The Loss of a Methyl Radical and the Retro Diels–Alder Reaction in the Electron Impact Mass Spectrometry of 2-Cyclohexen-1-ol and Related Compounds

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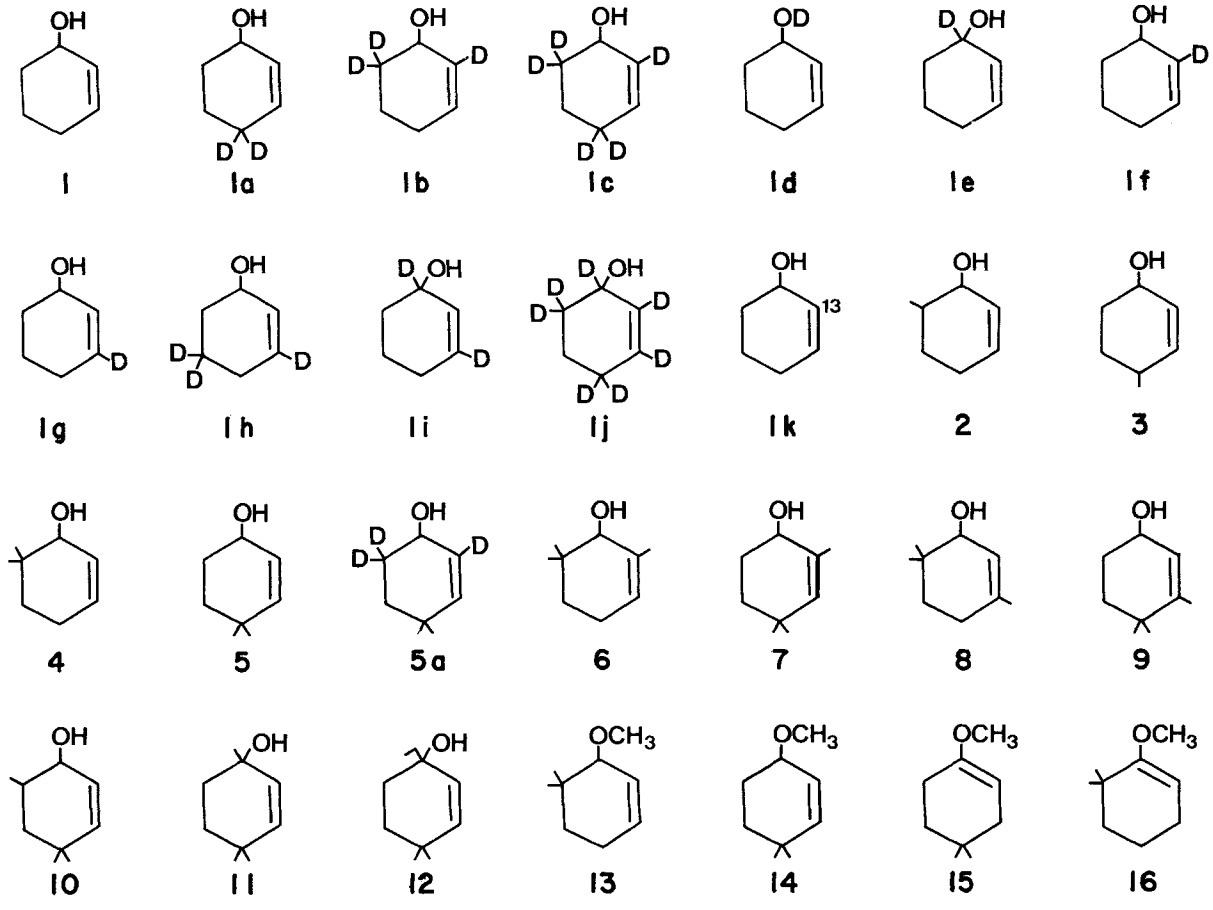
The electron impact mass spectra of 2-cyclohexen-1-ol and of several of its ^{2}H and ^{13}C labelled analogues show that the molecular ions lose a methyl radical by a completely different means from the mechanism described previously. Moreover, the retro Diels–Alder reaction also proceeds in a non-classical way; in addition to the elimination of an olefinic molecule from unrearranged molecular ions, a second more important route implies a formal 1,3 allylic rearrangement prior to the retro Diels–Alder reaction. The mass spectra of a series of alkyl substituted homologues show that the competition between the two processes is closely related to the size of the olefinic moiety that is expelled.

INTRODUCTION

During a study of the mass spectrometry of various benzoic esters we prepared the labelled compounds **1b, 1c** and **1e** and observed fortuitously that for all the labelled compounds the loss of a methyl radical from their molecular ions resulted in the expulsion of $CH_2D^{\cdot}$ almost exclusively. This was completely contrary to the apparently sound mechanism that had been proposed previously on the basis of deuterium labelling experiments[1] (Scheme 1) and prompted us to



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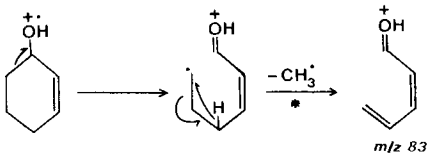


Scheme 1

study in more detail the electron impact (EI) mass spectrometry of 2-cyclohexen-1-ol.

The EI fragmentation of alicyclic α,β-unsaturated alcohols has received little attention and only some characteristic fragmentation modes have been discussed.[2–5] In the present work we have examined with the help of the labelled compounds **1a–1k** the formation of the most important ions which are found in the mass spectrum of 2-cyclohexen-1-ol (**1**). The ^{13}C labelled compound **1k** was prepared in order to confirm our results with respect to the loss of a methyl radical from the molecular ions. In addition we have also studied the mass spectra of a series of alkyl substituted homologues of **1** (**2–14**) and those of the two isomers **15** and **16** in order to gather some information on the two competitive retro Diels–Alder (RDA) reactions by which olefinic fragments are eliminated from the molecular ions. The various labelled compounds and the alkyl substituted homologues which have been studied are shown above; the isotopic compositions are given in the Experimental section.

