclo[3.2.1]oct-6-en-3-one* (**8**) were prepared by the zinc-copper couple route[4)]. No attempt was made to increase the yield (ca. 20–30% each) by using modified cyclodehalogenation procedures[6,10)]. *2,4-Dimethylbicyclo[3.2.1]oct-6-en-3-one*[3)] (**6**) and *2,2,4-trimethylbicyclo[3.2.1]oct-6-en-3-one* (**7**) were conveniently prepared by the NaI/Cu method[1,3)] in 90% and ca. 90% yield, respectively, on a 0.2 mol and larger scale. The zinc-copper couple technique gave more of the thermodynamically less stable axial epimers. Steam distillation with aqueous alkali (pH 10–11) is a convenient method for isolating the bicyclic ketones[6)] with little decomposition, although epimerisation of the methyl groups may occur, especially with ketone **6**.

Preparation of Tertiary Bicyclic Alcohols

3-Methylbicyclo[3.2.1]oct-6-en-3-ols **9**–**11**: 14.2 g (0.10 mol) of methyl iodide in 50 ml of absol. ether are stirred into a suspension of 2.4 g (0.1 mol) of magnesium turnings in 25 ml of absol. ether under nitrogen, with gentle boiling of the solvent. After refluxing for 0.5 h 10 ml of absol. toluene are added and the ether is distilled off (40–50 ml) to leave a thick broth which is cooled to 0 °C. 20 mmol of the corresponding bicyclo[3.2.1]oct-6-en-3-one in 15 ml of absol. toluene is added dropwise and the mixture is stirred for 4 h at 0 °C and 15 h at room temperature. The thick broth is poured onto 10 g of ice and 9 g of NH_4Cl in 9 ml of water are added. The organic layer is separated and the precipitate extracted with 3 portions of ether. The combined organic phase is washed with water and dried (Na_2SO_4). After removal of the solvent the residue is distilled at the Kugelrohr (60–100 °C, 1 Torr). Yields were determined by GC.

Separation of Alcohols and Ketones

a) The alcohols can be enriched or partially separated from the ketones by chromatography on 80 g silica gel with light petroleum/ether (10:1) as eluent.

b) Alternatively the alcohol/ketone mixture is dissolved in 20 ml of absol. ether and the solution is dropped into a suspension of 1 g of $LiAlH_4$ in 20 ml of absol. ether under nitrogen with gentle boiling of the ether. After stirring for 0.5 h at room temperature the mixture is cooled to 0 °C and then 10 g of ice water are dropped in, finally 50 ml of water. The precipitate is dissolved almost completely in 1 N HCl, and the organic phase is separated. The aqueous phase is extracted with 3 portions of ether and the combined organic phase is washed with aqueous $NaHCO_3$ and water and dried (Na_2SO_4). After removal of the solvent the residue is distilled at the Kugelrohr (60–100 °C, 1 Torr). The distillate is dissolved in 6.3 ml of absol. pyridine under nitrogen, and 1.2 ml of phosphoryl chloride are added dropwise at 0–5 °C (0.5–1 h). The reaction solution is stirred for 4 h at 25 °C, poured onto 10 g of ice and extracted three times with little ether. The combined ether layer is washed with 1 N H_2SO_4 and water and dried (Na_2SO_4). After removal of

*) *Note added in proof (27.8.1980):* Since our paper has been submitted, further bicyclo[3.2.1]octa-2,6-dienes have been prepared by Cope rearrangement of *cis*-divinylcyclopropanes. See *E. Piers* and *E. H. Ruediger*, J. Org. Chem. **45**, 1725 (1980) and references to earlier work cited therein. See also *G. W. Klumpp* et al., Rec. Trav. Chim. Pays-Bas **97**, 7 (1978).

the solvent the residue is distilled at the Kugelrohr, yielding the diene at 60 – 80 °C (water pump vacuum) and the alcohols at 60 – 100 °C/1 Torr. The fractions containing diene and alcohol are chromatographed on silica gel using pentane and ether for eluting the more polar alcohols. The eluates are dried (Na_2SO_4), freed from solvent, and distilled at the Kugelrohr.

2,2,3-Trimethylbicyclo[3.2.1]oct-6-en-3-ol (**9**): Following the general procedure 20 mmol of **5** were treated with methylmagnesium iodide in three different solvents. In toluene 2.1 g of ketone **5**

Solvent	Alcohol **9**		Ketone **5**	
	g	%	g	%
Et_2O	0.1	3	2.9	97
Et_2O	0.1	3	2.7	90
THF	0.1	3	2.5	83
Toluene	0.6 – 0.9	19 – 26	2.1 – 2.4	70 – 80

and 0.90 g of alcohol **9**, separated as described under b) above, gave 1.20 g of bicyclic diene **22** and 0.75 g (23%) of **9**, colorless solid at room temperature. – 90 MHz ^{1}H NMR (CCl_4): δ = 0.90 (s, 3H), 0.92 (s, 3H), 1.02 (s, 3H), 1.60 – 1.98 (m, 4H), 2.06 – 2.19 (m, 1H), 2.44 – 2.64 (m, 1H), 6.23 – 6.34 (m, 2H); the OH proton is obscured. – MS (70 eV): *m/e* = 166 (7%, M^+), 151 (5), 148 (47), 135 (13), 133 (70), 122 (18), 118 (28), 116 (16), 114 (15), 108 (83), 107 (63), 105 (83), 93 (100), 91 (80).

$C_{11}H_{18}O$ (166.3) Calcd. C 79.47 H 10.91 Found C 79.45 H 10.98

2,3,4-Trimethylbicyclo[3.2.1]oct-6-en-3-ol (**10**): The reaction was carried out in solvent ether on **6** to give 2.7 – 3.0 g of distillate (2.6 – 2.7 g of alcohol **10** and 0.2 – 0.3 g of ketone **6** by GC), which after chromatography according to b) yielded 2.5 g (75%) of **10**.

2α,3,4α-Trimethylbicyclo[3.2.1]oct-6-en-3-ol (**10a**): 90 MHz ^{1}H NMR (CCl_4): δ = 0.95 (d, *J* = 7 Hz, 6H), 1.00 (s, 3H), 1.56 (d, *J* = 9.5 Hz, 1H, H_{anti}), 1.59 – 1.88 (m, 2H), 2.06 (dt, *J* = 9.5 and 5 Hz, 1H, H_{syn}), 2.20 – 2.48 (m, 2H), 6.20 – 6.31 (m, 2H); the OH proton is obscured. – MS (70 eV): *m/e* = 166 (10%, M^+), 151 (9), 148 (6), 137 (9), 109 (15), 95 (39), 94 (76), 93 (18), 91 (16), 79 (100).

