Stereochemical Effects in the Mass Spectra of *endo*- and *exo*-2,3-Bismethoxycarbonylbicyclo[2.2.1]heptane and *endo*- and *exo*-2-Methoxycarbonylbicyclo[2.2.1]heptane

By **Teunis A. Eggelte** and **Nico M. M. Nibbering,*** Laboratory of Organic Chemistry, University of Amsterdam, Nieuwe Achtergracht 129, Amsterdam, The Netherlands

The *endo*- and *exo*-isomers of the title compounds show markedly different behaviour upon electron impact. The molecular ion of the *endo*-isomer of 2,3-bismethoxycarbonylbicyclo[2.2.1]heptane ($M^{+\cdot}$ 212) eliminates cyclopentadiene leading to the base peak at *m/e* 146; this decomposition occurs to a negligible extent for the molecular ion of the *exo*-isomer [*m/e* 146 (4%; after correction for natural ^{13}C contribution)], but expulsion of a resonance-stabilized cyclopentenyl radical is found instead, giving the base peak at *m/e* 145. A successive loss of methanol and carbon monoxide or keten from the molecular ion of the *endo*-isomer of 2-methoxycarbonylbicyclo[2.2.1]heptane ($M^{+\cdot}$ 154) leading to peaks at *m/e* 122, 94, and 80 is found. These reactions appear to be largely suppressed in the case of the corresponding *exo*-isomer. All these observations have been explained in terms of stereochemically controlled hydrogen migrations to the ester functions.

VARIOUS recent papers[1-10] have shown that mass spectrometry may serve as a useful tool in solving stereochemical problems, in particular when it refers to rigid cyclic systems. Several workers have recently

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[1] For a general review, see S. Meyerson and A. W. Weitkamp, *Org. Mass Spectrometry*, 1968, **1**, 659.

[2] K. Biemann in 'Mass Spectrometry of Organic Molecules,' ed. F. W. McLafferty, Academic Press, New York, 1963, pp. 591—596.

[3] J. Deutsch and A. Mandelbaum, *J. Amer. Chem. Soc.*, 1970, **92**, 4288.

[4] R. Furstoss, A. Heumann, B. Waegell, and J. Gore, *Org. Mass Spectrometry*, 1972, **6**, 1215.

[5] A. Buchs and E. Choirollais, *Helv. Chim. Acta*, 1973, **56**, 207.

[6] H. F. Grützmacher and K. H. Fechner, *Org. Mass Spectrometry*, 1973, **7**, 573.

[7] J. K. MacLeod and R. G. Wells, *J. Amer. Chem. Soc.*, 1973, **95**, 2387.

[8] A. Karpati and A. Mandelbaum, *Org. Mass Spectrometry*, 1971, **5**, 1345.

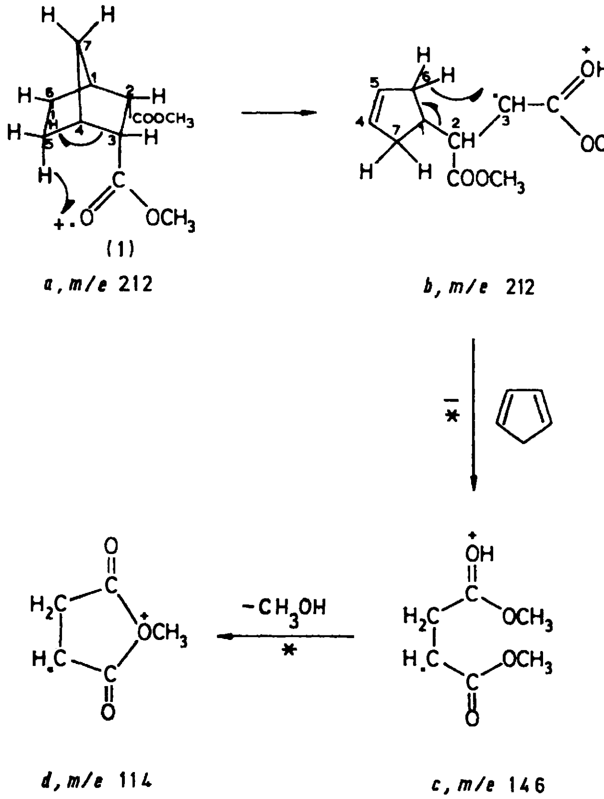
[9] A. W. J. D. Dekkers, N. M. M. Nibbering, and W. N. Speckamp, *Tetrahedron*, 1972, **28**, 1829.