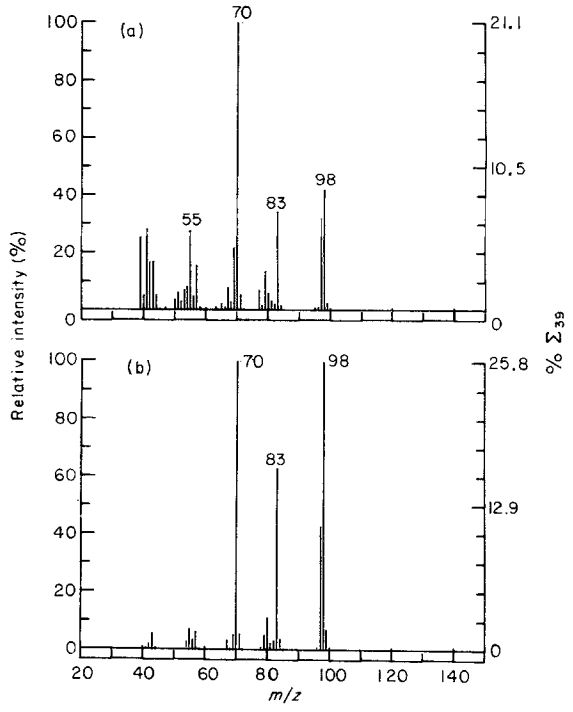


Figure 1. (a) 70 eV and (b) 12 eV mass spectra of 2-cyclohexen-1-ol.

RESULTS AND DISCUSSION

The 70 eV and 12 eV mass spectra of **1** are illustrated in Fig. 1, while the 70 eV mass spectra of the labelled compounds **1a–1k** are listed in Table 1. The 12 eV mass spectra yielded no additional information about the fragmentation modes. Therefore they are not presented here. Table 2 contains the 70 eV mass spectra of the alkyl substituted 2-cyclohexen-1-ols (**2–12**) and those of the methoxy compounds (**13–16**).

Table 1. 70 eV mass spectra of compounds 1a–1k normalized to base peak = 100.0

	Compound										
m/z	1a	1b	1c	1d[a]	1e	1f[a]	1g	1h	1i	1j	1k[a]
39	19.4	15.2	3.4	19.9	21.0	12.6	16.7	6.6	10.8	0.8	5.0
40	29.6	25.2	10.6	7.0	11.4	12.9	15.2	13.5	19.1	4.7	13.3
41	26.8	19.9	16.1	14.8	17.5	11.6	14.8	9.9	10.2	10.5	18.4
42	35.1	27.2	10.2	15.5	16.2	16.8	23.0	15.1	16.7	14.0	25.9
43	45.3	37.3	16.3	24.5	22.4	19.1	24.4	25.3	13.6	4.9	24.2
44	36.1	24.5	28.7	6.8	11.6	24.5	12.7	14.2	18.2	15.7	11.7
45	9.7	21.9	26.3	5.6	4.1	2.6	1.6	3.5	6.7	18.4	6.1
46	3.2	5.5	5.9	0.7	0.5	—	—	0.7	0.3	13.1	1.1
47	0.8	0.8	1.1	—	—	—	—	—	—	15.7	1.1
48	0.8	0.9	—	—	—	—	—	0.5	0.5	1.2	—
49	1.1	0.7	—	0.5	—	—	—	—	0.5	0.7	—
50	4.6	2.6	0.9	4.3	2.8	3.1	2.7	1.3	1.7	0.5	—
51	8.3	5.5	2.3	6.8	5.2	4.9	5.2	3.1	3.6	1.0	1.8
52	9.2	6.8	3.4	4.0	4.3	4.4	4.8	3.9	4.2	2.4	3.7
53	8.3	6.5	4.0	6.0	6.1	4.0	5.2	3.6	3.9	2.1	2.8
54	9.2	9.1	5.4	8.8	10.6	5.8	6.2	3.7	5.4	3.3	6.5
55	38.8	21.4	7.2	12.6	13.2	15.6	18.8	8.8	13.0	1.7	9.1
56	24.0	35.4	23.4	16.3	16.4	18.8	21.1	16.6	12.3	5.4	23.6
57	25.9	16.7	13.6	1.3	5.4	11.6	9.0	14.2	11.4	14.0	20.0
58	12.9	14.4	9.7	14.3	9.4	8.8	6.9	11.1	7.3	14.9	14.3
59	6.0	10.6	9.5	1.7	0.8	1.5	0.9	6.8	5.4	7.8	2.2
60	1.1	4.0	3.8	—	—	—	—	1.0	0.6	6.1	1.1
61	—	0.8	0.6	—	—	—	—	—	—	8.7	1.7
62	0.7	—	—	0.5	0.5	0.5	—	—	—	1.0	—
63	1.3	0.7	—	0.9	0.9	0.5	0.8	—	0.5	—	0.6
64	1.4	1.0	0.5	—	0.5	0.7	0.7	0.5	0.6	—	1.2

Table 1 (continued)

m/z	1a	1b	1c	1d[a]	1e	1f[a]	1g	1h	1i	1j	1k[a]
65	1.4	0.9	0.5	1.9	1.6	1.1	1.1	—	0.6	—	—
66	2.6	1.6	—	1.7	1.9	2.3	2.3	0.8	1.5	0.5	2.3
67	3.6	2.7	0.9	4.7	5.2	5.5	3.5	1.5	2.4	—	2.8
68	6.0	3.9	1.6	5.2	4.6	5.2	5.8	2.0	5.3	0.7	8.1
69	12.9	13.4	1.9	0.9	15.3	4.0	5.7	7.1	4.5	1.0	3.7
70	100.0	30.8	4.2	16.1	10.9	17.5	25.8	20.8	15.8	1.2	22.6
71	68.6	54.5	12.9	100.0	100.0	100.0	100.0	100.0	11.9	3.8	100.0
72	72.3	23.6	30.2	5.1	5.0	7.1	11.4	10.2	100.0	19.2	9.6
73	15.7	100.0	100.0	0.7	0.5	1.1	0.8	2.5	4.9	20.1	2.6
74	2.2	8.1	9.3	1.0	—	0.8	—	—	0.5	13.1	0.5
75	0.9	1.1	1.4	—	—	—	—	—	—	100.0	0.6
76	0.5	—	—	—	—	—	—	—	—	8.7	—
77	2.2	0.6	—	7.2	2.8	2.4	2.7	—	0.8	1.0	—
78	6.4	3.4	—	1.9	5.1	6.5	6.1	1.8	3.3	—	8.1
79	7.8	6.8	2.1	13.0	3.9	5.0	4.1	3.6	3.2	—	0.8
80	11.5	5.9	3.8	6.9	13.1	11.9	13.4	3.1	4.3	1.2	18.2
81	16.6	11.4	2.7	2.9	7.5	5.5	6.8	5.7	9.4	2.8	12.9
82	10.6	16.3	4.6	1.2	3.5	3.4	3.9	8.6	5.7	1.5	2.1
83	8.7	9.5	8.9	—	34.7	29.7	35.7	5.7	29.9	1.5	31.1
84	10.1	8.5	6.3	33.5	5.1	5.3	5.4	6.2	3.4	5.7	3.3
85	42.1	58.1	2.9	1.9	—	0.7	0.5	25.7	2.7	5.6	—
86	14.8	9.1	9.7	—	—	—	—	4.1	—	7.1	—
87	8.3	0.8	39.9	—	—	—	—	—	—	29.8	—
88	0.6	—	2.5	—	—	—	—	—	—	6.4	
89	—	—	—	—	—	—	—	—	—	1.9	—
90	—	—	—	—	—	—	—	—	—	0.5	—
95	—	—	—	—	—	—	—	—	—	—	0.7
96	0.9	—	—	1.1	0.7	0.8	0.9	—	—	—	4.6
97	2.3	1.0	—	—	2.6	2.0	2.4	0.5	0.6	—	5.9
98	19.4	1.6	0.5	31.9	28.1	30.7	27.7	0.7	4.9	—	30.8
99	25.9	8.8	0.8	41.4	42.1	43.3	38.5	4.8	25.2	—	39.1
100	56.1	47.2	2.1	2.7	2.8	3.6	4.8	26.2	44.5	0.5	3.6
101	20.3	59.7	17.4			0.7	—	39.5	3.0	1.4	0.8
102	10.1	7.5	13.8					4.4		5.9	
103	4.1	0.7	37.4							18.4	
104			2.5							8.7	
105										46.4	
106										3.3	