$C_{11}H_{18}O$ (166.3) Calcd. C 79.47 H 10.91 Found C 79.69 H 11.05

2,2,3,4-Tetramethylbicyclo[3.2.1]oct-6-en-3-ol (**11**): **7** was methylated with methylmagnesium iodide in three different solvents and the products separated as described under b) above.

Solvent	Distillate	Alcohol		Ketone **7**	
	g	g	%	g	%
Et_2O	3.25	0.46	13	2.79	85
THF	3.10	2.47	69[a]	0.73	22
Toluene	3.00	1.36	41	1.64	50

[a] In THF a major amount of epimeric alcohol is formed also (GC).

Distillation of a mixture of 1.36 g of **11** and 1.64 g of **7** gave three fractions: 1) 0.88 g of bicyclic diene **24**, 2) 1.04 g of diene **24**/alcohol **11** (1 : 1), and 3) 0.58 g of alcohol **11**. Chromatography of the second fraction gave a combined yield of 1.33 g of **24** and 1.10 g (31%) of *2,2,3,4α-tetramethylbicyclo[3.2.1]oct-6-en-3-ol* (**11**), colorless solid at room temperature. – 90 MHz ^{1}H NMR

(CCl_4): δ = 0.89 (s, 3H), 0.92 (s, 3H), 0.93 (d, *J* = 7 Hz, 3H), 1.02 (s, 3H), 1.63 – 2.03 (m, 3H), 1.96 (s, OH), 2.04 – 2.18 (m, 1H), 2.20 – 2.36 (m, 1H), 6.20 – 6.40 (m, 2H). – MS (70 eV): *m/e* = 180 (12%, M^+), 165 (6), 162 (5), 147 (7), 137 (15), 133 (6), 123 (7), 121 (6), 119 (7), 109 (33), 108 (82), 105 (10), 99 (10), 95 (25), 93 (100).

Preparation of Secondary Bicyclic Alcohols. 2,4-Methylated Bicyclo[3.2.1]oct-6-en-3-ols **12 – 15**

1) *Reduction with $LiAlH_4$:* 20 mmol of bicyclic ketone in 10 ml of absol. ether are dropped into a suspension of 0.50 g (85%, 11 mmol) or 1.00 g (22 mmol) of $LiAlH_4$ in 10 ml of absol. ether, with gentle refluxing of the solvent. After stirring for 0.5 h at room temperature the mixture is cooled to 0°C and 15 g of ice water are carefully dropped in. When evolution of hydrogen has ceased 200 – 250 ml of water are added; alternatively, when using 1.0 g $LiAlH_4$ one adds 50 ml of water and dissolves the resulting precipitate in 1 N H_2SO_4. After extracting with ether (3 ×) the combined organic phase is washed with water, dried (Na_2SO_4) and the solvent removed to leave a residue which is distilled at the Kugelrohr (100 – 130°C, water pump vacuum or 60 – 80°C, 1 Torr).

The alcohols can be separated partially by chromatography on silica gel (80 g, light petroleum/ether = 10:1). Before removing the solvent the solution must be dried (Na_2SO_4), because the bicyclic alcohols are volatile with water vapour and will be evaporated otherwise at the water pump together with the light petroleum.

2) *Reduction with i-Bu_2AlH*[11]: 100 ml of toluene are distilled under nitrogen until all water has been removed; 2 mmol of ketone are added to the resulting (90 ml) toluene and the solution is cooled to –78°C. After adding 7 ml of 1 M i-Bu_2AlH in toluene the solution is stirred for 0.5 h at –78°C, warmed to room temperature, and worked up by adding 5 g of ice/50 ml water, and extracting three times with a little ether. The ether extracts are washed with aqueous, saturated NaCl solution, dried (Na_2SO_4), and the solvent is removed at the water pump to leave a residue which is distilled at the Kugelrohr (60 – 80°C, 1 Torr).

2,2-Dimethylbicyclo[3.2.1]oct-6-en-3-ol (**12**): 3.0 g (20 mmol) of **5** were reduced as described above to yield a mixture of epimeric alcohols **12α**, **12β**. – MS (70 eV): *m/e* = 152 (12%, M^+), 137 (4), 134 (10), 119 (14), 109 (20), 93 (75), 91 (32), 86 (100).

$C_{10}H_{16}O$ (152.2) Calcd. C 78.90 H 10.59 Found C 78.35 H 10.59

$LiAlH_4$ (g)	Alcohol[a] (g)	Yield (%)	Ratio **12α**:**12β**[b]
0.5	2.86 – 2.87	94	0.83
1.0	2.93	96	0.67[c]
i-Bu_2AlH	0.27	90	3.6

[a] Colorless mixture of **12α**/**12β**, which is a solid at room temperature. – [b] Ratio determined by ^1H NMR (CCl_4, DMSO) and GC (SE 30, CWAX 20 M). – [c] In solvent THF the ratio of epimeric alcohols is the same.

Chromatography of 2.5 g of the alcohol (**12α**:**12β** = 0.67) yielded

2,2-dimethylbicyclo[3.2.1]oct-6-en-3α-ol (**12α**) (0.95 g), 90 MHz ^1H NMR (CCl_4): δ = 0.97 (s, 3H), 1.03 (s, 3H), 1.55 – 2.09 (m, 4H), 2.09 – 2.20 (m, 1H), 2.46 – 2.63 (m, 1H), 3.10 – 3.17 (m, 3β-H), 6.11 – 6.31 (m, 2H), and

2,2-dimethylbicyclo[3.2.1]oct-6-en-3β-ol (**12β**) (1.35 g), 90 MHz ^1H NMR (CCl_4): δ = 0.90 (s, 3H), 0.91 (s, 3H), 1.04 – 1.36 (m, 1H), 1.56 – 1.87 (m, 3H), 2.14 – 2.27 (m, 1H), 2.46 – 2.63 (m, 1H), 3.33 (dd, *J* = 6.5 and 10.5 Hz, 3α-H), 5.78 – 5.94 (m, 2H).