[10] A. van Wageningen, H. Cerfontain, and N. M. M. Nibbering, *Rec. Trav. chim.*, 1974, **93**, 43.

studied bicyclo[2.2.1]heptanols by mass spectrometry using deuterium labelling.[11,12] The availability of bicyclo[2.2.1]heptane substituted by one or two methoxycarbonyl groups in both *endo*- and *exo*-positions prompted us to investigate their mass spectra. Striking differences between the mass spectra of each pair of *endo*- and *exo*-isomers were found.

RESULTS AND DISCUSSION

endo- *and* exo-2,3-*Bismethoxycarbonylbicyclo*[2.2.1]-*heptane* (1) *and* (2).—Inspection of Table 1 shows that there is a marked difference between the mass spectra of the *endo*- and *exo*-isomers (1) and (2). The base peak in the spectrum of the *endo*-isomer (1) is found at *m/e* 146, but this peak has a very low relative intensity in the spectrum of the *exo*-isomer (2): in this case the base peak occurs at *m/e* 145 and its natural isotopic contribution accounts to the extent of 65% for the intensity of the peak at *m/e* 146, the remaining 35% being due to $C_6H_{10}O_4$ as shown by high resolution measurements. These observations can easily be rationalized when the stereochemistry of the compounds is considered.



SCHEME 1 Rationalization of the formation and decomposition of *m/e* 146 from the molecular ion of *endo*-2,3-bismethoxycarbonylbicyclo[2.2.1]heptane

TABLE 1

Mass spectra * of *endo*- (1), *exo*- (2), and *trans*- (3)-2,3-bismethoxycarbonylbicyclo[2.2.1]heptanes (mol. wt. 212) at 70 eV

m/e	(1)	(2)	(3)
	Relative intensity (%)		
182	3·7		6·4
181	33·8	26·0	56·4
180	16·4		97·7
154			3·7
153	6·3	10·5	35·7
152	10·1	3·2	54·7
151			9·0
148	10·0		18·4
147	7·7		8·0
146	100	11·5	100
145	28·4	100	51·1
139	4·1		18·4
138			9·4
137			6·6
125			9·1
124		4·7	85·3
121	6·4	9·3	19·9
120	3·5		7·3
115	6·6		6·7
114	83·9	15·6	84·8
113	50·5	64·8	50·6
111			4·9
96			4·7
94			6·1
93	13·6	17·0	42·4
92	5·1	3·4	12·1
91	9·3	8·6	22·7
87	29·0	29·0	62·0
85	3·2		4·9
81			6·2
80			3·4
79	6·8	7·1	19·3
78	3·2		6·4
77	9·0	8·9	20·9
75			3·4
74	3·8		6·6
68			8·2
67	14·6	14·2	32·3
66	37·9	14·1	53·2
65	5·8	6·4	17·3
59	12·6	12·1	28·1
58		4·1	5·3
55	10·5	5·9	16·9
53	5·6	5·6	13·9
52			3·1
51			4·2
45			4·8
44			9·2
43		11·5	13·6
41	9·3	8·4	22·8
40			6·9
39	7·8	9·1	20·7
31			3·8
29			6·3
28	4·9	22·9	76·7
27	4·3	6·0	12·5
26		4·5	13·5

* All peaks with relative intensity $\leqslant 3\%$ have been omitted.