[a] Spectrum corrected to 100% deuteration.

Table 2. 70 eV mass spectra of compounds 2–16 normalized to base peak = 100.0

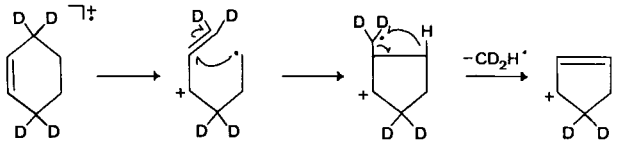
	Compound															
m/z	2	3	4	5	5a	6	7	8	9	10	11	12	13	14	15	16
39	19.5	17.0	7.9	11.3	9.6	8.6	11.9	5.9	9.8	7.6	12.1	6.9	6.4	13.2	11.3	16.6
40	4.2	4.7	1.7	2.7	8.6	1.5	2.0	1.0	1.7	1.4	2.1	1.2	1.1	2.3	1.7	3.7
41	23.1	24.3	12.7	23.5	18.3	14.3	20.8	10.7	18.4	16.9	20.4	11.6	11.1	23.0	16.5	28.3
42	18.5	9.4	7.7	6.1	11.7	1.4	1.9	0.8	2.3	3.0	2.1	1.0	0.7	2.1	1.7	3.1
43	18.2	26.4	12.0	22.9	18.8	19.4	57.9	14.6	20.7	25.3	76.1	18.3	2.3	43.4	58.4	10.5
44	3.1	5.1	1.1	2.7	7.1	2.6	2.6	1.2	1.1	1.4	3.0	0.7	—	2.2	4.3	1.3
45	2.6	2.7	0.8	1.7	7.6	1.5	3.4	0.6	1.9	1.8	3.6	0.8	2.0	9.9	3.1	12.2
46	—	—	—	—	1.3	—	—	—	—	—	—	—	—	—	—	—
47	—	—	—	0.5	—	—	—	—	—	—	—	—	—	—	—	—
48	—	—	—	0.7	—	—	—	—	—	—	—	—	—	—	—	—
50	2.0	1.8	0.5	1.0	0.9	0.5	0.8	—	0.6	0.5	1.0	0.5	—	0.9	0.6	0.9
51	4.1	4.2	1.7	2.9	2.3	1.8	3.0	1.2	2.3	1.8	3.4	2.1	1.1	3.3	1.8	3.1
52	1.7	2.1	0.6	1.5	2.7	0.7	1.4	0.5	1.0	0.7	1.6	1.0	0.5	1.7	1.2	1.6
53	6.9	9.8	2.7	5.9	4.3	3.9	6.7	2.6	4.9	4.7	7.3	4.1	2.6	7.3	5.9	8.5
54	1.7	3.2	0.6	1.9	5.6	1.6	2.3	0.9	1.7	1.6	3.0	0.9	1.3	8.6	15.5	2.5
55	16.5	32.4	6.2	24.6	10.2	14.3	15.2	6.0	17.0	16.1	19.1	11.2	3.7	9.3	8.6	19.2
56	4.9	7.6	2.4	5.6	18.8	11.3	3.9	8.5	4.3	7.5	2.1	1.1	1.9	1.6	1.7	2.8
57	7.3	24.7	9.9	12.9	15.8	4.5	5.2	3.4	5.4	3.8	3.0	9.2	0.5	1.1	1.1	1.7
58	3.4	12.8	0.6	2.9	7.1	—	0.5	—	0.7	1.0	2.8	0.6	0.7	1.6	—	0.5
59	1.7	0.7	—	1.6	2.1	0.5	1.2	0.7	0.9	1.2	1.5	1.0	1.0	1.9	0.7	8.1
60	—	—	—	—	1.1	—	—	—	—	—	—	—	—	—	—	—

Table 2 (continued)