2,4-Dimethylbicyclo[3.2.1]oct-6-en-3-ol (**13**): 3.0 g (20 mmol) of **6a – c** were reduced. 2.90 g of **13** (α:β = 2.2) were filtered through 20 g of silica gel with 200 ml of light petroleum, giving after

$LiAlH_4$ (g)	Alcohol (g)	Yield (%)	Ratio $\alpha:\beta$[a]
0.5	2.82 – 2.98	93 – 98[b]	2.2
1.0	2.81 – 2.94	92 – 97[c]	1.3[d]
i-Bu_2AlH	0.270	89	5

[a] Ratio $\alpha:\beta$ determined on CWAX 20 M. – [b] Colorless oil. – [c] Colorless oil containing colorless crystals. – [d] Analogous result in solvent THF. However, the yield of epimeric alcohols **13** was lower (2.68 g, 88%).

distillation 0.84 – 0.90 g of axial alcohol (GC: predominantly **13a α**, very little **13c α**). Elution with ether gave 1.90 – 1.96 g of **13** ($\alpha:\beta$ = 1), 1.50 g of which was chromatographed:

2α,4α-Dimethylbicyclo[3.2.1]oct-6-en-3α-ol (**13a α**) (0.66 g). – 90 MHz ^{1}H NMR (CCl_4): δ = 1.00 (d, *J* = 7 Hz, 6H), 1.58 (d, *J* = 9 Hz, H_{anti}), 1.74 – 2.06 (m, 2H, 2β-,4β-H), 2.07 – 2.39 (m, 3H), 3.51 (t, *J* = 5 Hz, 3β-H), 6.21 (m, 2H). Some spectra showed the OH proton at 1.42 (d, *J* = 12 Hz) and 3β-H at 3.51 (dt, *J* = 12 and 5 Hz) (see Table 5).

2α,4β-Dimethylbicyclo[3.2.1]oct-6-en-3α-ol (**13c α**) (0.16 g). – 90 MHz ^{1}H NMR (CCl_4): δ = 0.94 (d, *J* = 7.2 Hz, 3H), 1.08 (d, *J* = 7.5 Hz, 3H), 1.57 (d, *J* = 10 Hz, OH), 1.78 – 2.01 (m, 4H), 2.16 – 2.31 (m, 1H), 2.32 – 2.41 (m, 1H), 3.23 (dd, *J* = 5 Hz and 10 Hz, 1H), 6.01 – 6.31 (m, 2H).

Further eluates contained **13a β**, **b α**, **b β**, **c β** and were solid after removing the solvent. Recrystallization (light petroleum, b. p. 60 – 70 °C) yielded colorless needles of **13a β** and **c β** (identification by GC).

Assignment of 2,4-dimethylbicyclo[3.2.1]oct-6-en-3-ols (**13a α**, **a β**, **b α**, **b β**, **c α**, **c β**): 0.50 g (3.3 mmol) of ketone **6** in 5 ml of absol. ether were dropped into 0.35 g (7.7 mmol) of $LiAlH_4$ in 5 ml of absol. ether, and the reaction mixture was worked up as described above.

Reaction of 2α,4α-dimethylbicyclo[3.2.1]oct-6-en-3-one (**6a**)[3]: 0.39 g of distillate were obtained ($\alpha:\beta$ = 2.3). The solid residue was recrystallized from light petroleum (b. p. 60 – 65 °C) to give 0.07 g of **13a β**. Total yield: 0.46 g of **13a α** and **a β** (91%, **13a α**: **13a β** = 1.3). 0.33 g of epimeric alcohols were chromatographed on 20 g of silica gel using light petroleum/ether (10:1). The eluates were dried (Na_2SO_4) and after removal of the solvent distilled at the Kugelrohr, yielding *2α,4α-dimethylbicyclo[3.2.1]oct-6-en-3α-ol* (**13a α**) (0.20 g, oil) and *2α,4α-dimethylbicyclo[3.2.1]oct-6-en-3β-ol* (**13a β**) (0.10 g), colorless needles, m. p. 95 – 96 °C. – 90 MHz ^{1}H NMR (CCl_4): δ = 0.94 (d, *J* = 7 Hz, 6H), 1.32 (m, 2H, 2β-, 4β-H), 1.47 (d, *J* = 10 Hz, 1H, H_{anti}), 1.88 (dt, *J* = 10 and 5 Hz, 1H, H_{syn}), 2.38 (m, 2H, 1-, 5-H), 2.60 (t, *J* = 8.5 Hz, 1H, 3α-H), 5.88 (m, 2H).

Alternatively **13a β** was prepared from 15 g of **6a** (0.10 mol) by reduction with 46 g of sodium (2.0 mol) in 650 ml of ethanol under nitrogen. After all the sodium had dissolved, the solution was refluxed for 1 h, cooled, and diluted with 650 g of water. The resulting solution was continuously extracted with pentane for 10 h. The extract was washed with water and dried (Na_2SO_4). Removal of the solvent at reduced pressure gave a mixture of **13a β**: **13a α** = 4.5:1, 13.7 g (91%). Recrystallization from light petroleum (b. p. 40 – 60 °C) gave pure **13a β**, 8.35 g (74%). A further 1.65 g of **13a β** was obtained from the mother liquor.

2,2,4-Trimethylbicyclo[3.2.1]oct-6-en-3-ol (**14**): 3.28 g (20 mmol) of **7a**, **b** were reduced to give a mixture of epimeric alcohols **14**. – MS (70 eV): *m/e* = 166 (21%, M^+), 151 (7), 148 (12), 133 (12), 123 (12), 108 (29), 105 (14), 100 (100), 94 (80), 93 (94), 91 (27), 85 (30), 83 (31), 79 (65).

$C_{11}H_{18}O$ (166.3) Calcd. C 79.47 H 10.91 Found C 79.36 H 10.99

$LiAlH_4$ (g)	Alcohol[a] (g)	Yield (%)	Ratio α:β[b]
0.5	3.13	94	1.5
1.0	3.12	93	1.1[c]
i-Bu_2AlH	0.30	90	10.5

[a] Colorless oil. – [b] Ratio **14a α**: **14a β** and **14b α**: **14b β** (GC: CWAX 20 M). – [c] Same result in THF.

2.5 g of the mixture of alcohols was chromatographed:

2,2,4α-Trimethylbicyclo[3.2.1]oct-6-en-3α-ol (**14a α**): 1.10 g. – 90 MHz ^{1}H NMR (CCl_4): δ = 0.96 (d, *J* = 7 Hz, 3H), 0.97 (s, 3H), 1.03 (s, 3H), 1.67 – 2.00 (m, 2H), 2.20 – 2.36 (m, 1H), 6.15 – 6.31 (m, 2H), 3.10 (d, *J* = 5 Hz, 3β-H) or 3.10 (dd, *J* = 5 and 11.5 Hz, 3β-H), 1.38 (d, *J* = 11.5 Hz, OH) (see Table 5).