In the molecular ion of the *endo*-isomer (1) the hydrogen atom at C-5 (C-6) is ideally situated to be transferred to the charge-localized carbonyl oxygen of the ester group at C-3 (C-2) *via* a McLafferty rearrangement.[13] This reaction results in ring-opening of the six-membered ring, irrespective of whether the McLafferty rearrangement proceeds in a stepwise or concerted manner, the latter being depicted by sequence *a* ⟶ *b* in Scheme 1. The radical, located at C-3 (C-2) in ion *b*, may then abstract one of the allylic hydrogen atoms from the now equivalent positions 6 (5) and 7, followed by, or simultaneously accompanied with, cleavage of

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[11] D. R. Dimmel and J. M. Seipenbusch, *J. Amer. Chem. Soc.*, 1972, **94**, 6211.

[12] J. L. Holmes and D. McGillavry, *Org. Mass Spectrometry*, 1973, **7**, 559 and references cited therein.

[13] F. W. McLafferty, *Analyt. Chem.*, 1956, **28**, 306.

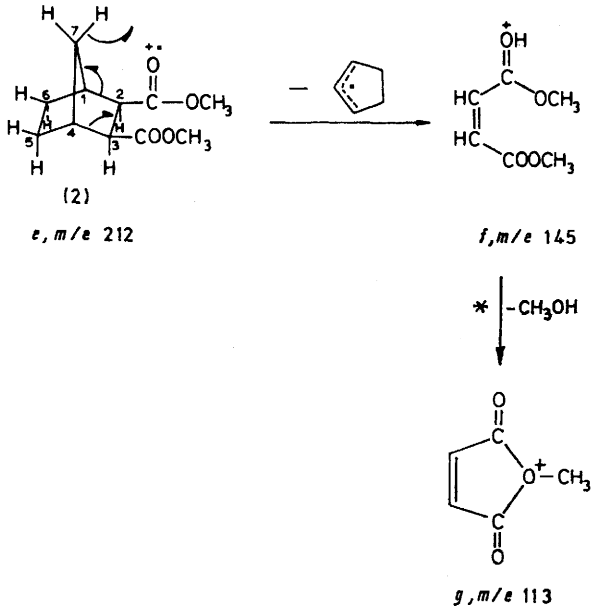
the C-1–C-2 bond (C-3–C-4 bond) to give ion *c* (Scheme 1). Expulsion of methanol from ion *c* results in the formation of ion *d*, corresponding with the peak at *m/e* 114, that appears to be present to a much lesser extent in the spectrum of the *exo*-isomer (2) (*cf.* Table 1). The most abundant ion, *m/e* 145, with elemental composition $C_6H_9O_4$ in the spectrum of the latter compound is most likely generated in one step from the molecular ion. This is not supported by the occurrence of metastable ions, because neither in the first nor in the second field-free regions of the mass spectrometers used is any metastable transition observed for the formation of the ion with *m/e* 145. Its elemental composition however demands a precursor ion containing four oxygen atoms. High resolution measurements of all peaks with *m/e* $\geqslant$146 have shown that the peak at *m/e* 146, consisting of 65% $^{13}C_1{}^{12}C_5H_9O_4$ and 35% $C_6H_{10}O_4$ (see above), and of course the molecular ion with *m/e* 212 ($M^{+\cdot}$, $C_{11}H_{16}O_4$), although being absent, meet this requirement.

Upon lowering the electron energy from 70 to 15 eV the ratio of intensities of the peaks *m/e* 145 and 146 remains unchanged, pointing to a one-step formation of the ion with *m/e* 145 from the molecular ion.* It may then arise from transfer of one of the hydrogen atoms from C-7 to one of the charge-localized carbonyl oxygen atoms of the ester groups.

Such a stereospecifically controlled migration opens the possibility for expulsion of a resonance-stabilized cyclopentenyl radical either through very fast consecutive steps or in a concerted way, the latter being depicted by sequence $e \longrightarrow f$ in Scheme 2. Expulsion of methanol from ion *f* results in the formation of ion *g*, corresponding with the peak at *m/e* 113. Thus migration of a hydrogen atom in a stereochemically suitable position to one of the carbonyl oxygens of the ester groups initiates the decomposition of the molecular ions both of the *endo*- and of the *exo*-isomer. After this migration the fate of the molecular ions is essentially determined by the possibility of expulsion of a stable neutral species.