m/z	2	3	4	5	5a	6	7	8	9	10	11	12	13	14	15	16
61	—	1.1	—	—	0.7	—	—	—	0.5	—	—	—	—	—	—	—
63	1.1	1.1	—	0.8	0.7	0.5	0.9	—	0.7	0.5	0.9	0.6	—	1.1	0.5	0.8
64	—	—	—	—	0.7	—	—	—	—	—	—	—	—	—	—	—
65	2.5	2.8	1.2	2.7	1.2	1.8	3.6	1.2	2.3	1.8	3.4	2.5	1.3	4.1	1.9	4.0
66	1.5	2.7	—	1.2	1.9	0.7	1.6	—	1.7	1.0	1.3	0.7	—	1.5	0.8	1.8
67	5.3	16.2	2.7	11.3	5.1	2.4	6.5	2.1	5.0	6.6	11.3	3.7	3.1	15.2	3.7	16.1
68	4.6	19.2	1.8	4.3	8.6	0.7	1.3	—	0.9	4.6	1.9	0.7	0.6	1.9	1.1	2.9
69	24.2	10.6	13.7	16.1	12.2	4.1	32.6	3.2	39.2	12.4	23.9	10.9	17.4	8.2	6.1	9.6
70	100.0	100.0	100.0	100.0	15.3	1.0	3.4	0.6	3.5	3.0	3.9	1.0	1.1	0.6	0.5	1.0
71	13.3	8.1	5.8	11.9	7.1	1.5	2.1	0.7	1.2	3.7	4.7	0.5	1.4	2.7	0.8	2.5
72	1.5	0.5	0.6	1.2	14.2	1.8	0.9	—	—	1.0	0.6	—	—	4.3	0.6	1.4
73	—	0.5	—	1.1	100.0	—	—	—	—	—	—	—	—	0.6	—	1.1
74	1.1	—	—	—	10.2	—	0.5	—	—	—	—	—	—	—	—	—
75	—	—	—	—	0.9	—	—	—	—	—	—	—	—	—	—	—
77	6.0	6.8	2.0	7.9	1.6	2.4	5.4	1.9	3.7	2.9	5.2	5.0	2.8	11.3	3.8	13.7
78	1.5	1.3	—	1.2	3.8	0.6	1.0	—	0.9	0.5	1.3	1.0	0.6	2.1	1.0	2.2
79	9.6	16.2	1.3	3.6	5.6	2.6	7.3	2.2	5.8	4.0	8.2	5.8	2.1	7.6	2.8	8.1
80	1.1	1.5	—	0.7	3.7	—	1.0	—	0.8	0.7	1.1	0.7	—	1.4	0.5	1.8
81	4.4	9.8	1.1	6.1	3.5	3.3	19.1	3.1	5.6	6.3	14.7	5.4	1.0	4.9	1.7	4.6
82	1.0	1.7	0.6	5.5	4.8	1.8	5.2	2.1	2.3	4.9	18.2	1.6	0.5	4.2	1.3	2.9
83	9.8	9.4	2.2	9.8	11.2	11.8	8.0	28.6	13.3	28.4	9.5	6.3	0.6	10.4	13.8	2.2
84	14.9	6.8	—	10.4	9.1	100.0	100.0	100.0	100.0	100.0	29.1	0.6	100.0	100.0	100.0	81.5
85	1.1	1.0	2.0	1.1	3.8	7.9	8.0	7.1	6.6	8.3	4.7	0.6	6.2	7.6	6.9	24.0
86	—	0.5	—	0.5	7.1	0.5	0.5	—	0.5	3.6	—	—	0.5	0.6	0.7	1.5
87	—	—	—	—	8.1	—	—	—	—	—	—	—	—	—	—	—
88	—	0.5	—	—	0.5	—	—	—	—	—	—	—	—	—	—	—
91	2.5	2.3	1.5	6.4	1.0	3.7	11.3	2.6	5.8	4.6	9.5	6.1	2.2	8.6	2.7	11.8
92	0.6	—	—	0.8	1.7	0.5	1.6	—	0.9	0.7	1.5	0.9	—	1.2	—	1.4
93	1.3	2.3	2.0	14.9	5.1	1.2	2.6	0.9	1.7	1.3	2.6	8.7	3.5	20.2	2.8	30.3
94	2.8	8.5	—	1.6	3.8	—	0.6	—	0.7	—	1.0	1.2	0.5	2.9	0.6	2.8
95	2.2	3.4	0.8	2.1	9.1	1.3	3.2	0.9	2.9	3.2	4.3	3.9	0.8	2.7	1.0	9.9
96	0.6	7.6	—	1.5	13.2	—	6.5	—	1.9	0.9	2.6	1.9	—	0.5	—	1.3
97	33.0	32.4	0.5	9.5	3.5	1.4	6.0	1.8	11.3	3.3	7.6	2.6	0.9	7.3	2.2	8.8
98	2.2	2.2	—	3.3	7.1	—	3.4	—	4.7	12.1	2.6	5.8	—	2.6	0.6	2.5
99	—	—	—	0.6	9.1	—	—	—	0.5	1.0	—	0.5	—	—	—	10.3
100	—	—	—	—	1.5	—	—	—	—	—	—	—	—	—	—	0.6
101	—	—	—	—	—	—	—	—	—	—	1.3	—	—	—	—	—
102	—	—	—	1.0	—	—	—	—	—	—	—	—	—	—	—	—
103	—	—	—	—	—	—	—	—	—	—	0.5	—	—	—	—	—
105	—	—	—	—	—	0.9	3.0	0.7	1.5	1.3	2.3	2.5	—	0.7	—	1.0
106	—	—	—	—	—	—	0.5	—	—	—	—	0.6	—	—	—	—
107	—	—	—	0.8	0.6	5.0	23.9	3.7	7.8	6.7	18.0	7.9	0.5	1.6	0.8	5.1
108	—	—	—	2.4	0.5	0.7	2.6	0.5	1.0	0.9	2.1	1.2	—	3.1	1.3	2.6
109	—	—	0.5	1.8	0.6	1.1	1.9	0.5	1.9	1.2	1.7	1.5	1.4	7.8	1.3	4.0
110	—	—	—	—	1.9	—	0.7	—	0.7	0.6	1.6	1.5	—	1.3	0.5	2.5
111	3.6	2.9	6.8	23.5	3.0	—	1.5	—	0.5	1.5	1.4	0.6	—	8.2	4.9	4.4
112	26.9	21.3	0.5	1.8	1.6	—	1.1	2.6	1.3	—	5.6	—	—	6.5	0.7	10.7
113	2.2	1.8	—	—	3.5	—	—	—	—	—	0.6	—	—	0.5	—	0.8
114		0.6	—	—	25.5	—	—	—	—	—	—	—	—	—	—	—
115			—	—	2.1	—	—	—	—	—	—	—	—	—	—	—
119			—	—	—	—	—	—	—	—	—	—	—	0.5	—	—
121			—	—	—	—	0.5	—	0.5	—	—	9.0	—	—	—	—
122			—	—	—	0.6	4.1	0.7	1.5	0.8	4.5	1.1	—	—		—
123			—	—	—	0.6	1.5	1.2	1.3	1.2	2.8	—	—	0.8	0.6	1.7
124			—	—	—	—	—	—	0.9	—	0.8	—	—	0.5	—	0.8
125			—	1.4	0.6	16.2	30.8	9.6	7.2	11.6	100.0	100.0	3.1	27.3	12.2	100.0
126			8.1	11.0	1.0	1.5	3.0	0.9	0.7	2.1	12.1	10.1	—	2.4	1.1	9.6
127			0.7	1.1	0.6	—	—	—	—	—	0.8	0.6	—	—	—	0.6
128					3.0	—	—	—	—	—	—	—	—	—	—	—
129					19.3	—	—	—	—	—	—	—	—	—	—	—
130					1.9	—	—	—	—	—	—	—	—	—	—	—
136						—	—	—	—	—	—	5.9	—	—	—	—
137						—	—	—	—	—	—	1.1	—	—	—	—
139						—	0.5	—	1.4	—	—	0.8	—	1.9	0.6	3.7
140						16.2	34.7	8.2	11.9	6.7	7.8	—	3.0	20.2	19.9	44.4
141						1.7	3.4	0.7	1.2	0.7	1.0	—	—	1.9	2.0	4.4
154												0.5				