2,2,4α-Trimethylbicyclo[3.2.1]oct-6-en-3β-ol (**14a β**): 0.65 g, solid at room temperature. – 90 MHz ^{1}H NMR (CCl_4): δ = 0.89 (s, 3H), 0.93 (d, *J* = 7 Hz, 3H), 0.93 (s, 3H), 1.17 – 1.89 (m, 3H), 2.17 – 2.40 (m, 2H), 2.82 (d, *J* = 9 Hz, 3α-H), 5.84 – 6.06 (m, 2H).

2,2,4β-Trimethylbicyclo[3.2.1]oct-6-en-3β-ol (**14b β**): 0.15 g, solid at room temperature. – 90 MHz ^{1}H NMR (CCl_4): δ = 0.88 (s, 3H), 0.99 (s, 3H), 1.04 (d, *J* = 7.5 Hz, 3H), 1.36 – 1.62 (m, 1H), 1.80 – 2.03 (m, 2H), 2.13 – 2.26 (m, 1H), 2.37 – 2.52 (m, 1H), 3.46 (d, *J* = 7 Hz, 3α-H), 5.83 – 6.03 (m, 2H).

Alcohol **14b α** was not isolated free from diastereoisomers.

2,2,4,4-Tetramethylbicyclo[3.2.1]oct-6-en-3-ol (**15 α, 15 β**): 3.56 g of **8** yielded 3.40 g (94%) of colorless oil (**15 α**: **15 β** = 1:4). *2,2,4,4-Tetramethylbicyclo[3.2.1]oct-6-en-3β-ol* (**15 β**): 90 MHz ^{1}H NMR (CCl_4): δ = 0.89 (s, 6H), 1.00 (s, 6H), 1.50 – 1.80 (m, 1H), 1.82 (s, OH), 2.01 (d, ^2J = 10 Hz, 1H, H_{anti}), 2.10 – 2.20 (m, 2H, 1-, 5-H), 3.03 (s, 1H, 3α-H), 5.96 (m, 2H). – MS (70 eV): *m/e* = 180 (5%, M^+), 143 (5), 137 (5), 132 (9), 114 (36), 108 (18), 93 (57), 71 (22), 66 (100).

Dehydration of Tertiary Bicyclic Alcohols

1) *Two Phase Method:* A solution of tertiary bicyclic alcohol in 5 ml of light petroleum is added to a solution of 2.4 g of *p*-toluenesulfonic acid in 5 ml water. The mixture is refluxed under nitrogen for 2 h, cooled to room temperature, neutralized with an aqueous solution of $NaHCO_3$, and the aqueous phase is extracted three times with a little pentane. The combined organic phase is washed with water, dried (Na_2SO_4), and the solvent is removed at the water pump at room temperature. The residue is distilled at the Kugelrohr (60 – 80 °C, water pump vacuum), the ratio of olefins being determined by ^{1}H NMR.

Dehydration of **10**: 0.86 g (5.2 mmol) of an epimeric mixture of tertiary alcohols **10** gave 0.67 g (86%) of *2,3,4-trimethylbicyclo[3.2.1]octa-2,6-diene* (**20**) (see Table 11) and methylene isomer **17** (see below) (86% total yield, **20**: **17** = 13:1).

Similarly, dehydration of a mixture of alcohols **11** (0.70 g, 3.8 mmol) yielded 0.62 g of *2,3,4,4-tetramethylbicyclo[3.2.1]octa-2,6-diene* (**21**) and methylene isomer **18** (total yield 98%, **21**: **18** = 6.3:1).

2) *Phosphoryl Chloride Method*

a) *Tertiary bicyclic alcohols:* 7.67 g (50 mmol) of $POCl_3$ is dropped into a solution of 10 – 50 mmol of tertiary bicyclic alcohol in 23.7 g (0.30 mol) of pyridine under nitrogen at 5 °C. The reaction solution is refluxed for 3 h, cooled to 0 °C, and poured carefully (0.5 – 1 h) onto 25 g of ice. The aqueous phase is extracted three times with a little pentane and the combined extracts

are washed with 1 N H_2SO_4, a saturated aqueous solution of NaCl, and dried (Na_2SO_4). After removal of the solvent at room temperature the residue is distilled at the Kugelrohr (60–80 °C, water pump vacuum). The ratio of endocyclic:exocyclic olefins is determined by ^1H NMR.

Dehydration of **10**: 8.30 g (50 mmol) of **10** yielded 5.39–6.71 g of dienes **20**:**17** (total yield 73–91%, **20**:**17** = 3.6:1). *Dehydration of* **11**: 1.80 g (10 mmol) of **11** gave 1.58 g of olefins **21** and **18** (total yield 92%, **21**:**18** = 1.4:1).

b) *Dehydration of secondary bicyclic alcohols* **12**–**15**: 3.83 g (25 mmol) of $POCl_3$ is dropped into a solution of 10 mmol of bicyclic alcohol in 11.8 g (0.15 mol) of pyridine at 5 °C under nitrogen. After being stirred for 4 h at room temperature the solution is cooled to 0 °C and poured carefully (0.5–1 h) onto 20 g of ice. The aqueous phase is extracted three times with a little pentane and the combined organic phase is washed with 1 N H_2SO_4, saturated aqueous NaCl solution, and dried (Na_2SO_4). After removal of the solvent at the water pump at room temperature the residue is distilled at the Kugelrohr (50–80 °C, water pump vacuum).

4,4-Dimethylbicyclo[3.2.1]octa-2,6-diene (**22**): Dehydration of **12** gave 0.94–1.18 g (70–88%) of colorless, volatile **22** which interestingly is a solid at 0 °C. – 90 MHz ^1H NMR (CCl_4): δ = 0.86 (s, 3H), 1.12 (s, 3H), 1.88–1.92 (m, 2H), 2.30–2.44 (m, 1H, 5-H), 2.44–2.64 (m, 1H, 1-H), 5.67 (dd, $J_{6,7}$ = 5.5, $J_{5,6}$ = 3 Hz, 1H, 6-H), 6.21 (dd, $J_{6,7}$ = 5.5, $J_{1,7}$ = 3 Hz, 1H, 7-H), 4.89 (dd, $J_{2,3}$ = 9.5, $J_{3,5}$ = 2 Hz, 1H, 3-H), 5.98 (dd, $J_{2,3}$ = 9.5, $J_{1,2}$ = 6 Hz, 1H, 2-H). – MS (70 eV): *m/e* = 134 (83%, M^+), 119 (100), 117 (16), 106 (19), 105 (22), 93 (29), 91 (64), 79 (16), 77 (22), 69 (18).