A resonance-stabilized cyclopentenyl radical cannot be eliminated from the molecular ion of the *endo*-isomer (1) in the way shown for the molecular ion of the *exo*-isomer (2) (compare Schemes 1 and 2). Instead, expulsion of a molecule of cyclopentadiene then takes place as rationalized in Scheme 1.

The spectrum of the *trans*-isomer (3) shows much more intense peaks at *m/e* 181, 180, 153, 152, and 124 than those of the *endo*- and *exo*-isomers (1) and (2) (*cf.* Table 1). This could be due to reduced interaction between the ester groups in the *trans*-isomer (3) in comparison with the *endo*- and *exo*-isomers (1) and (2). It is interesting to note that the reactions given in Schemes 1 and 2 are both operative in the breakdown of the molecular ion of the *trans*-isomer (3); the ratio of the relative intensities of *m/e* 145 and 146 is higher than that found in the spectrum of the *endo*-isomer.



SCHEME 2 Rationalization of the loss of a cyclopentenyl radical from the molecular ion of *exo*-2,3-bismethoxycarbonylbicyclo-[2.2.1]heptane and further decomposition of the generated ion

TABLE 2

Mass spectra * of *exo*- (4) and *endo* (5)-2-methoxycarbonylbicyclo[2.2.1]heptanes (mol. wt. 154) at 70 eV

	(4)	(5)		(4)	(5)
m/e	Relative intensity (%)		*m/e*	Relative intensity (%)	
125	14·5	7·4	68	12·8	23·1
123	6·9	29·1	67	36·4	81·2
122	8·2	78·8	66	14·3	25·8
113	6·3	26·1	65	5·0	14·5
111	3·8	5·4	59	5·1	13·3
100	4·9	6·7	57		7·5
96	5·9	5·9	55	12·3	38·0
95	56·5	56·5	54		11·6
94	10·8	41·0	53	7·8	23·8
93	8·7	12·9	52		4·8
91	3·8	8·1	51		7·6
88	5·0	13·9	45		3·5
87	100	100	44		7·7
81	9·1	74·4	42		4·0
80	12·1	85·0	41	16·5	43·5
79	13·4	30·4	40	3·9	6·9
78		8·5	39	13·6	39·6
77	6·1	14·9	32	5·2	
75		7·7	29	3·4	12·3
74		23·8	28	27·3	21·8
71		3·8	27	7·8	27·8
69		5·2			

* All peaks with relative intensity $\leqslant$3% have been omitted.

endo- *and* exo-2-*Methoxycarbonylbicyclo*[2.2.1]*heptane*.—The principles outlined above are also demonstrated