Loss of a methyl radical

The loss of $CH_3^{\cdot}$ from the metastable molecular ions of **1** generates the *m/z* 83 ions (34% rel. int; *m** 98 → 83, calc. 70.30, obs. 70.3). By analogy with the mechanism reported for the loss of $CH_3^{\cdot}$ from cyclohexene,[6] Aplin *et al.*[1] proposed the mechanism shown in Scheme 1. Field ionization kinetic studies showed later that such a mechanism could not explain the results that were obtained with 3,3,6,6-d_4-cyclohexene.[7] Short-lived molecular ions ($\leq 10^{-11}$ s) lose mainly $CHD_2^{\cdot}$, which clearly indicates that two allylic H atoms are eliminated from the unlabelled molecules. Derrick *et al.*[7] have proposed the mechanism illustrated in Scheme 2 as an explanation.



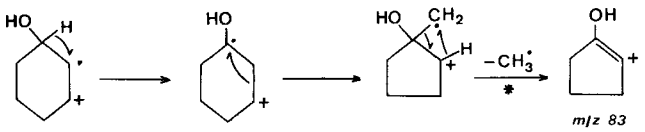
Scheme 2

For long-lived molecular ions ($\geq 10^{-9}$ s) the loss of the methyl radical occurs after an almost complete H/D randomization. Both the 70 eV and the 12 eV EI mass spectra of the labelled cyclohexene also showed extensive randomization in the molecular ions prior to their decomposition; this was attributed to a 1,3 allylic rearrangement reaction.[7] All these findings point clearly to the fact that one cannot compare the behaviour of **1** with that of cyclohexene in respect of the loss of $CH_3^{\cdot}$ from the molecular ions.

As our results with the labelled compounds **1b**, **1c** and **1e** were in complete disagreement with the mechanism of Scheme 1, we prepared the additional labelled compounds shown above in order to determine unequivocally the origins of the atoms expelled as $CH_3^{\cdot}$. The shifts of *m/z* 83 are listed in Table 3; they show clearly that most of the $CH_3^{\cdot}$ fragments which are expelled contain the C-2 atom together with the hydrogen atoms from C-1, C-2 and C-3. This rather unexpected elimination of $CH_3^{\cdot}$ is of course difficult to rationalize by a single mechanism. Any process beginning with an allylic cleavage or with a 1,3 allylic rearrangement cannot explain our results. A mechanism such as the one illustrated in Scheme 3 might formally offer a plausible explanation. Other

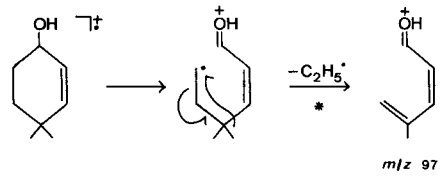
Table 3. Shifts of *m/z* 83 in the 70 eV mass spectra of the labelled compounds 1a–1k

Compound \ *m/z*	83	84	85	86	87	88
1a			100			
1b	3	5	87	4		
1c			3	10	86	1
1d		100				
1e	92	8				
1f	91	9				
1g	91	9				
1h			95	5		
1i	89	4	7			
1j					92	8
1k	95	5				



Scheme 3

mechanisms could be envisaged, but they would be more hypothetical as for example the one in Scheme 3. The various methyl substituted 2-cyclohexen-1-ols (**2–11**) also exhibit in their mass spectra peaks corresponding to $[M-CH_3]^+$ ions, as is apparent from Table 2. However, they always correspond to the loss of a substituent; the metastable peaks are also much less intense than in the case of the expulsion of $CH_3^{\cdot}$ from **1**. The mass spectrum of the labelled compound **5a** where the $[M-CH_3]^+$ ions fully retain the deuterium atoms partly corroborates this assumption. Another salient feature is the ease with which a substituent is lost when it is attached to C-1. The $[M-CH_3]^+$ ions give the base peak in the spectrum of **11**, carrying 20% of the Σ_{39} total ion current. Similarly, the loss of the C-1 ethyl substituent from **12** also generates the base peak (33% Σ_{39}). Moreover, a comparison of the mass spectra of **2–5** shows that the elimination of the C-4 allylic substituent is also slightly favoured.



Scheme 4

Although the mechanism shown in Scheme 1 is clearly not operating in the fragmentation of 2-cyclohexen-1-ol, one could nevertheless envisage a migration of a $CH_3^{\cdot}$ radical from C-4 to C-6 in order to account for the loss of the fragments $CH_3CH_2^{\cdot}$ and $CH_3CD_2^{\cdot}$ from **5** and **5a** respectively; both of these fragmentations are accompanied by the appropriate metastable peaks (*m** 126 → 97, calc. 74.67, obs. 74.8 and *m** 129 → 98, calc. 74.45, obs. 74.5). This mechanism is illustrated in Scheme 4; however, it is not the only one which gives rise to the formation of the $[M-C_2H_5]^+$ ion from **5**. In fact, **5a** also eliminates a $C_2H_4D^{\cdot}$ fragment to the extent of about 50%, indicating that another complex mechanism is involved in the formation of the $[M-C_2H_5]^+$ ions from compound **5**.