$C_{10}H_{14}$ (134.2) Calcd. C 89.49 H 10.51 Found C 88.72 H 10.60

Dehydration of **13** gave 0.94–1.13 g of bicyclic diene **23**α and a minor amount of **23**β (70–84%). If pure **13**aα and/or **13**aβ is dehydrated, only **23**α is formed. *2,4α-Dimethylbicyclo[3.2.1]octa-2,6-diene* (**23**α): 90 MHz ^1H NMR (CCl_4): δ = 0.85 (d, *J* = 7.5 Hz, 3H), 1.69 (t, *J* = 1.5 Hz, 3H), 1.73–1.91 (m, 1H, H_{anti}), 1.93–2.17 (m, 1H, H_{syn}), 2.22–2.50 (m, 2H), 2.60–2.79 (m, 1H), 5.59 (dd, $J_{6,7}$ = 5.5, $J_{5,6}$ = 3 Hz, 1H, 6-H), 6.32 (dd, $J_{6,7}$ = 5.5, $J_{1,7}$ = 3 Hz, 1H, 7-H), 4.60–4.73 (m, 1H).

2,4β-Dimethylbicyclo[3.2.1]octa-2,6-diene (**23**β): Inter al. δ = 1.09 (d, *J* = 7.3 Hz, 3H), 5.74 (dd, $J_{6,7}$ = 5.5, $J_{5,6}$ = 3 Hz, 1H, 6-H), 6.17 (dd, $J_{6,7}$ = 5.5, $J_{1,7}$ = 3 Hz, 1H, 7-H). – MS (70 eV): *m/e* = 134 (71%, M^+), 119 (100), 106 (27), 91 (60), 79 (21), 77 (23), 69 (14), 66 (27).

$C_{10}H_{14}$ (134.2) Calcd. C 89.49 H 10.51 Found C 88.40 H 10.69

2,4,4-Trimethylbicyclo[3.2.1]octa-2,6-diene (**24**): Dehydration of **14** gave 0.81–1.12 g (54–76%) of **24**. – 90 MHz ^1H NMR (CCl_4): δ = 0.84 (s, 3H), 1.09 (s, 3H), 1.65 (d, *J* = 1.2 Hz, 3H), 1.86–1.96 (m, 2H), 2.30–2.44 (m, 2H), 4.53–4.64 (m, 1H, 3-H), 5.61 (dd, $J_{6,7}$ = 5.5, $J_{5,6}$ = 3 Hz, 1H, 6-H), 6.23 (dd, $J_{6,7}$ = 5.5, $J_{1,7}$ = 3 Hz, 1H, 7-H). – MS (70 eV): *m/e* = 148 (50%, M^+), 133 (100), 128 (18), 122 (16), 117 (16), 115 (18), 107 (30), 105 (64), 94 (66), 92 (64), 83 (13), 79 (16), 77 (29).

$C_{11}H_{16}$ (148.3) Calcd. C 89.12 H 10.88 Found C 88.68 H 10.90

In an orienting experiment dehydration of **15** with $POCl_3$/pyridine under reflux gave **21** and **25** in low yield.

Preparation of 3-Methylenebicyclo[3.2.1]oct-6-enes[5] **16**–**18**: Titanium tetrachloride (11 ml of a 1 M solution in CH_2Cl_2) is dropped slowly (0.25 h) into a suspension of 2.95 g (45 mmol) of zinc dust and 2.60 g (15 mmol) of dibromomethane in 50 ml of absol. THF under nitrogen. The solution warms and turns dark brown. After 0.25 h 10 mmol of bicyclic ketone in 10 ml of absol. THF are dropped in (0.5 h). After being stirred for 24 h at 25 °C the solution is worked up by

pouring onto 50 g of ice, filtering the precipitate formed, and washing three times with dichloromethane. The organic phase of the filtrate is separated, the aqueous layer extracted three times with dichloromethane, and the combined organic layer is washed with water and dried (Na_2SO_4). After removal of dichloromethane the residue is distilled at the Kugelrohr (60 – 80 °C, water pump vacuum). As the distillate still contains bicyclic ketone (GC, IR), it is taken up in 10 ml of absol. ether and dropped into a suspension of 0.30 g of $LiAlH_4$ in 10 ml of absol. ether under nitrogen (0.5 h). After stirring for 0.5 h at 25 °C the solution is cooled to 0 °C and treated cautiously with 10 g of ice water. After evolution of hydrogen has ceased, 200 ml of water are added. After separation of the organic layer the aqueous phase is extracted three times with pentane and the combined organic phase is washed with aqueous saturated NaCl solution and dried (Na_2SO_4). The solvent is distilled off, and the remainder is concentrated briefly at the water pump at room temperature and then filtered over 20 g of silica gel with pentane, the alcohols being eluted with ether. The eluates are dried (Na_2SO_4) and after evaporation of the solvent the residue is distilled at the Kugelrohr using water pump vacuum (methylenebicyclics b. p. 60 – 80 °C, alcohols b. p. 100 – 130 °C).

2,2-Dimethyl-3-methylenebicyclo[3.2.1]oct-6-ene (**16**): Reaction of **5** according to the general procedure gave 0.12 g of alcohol **12**α,β (8%) and 1.08 g (71%) of **16**, which, like diene **22**, is a colorless solid at 0 °C. – 90 MHz ^{1}H NMR (CCl_4): δ = 1.03 (s, 3H), 1.13 (s, 3H), 1.26 – 2.42 (m, 5H), 2.42 – 2.62 (m, 1H), 4.54 (br d, *J* = 1.5 Hz, 1H), 4.65 (t, *J* = 1.5 Hz, 1H), 5.79 (dd, *J* = 5.8 and 2.8 Hz, 1H), 5.93 (dd, *J* = 5.8 and 2.8 Hz, 1H). – MS (70 eV): *m/e* = 148 (43%, M^+), 133 (50), 119 (17), 115 (13), 107 (76), 105 (93), 92 (48), 91 (53), 83 (90), 79 (59), 77 (38), 67 (98), 66 (100).

$C_{11}H_{16}$ Calcd. 148.1252 Found 148.1250 (MS)

2,4-Dimethyl-3-methylenebicyclo[3.2.1]oct-6-ene (**17**αα, **17**ββ, **17**αβ): Methylenation of **6** gave 0.11 – 0.22 g of alcohols **13a**α – **13c**β (6 – 13%) and 0.94 – 1.13 g (64 – 76%) of **17**αα, **17**ββ and **17**αβ. GC retention times on a SE 30 column: **17**αβ < **17**ββ < **17**αα. – 90 MHz ^{1}H NMR (CCl_4) of **17**αα: δ = 0.99 (d, *J* = 6.8 Hz, 6H), 1.52 – 1.72 (m, 1H), 1.86 – 2.12 (m, 1H), 2.10 – 2.50 (m, 4H), 4.67 (t, *J* = 1.9 Hz, 2H), 5.82 (br s, 2H). **17**ββ: 1.13 (d, *J* = 7.2 Hz, 6H). **17**αβ: 0.97 (d, *J* = 6.8 Hz, 3H), 1.19 (d, *J* = 7.3 Hz, 3H). – MS (70 eV): *m/e* = 148 (28%, M^+), 133 (31), 119 (55), 107 (100), 105 (38).