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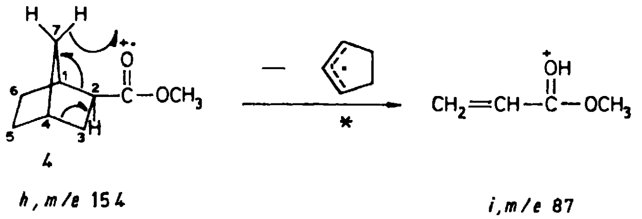
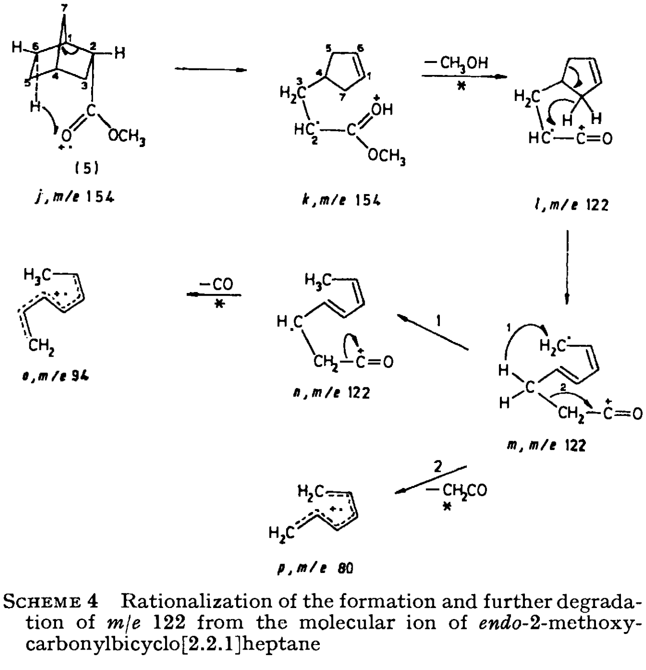
* In the mass spectrum of the *endo*-isomer (1) a peak at *m/e* 145 with the elemental composition $C_6H_9O_4$ is also present (*cf.* Table 1). Again, neither in the first, nor in the second field-free regions of the mass spectrometers used is any metastable transition observed for its formation. High resolution measurements of all peaks with *m/e* $\geqslant$146 have shown that the ion with *m/e* 145 can only be formed from the molecular ion and/or from *m/e* 146, as these contain four oxygen atoms. In this case a 25% decrease is found for the ratio of intensities of the peaks *m/e* 145 and 146, when the electron energy is lowered from 70 to 15 eV. This observation can be explained by a two-step formation of *m/e* 145 from the molecular ion *via* *m/e* 146 as well as by an energetically unfavoured one-step formation of *m/e* 145 from the molecular ion (*e.g.* expulsion of a cyclopentenyl radical, not stabilized by resonance; see text).

by the pronounced differences in the spectra of the *exo*- and *endo*-monoesters (4) and (5) presented in Table 2. The formation of the base peak at *m/e* 87 in the spectrum of the *exo*-isomer (4) (*cf.* Table 2) is again due to the expulsion of a resonance-stabilized cyclopentenyl radical, initiated by transfer of a hydrogen atom from C-7 to the charge-localized carbonyl oxygen atom of the ester group as shown in Scheme 3.



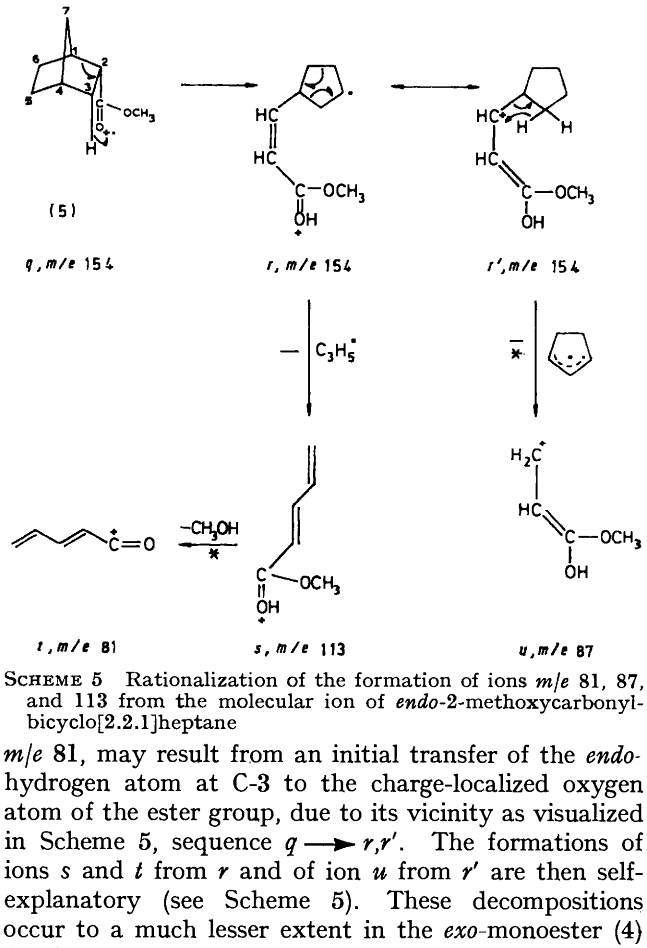
Scheme 3 Rationalization of the loss of a cyclopentenyl radical from the molecular ion of *exo*-2-methoxycarbonylbicyclo-[2.2.1]heptane