The retro Diels–Alder fragmentation

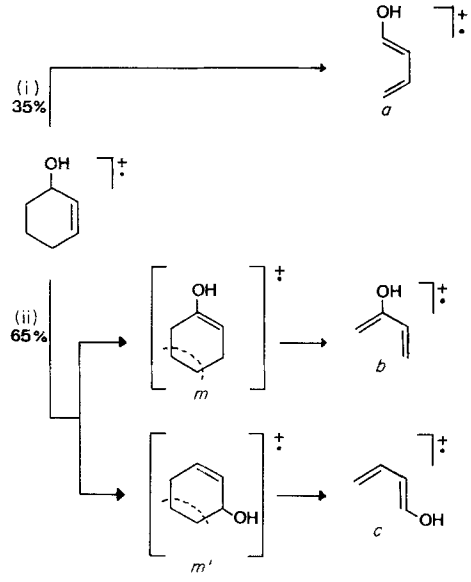
The *m/z* 70 ion which by high resolution studies has the elemental composition C_4H_6O yields the base peak in the spectrum of 2-cyclohexen-1-ol; it is formed by the loss of ethylene via a RDA reaction.[6,8] The mass shifts of *m/z* 70 which are observed in the spectra of the deuterium labelled compounds are reported in Table 4. They indicate the existence of two competing processes and also the absence of any H/D scrambling prior to the fragmentation. Process (i) shown in Scheme 5 accounts for 35% of the *m/z* 70

Table 4. Shifts of *m/z* 70 in the 70 eV mass spectra of the labelled compounds 1a–1k

Compound	m/z 70	71	72	73	74	75
1a	65		35			
1b		35		65		
1c				100		
1d		100				
1e		100				
1f		100				
1g		100				
1h		100				
1i			100			
1j						100
1k		100				

ions and process (ii), which leads to the elimination of the C-4 and C-5 atoms, is responsible for 65% of the *m/z* 70 ions that are formed. The second route requires that the molecular ions undergo an allylic isomerization via a 1,3 shift of the C-1 hydrogen atom or of the hydroxyl group. Similar isomerizations have already been observed. In the fragmentation of cyclohexene for example,[7] the molecular ions probably undergo many fast consecutive 1,3 allylic rearrangements and this results in a partial randomization of the hydrogen atoms prior to the RDA reaction. The mass spectra of other systems containing the cyclohexene ring, like those of $\Delta^{4(8)}$-menthene[9] and various methylcyclohexenes[10] can also be explained by the existence of allylic rearrangement reactions. Studies of the fragmentation of tetraline have shown that two processes are responsible for the loss of ethylene from the molecular ions.[11,12] At first thought to be the result of partial isomerization of the tetraline molecular ions into tetrahydroazulene ions[11] it was suggested later that two consecutive 1,2 shifts of the hydrogen atoms might account for the observed results.[13]

The simplest cyclohexene derivative containing an allylic hydroxyl group which has been studied with regard to the RDA reaction is the tetralol system.



Scheme 5

Thus, 4,4-dimethyl-1-tetralol loses an isobutene moiety containing both C-3 and C-4, instead of C_2H_4 as would be expected.[14] If one regards this elimination as a formal RDA reaction then a 1,3 shift of an H atom or of the OH group, must precede the reaction. According to what is expected from a classical RDA reaction, 2,2-dimethyl-1-tetralol eliminates only isobutene. A detailed study of 1-tetralol[15] has also shown that competing reactions similar to those illustrated in Scheme 5 for the case of 2-cyclohexen-1-ol operate in a 1:3 ratio in favour of the non-classical elimination of C_2H_4 via the formal RDA reaction. Metastable ions and kinetic energy release measurements indicate that the structure of the ions formed through process (ii) correspond to type *b* shown in Scheme 5, i.e. that it is a hydrogen atom which shifts rather than the hydroxyl group. The mechanism of this double bond migration, provided it really takes place, is still subject to much controversy; it is difficult, however, to find out if it results from a concerted 1,3 shift or from two consecutive 1,2 shifts. Moreover, one should also consider the possibility that other groups might migrate.

The results which we have obtained with the labelled 2-cyclohexen-1-ol compounds and with the numerous alkyl substituted homologues provide some relevant information on this topic, namely with regard to the influence of the size of the expelled olefinic moiety and the migration of alkyl groups. It should be stressed that one cannot distinguish between the migration of the hydrogen atom from C-1 to C-3 and the same migration of the OH radical; these two different migrations would lead to the intermediate structures *m* and *m'* respectively (Scheme 5). Although the dienes *b* and *c* are different, all the labelled compounds lead to the same isotopic content in each case. The *m/z* 70 ion of **1** loses a $CH_3^{\cdot}$ radical (m^* 70 → 55, calc. 43.21, obs. 43.2) and also a hydrogen atom, but these two fragmentations cannot be used to determine the most probable structure of the precursor ion *m/z* 70 because of the formation of these ions through competing reactions and the H/D scrambling that takes place prior to their formation. However, it seems much more probable that the process involves the 1,3 shift of a hydrogen atom, as is the case with 1-tetralol,[13] rather than that of the OH$^{\cdot}$ radical.

The results listed in Table 5 show clearly that the loss of the larger substituent via a formal RDA reaction is always strongly favoured. Thus, the rearrangement reaction which accounts for 65% of the *m/z* 70 ions formed from **1** increases sharply in importance in the fragmentation of **3**, **5**, **7**, **9**, and **10**. The rearrangement process is completely suppressed in the fragmentation of **4** and **6** and drastically reduced in the case of **2** and **8**.

The mass spectra of **11** and **12** show that the double bond rearrangement may also involve the migration of an alkyl radical. However, a comparison of the spectra of **5**, **11** and **12** shows that the importance of the rearrangement reaction decreases as the C-1 substituent becomes larger. Finally, all of the above observations are also valid for the elimination of olefinic moieties from the methoxy compounds **13**–**16**. Compound **16** loses predominently C_4H_8 and requires a

Table 5. Influence of the size of the expelled olefin molecule on the RDA fragmentation processes (i) and (ii) of Scheme 5

	Process (i)		Process (ii)	
Compound	Olefin expelled	Relative abundance	Olefin expelled	Relative abundance
1	C_2H_4	35	C_2H_4	65
2	C_3H_6	87	C_2H_4	13
3	C_2H_4	6	C_3H_6	94
4	iso-C_4H_8	100	C_2H_4	0
5	C_2H_4	3	iso-C_4H_8	97
6	iso-C_4H_8	100	C_2H_4	0
7	C_2H_4	1	iso-C_4H_8	99
8	iso-C_4H_8	97	C_2H_4	3
9	C_2H_4	1	iso-C_4H_8	99
10	C_3H_6	11	iso-C_4H_8	89
11	C_2H_4	16	iso-C_4H_8	84
12	C_2H_4	19	iso-C_4H_8	81
13	iso-C_4H_8	100	C_2H_4	0
14	C_2H_4	6	iso-C_4H_8	94
15	iso-C_4H_8	100	C_2H_4	0
16	C_2H_4	11	iso-C_4H_8	89

C_2H_4 = ethene; C_3H_6 = propene; iso-C_4H_8 = 2-methylpropene.