$C_{11}H_{16}$ Calcd. 148.1252 Found 148.1251 (MS)

2,2,4α-Trimethyl-3-methylenebicyclo[3.2.1]oct-6-ene (**18**α): Methylenation of 7 gave 0.16 g (10%) of alcohols **14a**α – **14b**β and 0.85 – 0.92 g (57 – 62%) of **18**α, **18**β. GC retention time SE 30: **18**β < **18**α. – 90 MHz ^{1}H NMR (CCl_4) of **18**α: δ = 1.00 (d, *J* = 6.8 Hz, 3H), 1.04 (s, 3H), 1.15 (s, 3H), 1.58 – 1.84 (m, 1H), 1.98 (d, ^2J = 10 Hz, 1H), 2.05 – 2.22 (m, 1H), 2.26 – 2.56 (m, 2H), 4.64 (d, *J* = 2 Hz, 1H), 4.77 (d, *J* = 2 Hz, 1H), 5.82 (dd, *J* = 5.8 Hz, *J* = 2.8 Hz, 1H), 5.94 (dd, *J* = 5.8 Hz, *J* = 2.8 Hz, 1H). **18**β was also present (GC and ^{1}H NMR signals due to methyl protons). – MS (70 eV): *m/e* = 162 (55%, M^+), 147 (81), 133 (16), 121 (69), 119 (91), 107 (27), 105 (64), 96 (35), 93 (45), 91 (72), 81 (96), 79 (51), 77 (58), 68 (43), 66 (37), 55 (80), 53 (44), 41 (100).

$C_{12}H_{18}$ Calcd. 162.1408 Found 162.1412 (MS)

Silver Nitrate Complexes: 2.13 g of silver nitrate (12.5 mmol) are dissolved with gentle warming in 1.4 ml of distilled water. 10 mmol of bicyclic olefin (Note 1) are added dropwise. The solution warms up and after a short period a colorless to light yellow paste is formed which is suction filtered (ca. 1 h at the water pump). The filtered aqueous phase and the mother liquor (after recrystallization) are diluted with 5 – 10 ml of water and extracted several times with a little pentane. The combined extracts are washed with water and dried (Na_2SO_4) for recovery of the olefin. The paste is dissolved in methanol (40 °C) and the solution is filtered. On cooling the

colorless silver nitrate complex crystallizes. It is suction filtered and washed with a little methanol (Note 2).

Notes. 1) The bicyclic dienes must be freshly distilled. Otherwise precipitation of silver occurs.

2) On concentrating the methanol solution the temperature must not exceed 20 °C, as otherwise the bicyclic diene is evaporated with the methanol.

2,2-Dimethylbicyclo[3.2.1]oct-6-en-3-one-silver nitrate (1/1) (**5-A**): Addition of 1.50 g of **5** did not give rise to a precipitate. After adding 2 ml of water and cooling to 0 °C for 3 h 0.70 g of complex **5-A** was obtained. The experiment was repeated by adding 1.50 g of **5** as before, and seeding the mother liquor with crystals of **5-A**. After 0.5 h 2.40 g (75%) of **5-A** was suction filtered. From the aqueous layer 0.14 g of **5** (10%) and from the mother liquor another 0.30 g of **5** (20%) were recovered. Recrystallization gave 1.96 g (61%) of **5-A**, m. p. 127 °C (dec.). – 90 MHz ^{1}H NMR (CD_3CN): δ = 0.98 (s, 3H), 1.17 (s, 3H), 2.04 – 2.27 (m, 1H), 2.37 – 2.56 (m, 2H), 2.71 – 2.90 (m, 1H), 6.01 – 6.26 (m, 2H). The signals for the other protons were obscured by CD_3CN.

$C_{10}H_{14}O \cdot AgNO_3$ (320.1) Calcd. C 37.52 H 4.41 N 4.37 Found C 37.07 H 4.50 N 4.34

2,4-Dimethylbicyclo[3.2.1]oct-6-en-3-one-silver nitrate (1/1) (**6a-A, 6c-A**): 7.50 g of **6** (**6a** : **6b** = 4 : 1) gave 12.1 g (76%) of a colorless paste, 11.6 g (73%) of **6a-A** after recrystallization. (From the aqueous phase and mother liquor 1.90 g of **6** (**6a** : **6b** = 1 : 2) (25%) are recovered). *2α,4α-Dimethylbicyclo[3.2.1]oct-6-en-3-one-AgNO$_3$* (**6a-A**), m. p. 140 °C (dec.). – 90 MHz ^{1}H NMR (CD_3CN): δ = 0.95 (d, *J* = 7 Hz, 6H), 2.40 – 2.67 (m, 2H), 2.67 – 2.82 (m, 2H), 6.13 (m, 2H). The signals of H_{syn}, H_{anti} were obscured by CD_3CN.

$C_{10}H_{14}O \cdot AgNO_3$ (320.1) Calcd. C 37.52 H 4.41 N 4.37 Found C 37.45 H 4.39 N 4.32

2α,4β-Dimethylbicyclo[3.2.1]oct-6-en-3-one (**6c**) formed a silver nitrate complex **6c-A**. On rapid precipitation of the complex (the paste was suction filtered quickly after addition of ketones **6a – c**) and slow recrystallization, epimeric ketone **6c** was enriched in the aqueous phase and mother liquor. On slow precipitation (the paste was suction filtered 0.5 h after addition of ketones **6a – c**), ketone **6a** and **6c** crystallized together as complexes **6a-A** and **6c-A**. – 90 MHz ^{1}H NMR of **6c-A** (CD_3CN): inter al. δ = 0.96 (d, *J* = 7 Hz, 3H), 1.17 (d, *J* = 7.5 Hz, 3H).