In the molecular ion of the *endo*-isomer (5) the hydrogen atom at C-6 is ideally situated to be transferred to the carbonyl oxygen atom of the ester group. This migration, however, cannot result in the expulsion of a resonance-stabilized cyclopentenyl radical; instead, it induces the loss of methanol from the molecular ion, this now being a favoured decomposition pathway (*cf.* Scheme 4, sequence *j* ⟶ *k* ⟶ *l*) and giving an intense peak at *m/e* 122 (*cf.* Table 2). This reaction is followed by expulsion of carbon monoxide or of keten, as evidenced by metastable transitions, to give the peaks at *m/e* 94 and 80 (*cf.* Table 2). The relative intensities of these peaks are very low in the spectrum of the *exo*-monoester (4) (*cf.* Table 2). These corresponding reactions have been rationalized by the sequences *l* ⟶ *m* ⟶ *n* ⟶ *o* and *l* ⟶ *m* ⟶ *p* in Scheme 4 and are thought to be induced *via* abstraction of one of the four allylic hydrogen atoms by the radical centre in ion *l*.



Scheme 4 Rationalization of the formation and further degradation of *m/e* 122 from the molecular ion of *endo*-2-methoxycarbonylbicyclo[2.2.1]heptane

It is interesting to note that neither ion *k* nor ion *l* eliminates cyclopentadiene because then ions would be generated with radical centres (primary!) not stabilized by an adjacent ester group as in the case of *endo*-diester (1) (*cf.* ion *c* in Scheme 1). Nevertheless, expulsion of a cyclopentenyl radical from the molecular ion of the *endo*-monoester (5) appears to be a very favoured reaction, as the base peak in its spectrum is found at *m/e* 87 (*cf.* Table 2). Its formation as well as the generation of the ion with *m/e* 113, the precursor of the ion with *m/e* 81, may result from an initial transfer of the *endo*-hydrogen atom at C-3 to the charge-localized oxygen atom of the ester group, due to its vicinity as visualized in Scheme 5, sequence *q* ⟶ *r*,*r'*. The formations of ions *s* and *t* from *r* and of ion *u* from *r'* are then self-explanatory (see Scheme 5). These decompositions occur to a much lesser extent in the *exo*-monoester (4) (*cf.* Table 2) because of the very favoured loss of a resonance-stabilized cyclopentenyl radical (Scheme 3).



Scheme 5 Rationalization of the formation of ions *m/e* 81, 87, and 113 from the molecular ion of *endo*-2-methoxycarbonylbicyclo[2.2.1]heptane

EXPERIMENTAL

The mass spectra, all taken at 70 eV unless otherwise stated, were obtained with A.E.I. MS 902 and Varian-MAT 711 double focusing mass spectrometers, the latter being coupled with a Spectro system 100. Samples were introduced in the first instrument *via* the all-glass heated inlet system at 150° (ion source at 150°) and in the second instrument *via* the heatable reference inlet system at 150° (ion source at 200°). No essential differences between the mass spectra from both instruments were found.

All high resolution measurements were performed with the Varian-MAT 711 instrument.

Diesters (1) and (2) were obtained by refluxing the corresponding anhydrides[14] in methanol in the presence of sulphuric acid. The *trans*-compound (3) was obtained by isomerization of one of the ester groups in compound (1) with NaOMe–MeOH. The monoesters (4) and (5) were obtained by a Diels–Alder reaction of cyclopentadiene with methyl acrylate,[15] followed by separation of the *endo*- and *exo*-isomers by g.l.c. on a 15% Carbowax column (140°) and subsequent hydrogenation in the presence of 10% Pd–C catalyst.

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[3/1950 *Received, 24th September*, 1973]

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[14] D. Craig, *J. Amer. Chem. Soc.*, 1951, **73**, 4889.

[15] J. A. Bearson, Z. Hamlet, and W. A. Mueller, *J. Amer. Chem. Soc.*, 1964. **84**. 297.