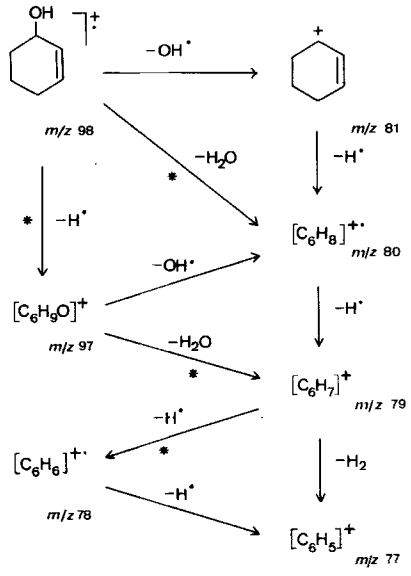
reverse migration of the double bond. Thus, a formal 1,3 hydrogen or alkyl shift might indeed offer a satisfactory explanation of the results we report here.

All these considerations point to the conclusion that two competitive reactions are responsible for the loss of olefinic molecules from the molecular ions of cyclohexenic systems. One operates on unrearranged molecular ions while the other requires one or more double bond migrations to occur before the RDA reaction takes place. The kinetics and the relative importance of the two types of RDA eliminations depend on the size of the substituent and on its position in the ring. Unsubstituted and alkyl substituted systems[9,10] undergo several successive and slow migrations of the double bond whereas more crowded systems containing large substituents, for example 3,6-diphenyl-5-aryl-4-amino-1-cyclohexenes,[16] show no rearrangement at all. On the other hand, only one double bond migration can take place in α,β-unsaturated cyclohexenol; it leads to the enol form of cyclohexenone which, as is well known, does not convert itself spontaneously to the keto form.[17] Since no metastable peak is observed for the RDA fragmentation of the enol form and since the relative importance of the two processes is almost the same at 12 eV and at 70 eV, the rearrangement must be a fast process. Thus, the activation energies and the variation of the rate constants versus the internal energy of the molecular ions should be quite similar for the two competing RDA reactions. The lability of the C-1 hydrogen atom is certainly responsible for the ease with which the rearrangement takes place as well as for its specificity.

Formation of some of the other ions

The formation of m/z 97 from **1** would *a priori* be explained easily by the loss of the C-1 H atom; both its allylic position and the effect of the hydroxyl substituent should favour its elimination. However, an examination of the spectra of the deuterated molecules does not support a preferential loss from C-1. It is indeed difficult to calculate the participation of all the different H atoms in this elimination, mainly because of the incomplete labelling of some molecules and also because of the unknown isotope effect. Nevertheless, it can be seen easily from the various mass shifts that the lost hydrogen atom comes mainly from the C-4 position.

Another group of less important peaks covers the mass range from m/z 77 to m/z 81 in the spectrum of unlabelled 2-cyclohexen-1-ol. In the 70 eV spectrum m/z 79 predominates; a metastable peak (m^* 97→79, calc. 64.34, obs. 64.4) shows that it is at least partly due to the loss of H_2O from the $[M-H]^+$ ions; the spectrum of **1d** confirms that no rearrangement affects the hydroxyl H atom before the elimination. A $[M-H_2O]^{+\cdot}$ ionic species is also formed directly from $[M]^{+\cdot}$ (m^* 98 → 80, calc. 65.31, obs. 65.3) and it gives the most important signal in the m/z 77 to 81 region at 12 eV. Scheme 6 gives the most plausible origins of all these ions.



Scheme 6

Finally, the m/z 69 and 55 ions originate from the two precursors *a* and *b* shown in Scheme 5. The two possible structures for the precursor ions and the presence of interfering peaks makes it hazardous to postulate fragmentation modes, despite the data which we have for the many deuterated compounds.

EXPERIMENTAL

Low resolution mass spectra were recorded on a Varian CH-4 instrument. The temperature of the heated inlet system was kept at 100 °C and that of the ion source at 120 °C. High resolution measurements were performed on a Varian SM-1-B spectrometer with the ion source temperature at 150 °C and that of the

heated inlet system at 120 °C. The isotopic compositions of the labelled derivatives were determined (except for **1d**) from the mass spectra of their benzoate esters which, unlike the alcohols, exhibit negligible $[M-H]^+$ ions. All the compounds were purified by vacuum distillation and preparative gas chromatography; nuclear magnetic resonance spectroscopy was used to ascertain the position of the label incorporation.

2-Cyclohexen-1-ol (1). $LiAlH_4$ reduction of 2-cyclohexen-1-one according to the procedure of Hammond and Warkentin[18] afforded **1**.

2,6,6-d_3-2-Cyclohexen-1-ol (1b). A mixture of 2-cyclohexen-1-one (3 g) and sodium carbonate (150 mg) in D_2O (3 cm^3) was stirred at 40 °C for 3 h. After extraction into dry ether, the solution was neutralized with D_2O diluted d_2-sulfuric acid, washed with D_2O, dried ($MgSO_4$) and the ether removed. The exchange process was repeated five times and the labelled ketone was purified by vacuum distillation. $LiAlH_4$ reduction of this ketone gave **1b** with an isotopic composition of 6% d_4, 86% d_3 and 8% d_2.

2,4,4,6,6-d_5-2-Cyclohexen-1-ol (1c). This compound was obtained by $LiAlH_4$ reduction of 2,4,4,6,6-d_5-2-cyclohexen-1-one prepared according to the method given by Lambert and Clikeman[19] (85% d_5, 13% d_4, 2% d_3).

4,4-d_2-2-Cyclohexen-1-ol (1a). 2,4,4,6,6-d_5-2-Cyclohexen-1-one[19] was back-exchanged with H_2O using the procedure described for the preparation of **1b** to give 4,4-d_2-2-cyclohexen-1-one. Reduction of this ketone by $LiAlH_4$ afforded **1a** (5% d_5, 11% d_4, 17% d_3, 67% d_2).

***O*-*d*-2-Cyclohexen-1-ol (1d).** This derivative was prepared from 2-cyclohexen-1-one by $LiAlH_4$ reduction followed by D_2O hydrolysis. Before recording its mass spectrum the ion source of the instrument had been equilibrated with D_2O. The isotopic composition was 72% d_1 and 28% d_0.

1-d_1-2-Cyclohexen-1-ol (1e). Reduction of 2-cyclohexen-1-one by $LiAlD_4$ gave **1e** (99% d_1, 1% d_0).