2,2,4α-Trimethylbicyclo[3.2.1]oct-6-en-3-one-silver nitrate (1/1) (**7a-A**): The reaction of **7** gave 3.01 – 3.30 g (90 – 98%) of a colorless paste, 2.48 – 2.67 g (74 – 80%) of colorless crystals of **7-A** after recrystallization, 0.16 – 0.30 g (10 – 20%) of ketone **7** being recovered from the aqueous phase and mother liquor. – 90 MHz ^{1}H NMR (CD_3CN) of **7a-A**: δ = 0.96 (d, *J* = 6.7 Hz, 3H), 0.98 (s, 3H), 1.20 (s, 3H), 2.19 – 2.39 (m, 2H), 2.39 – 2.57 (m, 1H), 2.58 – 2.80 (m, 2H), 6.06 – 6.28 (m, 2H). The signal for H_{syn} was upfield from H_{anti} and obscured by solvent. The epimeric complex **7b-A** was also formed as could be seen most clearly by cleavage to **7b** (see below).

4,4-Dimethylbicyclo[3.2.1]octa-2,6-diene-silver nitrate (1/1) (**22-A**): 2.98 g (98%) of paste gave 1.62 g (53%) of **22-A** after recrystallization, 0.41 g (31%) of **22** being recovered. **22-A** had m. p. 153 °C (dec.). – 90 MHz ^{1}H NMR (CD_3CN): δ = 0.90 (s, 3H), 1.12 (s, 3H), 2.57 – 2.72 (m, 1H), 5.02 (dd, $J_{2,3}$ = 9.5, $J_{3,5}$ = 2 Hz, 1H, 3-H), 5.98 (dd, $J_{2,3}$ = 9.5, $J_{1,2}$ = 6 Hz, 1H, 2-H), 5.88 (dd, $J_{6,7}$ = 5.5, $J_{5,6}$ = 3 Hz, 1H, 6-H), 6.42 (dd, $J_{6,7}$ = 5.5, $J_{1,7}$ = 3 Hz, 1H, 7-H). The other signals were obscured by solvent CD_3CN.

$C_{10}H_{14} \cdot AgNO_3$ (304.1) Calcd. C 39.50 H 4.64 N 4.61 Found C 38.75 H 4.63 N 4.67

2,4-Dimethylbicyclo[3.2.1]octa-2,6-diene-silver nitrate (1.5 – 2/1) (**23-A**): 2.00 – 2.02 g (84 – 85%) gave 1.52 – 1.60 g (64 – 68%) of **23-A** after recrystallization, 0.39 – 0.41 g (29 – 31%) of **23** being recovered from the aqueous phase and the mother liquor. **23α-A** had m. p. 115 °C. –

90 MHz ^{1}H NMR (CD_3CN): inter al. δ = 0.85 (d, J = 7.5 Hz, 3H), 1.70 (t, ^4J = 1.5 Hz, 3H), 2.66 – 2.86 (m, 1H), 4.67 – 4.80 (m, 1H, 3-H), 5.73 (dd, $J_{6,7}$ = 5.5, $J_{5,6}$ = 3 Hz, 1H, 6-H), 6.48 (dd, $J_{6,7}$ = 5.5, $J_{1,7}$ = 3 Hz, 1H, 7-H). The signals of four protons were obscured by CD_3CN and traces of water. **23 β-A**: δ = 1.09 (d, J = 7 Hz, 3H), 5.79 (dd, $J_{6,7}$ = 5.5, $J_{5,6}$ = 3 Hz, 1H, 6-H), 6.35 (dd, $J_{6,7}$ = 5.5, $J_{1,7}$ = 3 Hz, 1H, 7-H).

2,4,4-Trimethylbicyclo[3.2.1]octa-2,6-diene-silver nitrate (1.5 – 2/1) (**24-A**): 2.90 g of colorless paste, 0.15 g (10%) of recovered **24**, and 2.08 g (86%) of colorless crystals of **24-A**, m. p. 118 °C. – 90 MHz ^{1}H NMR (CD_3CN): δ = 0.87 (s, 3H), 1.11 (s, 3H), 1.79 (d, ^4J = 1.5 Hz, 3H), 2.33 – 2.58 (m, 2H), 4.50 – 4.61 (m, 1H, 3-H), 5.82 (dd, $J_{6,7}$ = 5.5, $J_{5,6}$ = 3 Hz, 1H, 6-H), 6.36 (dd, $J_{6,7}$ = 5.5, $J_{1,7}$ = 3 Hz, 1H, 7-H). In solvent MeOD the signals for H_{syn} and H_{anti} were no longer obscured and appeared in the range 1.8 – 2.1 ppm.

Cleavage of silver nitrate complexes: The colorless silver nitrate complex is dissolved in water and pentane. The organic layer is separated, the aqueous layer is extracted twice with pentane and the combined organic phase is washed with water and dried (Na_2SO_4). After removal of the solvent the residue is distilled at the Kugelrohr.

Note: Should the dissolution of the silver nitrate complexes be difficult (complexes **20-A** and **21-A** dissolve only very slowly after several weeks), dilute aqueous ammonia can be added.

Recovery of 2,3,4,4-tetramethylbicyclo[3.2.1]octa-2,6-diene (**21**) *from its $AgNO_3$ Complex* **21-A**:

Complex **21-A**	2.58 g	4.40 g	4.15 g
Distillate **21**	1.74 g (99%)	2.70 g (93%)	2.50 g (92%)

Recovery of 2,2,4-trimethylbicyclo[3.2.1]oct-6-en-3-one (**7**) *from* **7-A**: 3.11 g of freshly precipitated complex **7-A** (dried at the water vacuum pump) were treated with 10 ml of absol. ether. The precipitate (mainly $AgNO_3$) was suction filtered, and the ether was removed to leave a residue which was distilled at the Kugelrohr (100 – 130 °C, water pump) giving 1.31 g (86%) of an epimeric mixture of ketones **7a** + **7b**. In another experiment 3.34 g of **7-A** were decomposed with water and ether to yield 1.48 – 1.56 g (90 – 95%) of colorless, pure ketone **7**.

Epoxidation[12]: 10 mmol of olefin in 100 ml of dichloromethane and 30 ml of 5% aqueous $NaHCO_3$ solution are stirred vigorously, whilst 2.03 g (85%, 10 mmol) of *m*-chloroperbenzoic acid are added in portions. The mixture is stirred for 1 h at room temperature, the organic phase is separated, and the aqueous layer is extracted once with 10 ml of dichloromethane. The combined organic phase is washed with 30 ml of 1 N NaOH, 30 ml of water, and dried (Na_2SO_4).

2,4,5,5-Tetramethyl-3-oxa-exo-tricyclo[4.2.1.0^{2,4}]non-7-ene (**26**): The crude product was purified by distillation (Kugelrohr, 80 – 100 °C, water pump) or by chromatography (80 g of silica gel, light petroleum/ether = 10:1) to yield 1.20 – 1.42 g (67 – 80%) of **26**. – 90 MHz ^{1}H NMR (CCl_4): δ = 0.86 (s, 3H), 1.06 (s, 3H), 1.08 (s, 3H), 1.24 (s, 3H), 1.24 – 1.50 (m, 1H), 1.90 – 2.12 (m, 2H), 2.34 – 2.48 (m, 1H), 5.87 (dd, J = 5.5 and 3 Hz, 1H, 7-H), 6.11 (dd, J = 5.5 and 3 Hz, 1H, 8-H). – MS (70 eV): *m/e* = 178 (72%, M^+), 163 (100), 160 (15), 145 (19), 141 (27), 139 (98), 136 (59), 135 (59), 134 (49), 121 (43), 119 (26), 111 (55), 109 (53), 107 (37), 91 (24).

6α,8α-Dimethyl-3-oxatricyclo[3.3.1.0^{2,4}]nonan-7-one (**27**): 0.50 g of **6a** (1/3 of general procedure) was used. After 6 h at room temperature *m*-chloroperbenzoic acid was still present (iodine starch test). Epoxidation was complete after refluxing for 2 h. Recrystallization (light petroleum, b. p. 60 – 70 °C) gave 0.40 g (91%) of **27**, colorless needles. – 90 MHz ^{1}H NMR (CCl_4): δ = 1.16 (d, J = 7 Hz, 6H), 1.42 – 1.60 (m, 1H, H_{anti}), 1.67 – 1.97 (m, 1H, H_{syn}),

2.40 – 2.70 (m, 4H), 3.33 (s, 2H). – MS (70 eV): *m/e* = 166 (18%, M^+), 137 (5), 135 (5), 122 (9), 109 (100), 107 (13), 95 (79).

$C_{10}H_{14}O$ (166.2) Calcd. C 72.26 H 8.49 Found C 72.33 H 8.42

2,4,5,5-Tetramethyl-3-oxatricyclo[4.2.1.0^{2,4}]non-7-ene-silver nitrate (1/1) (**26** · $AgNO_3$): The preparation followed the general procedure, 1.78 g (10 mmol) of **26** being allowed to react with aqueous $AgNO_3$ to yield 3.28 – 3.40 g of a colorless paste, which dissolved only slowly in methanol (40 °C, 0.25 h). Recrystallization gave 3.06 – 3.22 g (88 – 92%) of colorless crystals. – 90 MHz ^{1}H NMR (CD_3OD): δ = 0.93 (s, 3H), 1.12 (s, 3H), 1.14 (s, 3H), 1.32 (s, 3H), 1.32 – 1.59 (m, 1H, H_{syn}), 1.99 – 2.19 (m, 2H), 2.51 – 2.64 (dd, *J* = 2.5 and 5 Hz, 1H, 1-H), 6.15 (dd, $J_{7,8}$ = 5.5, $J_{6,7}$ = 2.5 Hz, 1H, 7-H), 6.38 (dd, $J_{7,8}$ = 5.5, $J_{1,8}$ = 2.5 Hz, 1H, 8-H).

$C_{12}H_{18}O \cdot AgNO_3$ (348.2) Calcd. C 41.40 H 5.21 N 4.02 Found C 41.73 H 5.25 N 3.99

Cleavage of silver nitrate complex **26** · $AgNO_3$: 3.09 g (8.9 mmol) of **26** · $AgNO_3$ were dissolved in dilute aqueous ammonia/ether and the solution was extracted three times with ether. The combined extracts were washed with water, dried (Na_2SO_4), and the solvent removed to leave a residue which after distillation at the Kugelrohr (80 – 100 °C, water pump) gave 1.48 g (94%) of **26**.

Reaction of **21** *with oxygen:* In a 50 ml flask the solution of 50 mg of **21** in 5 ml of CCl_4 was stirred under atmospheric oxygen for 1 week in the dark. 100 MHz ^{1}H NMR (CCl_4) indicated a ratio bicyclic diene **21** : epoxide **26** = 4.5 : 1.

References

[1] Part 20: *M. R. Ashcroft* and *H. M. R. Hoffmann,* Org. Synth. **58**, 17 (1978); Part 19, see ref.[3].

[2] *H. M. R. Hoffmann, D. R. Joy,* and *A. K. Suter,* J. Chem. Soc. B **1968**, 57.

[3] *D. I. Rawson, B. K. Carpenter,* and *H. M. R. Hoffmann,* J. Am. Chem. Soc. **101**, 1786 (1979). Axial methyl protons show greater coupling ^3J than equatorial methyl protons in other cyclohexanes. See *L. M. Jackman* and *S. Sternhell,* Applications of NMR Spectroscopy in Organic Chemistry, 2nd edit., p. 298, Pergamon Press, Oxford 1969; *F. Johnson, N. A. Starkovsky,* and *W. D. Gurowitz,* J. Am. Chem. Soc. **87**, 3492 (1965).

[4] *H. M. R. Hoffmann, K. E. Clemens,* and *R. H. Smithers,* J. Am. Chem. Soc. **94**, 3940 (1972); see also ref.[6].

[5] *K. Takai, Y. Hotta, K. Oshima,* and *H. Nozaki,* Tetrahedron Lett. **1978**, 2417.

[6] *H. M. R. Hoffmann* and *M. N. Iqbal,* Tetrahedron Lett. **1975**, 4487.

[7] See also *J. B. Stothers, J. R. Swenson,* and *C. T. Tan,* Can. J. Chem. **53**, 581 (1975).

[8] *R. L. Sowerby* and *R. M. Coates,* J. Am. Chem. Soc. **94**, 4758 (1972).

[9] The autoxidation of cyclobutadienes (*G. Maier,* Angew. Chem. **86**, 491 (1974); Angew. Chem., Int. Ed. Engl. **13**, 425 (1974); *A. Krebs* et al., Liebigs Ann. Chem. **1979**, 473; Tetrahedron Lett. **1980**, 3171) and ketenes (*N. J. Turro, M. F. Chow,* and *Y. Ito* in Singlet Oxygen, p. 174, *B. Ranby* and *J. F. Rabek* eds., Wiley-Interscience, Chichester 1978) has been investigated. See also *M. A. Pericás* and *F. Serratosa,* Tetrahedron Lett. **1978**, 4969.

[10] *R. J. Giguere, D. I. Rawson,* and *H. M. R. Hoffmann,* Synthesis **1978**, 902.

[11] *E. Winterfeldt,* Synthesis **1975**, 617.

[12] *W. K. Anderson* and *T. Veysoglu,* J. Org. Chem. **38**, 2267 (1973).

[37/80]