2-d_1-2-Cyclohexen-1-ol (1f). 1,3-Cyclohexanedione (3 g) was exchanged twice in D_2O (10 cm^3) at room temperature for 6 h. Extraction into chloroform and usual work-up yielded the 2,2-d_2 diketone. This labelled compound (2 g) was heated to reflux overnight with 700 mg of $LiAlH_4$ in 30 cm^3 of dry ether. After cautious addition of water and dilute HCl, the solution was extracted with ether. Work-up of the ethereal solution gave 1.2 g of **1f** (1% d_2, 44% d_1, 55% d_0).

3-d_1-2-Cyclohexen-1-ol (1g). The 3-d_1 derivative of 2-cyclohexen-1-one was prepared from 3-ethoxy-2-cyclohexen-1-one by $LiAlD_4$ reduction and hydrolysis according to the procedure of Baldwin and Kaplan;[20] it was then converted to **1g** in the usual way (7% d_2, 92% d_1, 1% d_0).

3,5,5-d_3-2-Cyclohexen-1-ol (1h). 1,4-Cyclohexanedione monoethylene acetal was prepared from the corresponding diketone according to the procedure of Courtot[21] and exchanged in a mixture of CH_3OD, D_2O and CH_3ONa using the method described by Gray *et al.*[22] for 4-benzyloxycyclohexanone. The d_4 ketone was then reduced by $LiAlH_4$ to afford 3,3,5,5-d_4-4-hydroxycyclohexanone ethylene acetal which was converted to 3,3,5,5-d_4-4-tosyloxycyclohexanone ethylene acetal.

This tosylate was transformed into 3,5,5-d_3-3-cyclohexen-1-one ethylene acetal by the procedure of Owen and Robins.[23] Heating of this compound in dilute acetic acid at 80 °C for 12 h led to the hydrolysis of the acetal function and simultaneous isomerization of the double bond yielding 3,5,5-d_3-2-cyclohexen-1-one which was reduced to give **1h** (6% d_4, 86% d_3 8% d_2).

1,3-d_2-2-Cyclohexen-1-ol (1i). $LiAlD_4$ reduction of 3-d_1-2-cyclohexen-1-one, intermediate in the preparation of **1g**, yielded **1i** (99% d_2, 1% d_1).

1,2,3,4,4,6,6-d_7-2-Cyclohexen-1-ol (1j). $LiAlD_4$ reduction and subsequent hydrolysis of 2,4,4,6,6-d_5-3-methoxy-2-cyclohexen-1-one[19] afforded 2,3,4,4,6,6-d_6-2-cyclohexen-1-one which was then reduced to **1j** by $LiAlD_4$ (88% d_7, 11% d_6, 1% d_5).

2-[^{13}C]-2-Cyclohexen-1-ol (1k). Methyl 6-[^{13}C]-5-ketohexanoate was prepared from glutaric acid monomethyl ester chloride and [^{13}C]methyl iodide according to the procedure of von Rudloff.[24] This ester was converted to 2-[^{13}C]-1,3-cyclohexanedione by the procedure of Müller,[25] and the diketone was transformed into 2-[^{13}C]-2-cyclohexen-1-one by the procedure of Baldwin and Kaplan.[20] $LiAlH_4$ reduction of the labelled ketone gave **1k** (59% ^{13}C).

6-Methyl-2-cyclohexen-1-ol (2). Birch reduction of the *o*-toluidine by the method of Stork and White[26] afforded 6-methyl-2-cyclohexen-1-one which was then reduced to **2** by $LiAlH_4$.

4-Methyl-2-cyclohexen-1-ol (3). 4-Methylcyclohexanone was transformed into 4-methyl-2-bromocyclohexanone according to the procedure of Colonge and Dubin.[27] The bromoketone was dehydrobrominated by the method of Stotter and Hill.[28] 4-Methyl-2-cyclohexen-1-one obtained was then reduced by $LiAlH_4$ to give **3**.

6,6-Dimethyl-2-cyclohexen-1-ol (4). 2,2-Dimethylcyclohexanone was brominated and dehydrobrominated as for compound **3**. Reduction by $LiAlH_4$ of 6,6-dimethyl-2-cyclohexen-1-one afforded **4**.

4,4-Dimethyl-2-cyclohexen-1-ol (5). 4,4-Dimethyl-2-cyclohexen-1-one, prepared according to Dauben *et al.*,[29] was reduced by $LiAlH_4$ to give **5**.

2,6,6-d_3-4,4-Dimethyl-2-cyclohexen-1-ol (5a). 4,4-Dimethyl-2-cyclohexen-1-one[29] was exchanged in D_2O

containing potassium carbonate according to the procedure of Wiemann *et al.*[30] The 2,6,6-d_3 ketone was then reduced by $LiAlH_4$ to **5a** (95% d_3, 5% d_2).

2,6,6-Trimethyl-2-cyclohexen-1-ol (6). 2,2,6-Trimethylcyclohexanone was converted into 2,6,6-trimethyl-2-cyclohexen-1-one by the procedure described for **3** and reduced to **6** by $LiAlH_4$.

2,4,4-Trimethyl-2-cyclohexen-1-ol (7). 2,4,4-Trimethyl-2-cyclohexen-1-one was obtained from ethylvinylketone and isobutyraldehyde using the method of Dauben *et al.*;[29] **7** was then prepared by reduction with $LiAlH_4$.

3,6,6-Trimethyl-2-cyclohexen-1-ol (8). This compound was obtained by $LiAlH_4$ reduction of the corresponding ketone which was provided by Dr P. Margaretha from the University of Strasbourg (France).

3,4,4-Trimethyl-2-cyclohexen-1-ol (9) and 4,4,6-trimethyl-2-cyclohexen-1-ol (10). These two alcohols were obtained by $LiAlH_4$ reduction of the corresponding ketones which were prepared according to Dauben *et al.*[29]

1,4,4-Trimethyl-2-cyclohexen-1-ol (11) and 1-ethyl-4,4-dimethyl-2-cyclohexen-1-ol (12). Compounds **11** and **12** were obtained from 4,4-dimethyl-2-cyclohexen-1-one[29] using methyl iodide and ethyl bromide respectively according to the procedure of Wenkert *et al.*[31]

4,4-Dimethyl-3-methoxy-1-cyclohexene (13) and 6,6-dimethyl-3-methoxy-1-cyclohexene (14). These two compounds were prepared from the corresponding alcohols, methyl iodide, sodium hydride and dimethylsulfoxide in the usual way.

4,4-Dimethyl-1-methoxy-1-cyclohexene (15) and 6,6-dimethyl-1-methoxy-1-cyclohexene (16). According to Whol's procedure,[32] 4,4-dimethylcyclohexanone and 2,2-dimethylcyclohexanone were reacted with trimethylorthoformate to give **15** and **16** respectively.

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