# FRAGMENTATION OF ORGANIC COMPOUNDS ON ELECTRON-IMPACT—V:\*

## 1,1-DICHLOROCYCLOPROPANES

## D. S. WEINBERG, C. STAFFORD and M. W. SCOGGINS Research and Development Division, Phillips Petroleum Company, Bartlesville, Oklahoma, USA

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Abstract—The mass spectral fragmentation reactions of twenty-one 1,1-dichlorocyclopropanes prepared from various isomeric octenes are discussed. The most characteristic reaction may be represented as follows:

$$\begin{array}{c} Cl & Cl \\ H \\ R_1 R_2 C - C \\ R_3 R_4 \\ R_4 \\ R_4 \\ R_4 \end{array} \xrightarrow{(-)^{-1}} C - R_5 \longrightarrow [R_1 R_2 C = CHR_3]^{+} \text{ and } [R_4 R_5 C = CCl_2]^{+}$$

The importance of this fragmentation and the distribution of the positive charge between the species produced is a function of the degree of branching in the molecule. The more highly branched isomers produce less characteristic fragmentation patterns.

The identification of isomeric octenes from the fragmentation patterns of the corresponding 1,1-dichlorocyclopropanes is discussed.

#### INTRODUCTION

ISOMERIC olefins which differ only in the position of a carbon-carbon double bond frequently produce similar mass spectra.<sup>2-5</sup> Consequently it is difficult or impossible to locate the position of a double bond in an olefin by mass spectral techniques. Recently investigators have examined the mass spectra of several olefin derivatives in order to determine if olefins could be characterized from the fragmentation patterns of their derivatives.<sup>6-11</sup> These efforts have met with some success, but many of the procedures are inconvenient because more than one step is required in the preparation of the derivatives or the interpretation is difficult because the critical mass spectral peaks are not very intense.

We have recorded the mass spectra of twenty-one 1,1-dichlorocyclopropane derivatives prepared in one step from various isomeric octenes and chloroform in order to determine the nature of the fragmentation reactions which occur on electronimpact and to determine if correlations could be established which would be useful in locating the position of the double bond in the parent olefin. Our results are reported in this paper.

## **RESULTS AND DISCUSSION**

## Fragmentation reactions of 1,1-dichlorocyclopropanes

The 1,1-dichlorocyclopropanes are listed in Table 1 and the partial mass spectra are tabulated in Tables 2A, 2B, and 2C. The compositions of all of the ions discussed

\* For Part IV, see Ref. 1.

Number	Compound	Boiling point		
(1)	1,1-Dichloro-2-hexylcyclopropane	80·0° (7·5 mm)		
(II)	1,1-Dichloro-2-(1',2'-dimethylbutyl)cyclopropane	69·8° (8·0 mm)		
(III)	1,1-Dichloro-2-methyl-2-pentylcyclopropane	70·8° (5·1 mm)		
(IV)	1,1-Dichloro-2-ethyl-2-butylcyclopropane	67·0° (4·5 mm)		
(V)	1,1-Dichloro-2-methyl-2-(3'-methylbutyl)cyclopropane	63·2° (4·5 mm)		
(VI)	1,1-Dichloro-2-methyl-2-(1'-methylbutyl)cyclopropane	60·8° (3·5 mm)		
(VII)	1,1-Dichloro-2-methyl-2-(1'-ethylpropyl)cyclopropane	61·2° (4·0 mm)		
(VIII)	1,1-Dichloro-2-methyl-2-(2',2'-dimethylpropyl)cyclopropane	58·0° (7·0 mm)		
(IX)	1,1-Dichloro-2-methyl-3-pentylcyclopropane	74·2° (8·0 mm)		
(X)	1,1-Dichloro-2-ethyl-3-butylcyclopropane	63·0° (5·3 mm)		
(XI)	1,1-Dichloro-2,3-dipropylcyclopropane	65·0° <b>(6·0</b> mm)		
(XII)	1,1-Dichloro-2-propyl-3-(1'-methylethyl)cyclopropane	72·0° (9·0 mm)		
(XIII)	1,1-Dichloro-2,3-di-(1'-methylethyl)-cyclopropane	71·3° (12·2 mm)		
(XIV)	1,1-Dichloro-2-methyl-3-(1'-ethylpropyl)cyclopropane	62·0° (6·5 mm)		
(XV)	1,1-Dichloro-2,3-dimethyl-2-(1'-methylpropyl)cyclopropane	65·0° (7·5 mm)		
(XVI)	1,1-Dichloro-2,3,3-triethylcyclopropane	53·8° (6·0 mm)		
(XVII)	1,1-Dichloro-2,2-dimethyl-3-(2'-methylpropyl)cyclopropane	61·0° (6·5 mm)		
(XVIII)	1,1-Dichloro-2,2-dimethyl-3-butylcyclopropane	67·4° (7·9 mm)		
(XIX)	1,1-Dichloro-2,2-dimethyl-3-(1',1'-dimethylethyl)cyclopropane	47·6° (4·6 mm)		
(XX)	1,1-Dichloro-2,2,3-trimethyl-3-propylcyclopropane	70·6° (5·5 mm)		
(XXI)	1,1-Dichloro-2,2-dimethyl-3,3-diethylcyclopropane	61·0° (6·0 mm)		

TABLE 1. IDENTIFICATION OF 1,1-DICHLOROCYCLOPROPANES

were determined from isotope peak distributions or by high resolution mass measurements.

1,1-Dichloro-2-alkylcyclopropanes. Compounds I and II do not produce abundant chlorine-containing ions on electron-impact. Very small peaks at m/e 179, m/e 165 and m/e 137 present in the spectrum of II result from the loss of a methyl, ethyl and butyl group, respectively. The absence of a peak at m/e 151 in the spectrum of II and all of these peaks in the spectrum of I suggests that these ions are produced by simple cleavage of the molecular ion at points of branching. A weak peak is also produced at m/e 123 by elimination of a chlorine atom plus hydrogen chloride from the molecular ions.

The ion at m/e 98 (C<sub>7</sub>H<sub>14</sub>) is present in low abundance in the spectra of both compounds. It may arise in the following manner:



An analogous fragmentation process has been observed by Djerassi and his co-workers in the fragmentation of aliphatic epoxides.<sup>12</sup> They suggested that this fragmentation is 'unique to epoxides', but it appears that the fragmentation may be characteristic of compounds which contain a C-alkyl substituted, saturated, three-membered ring system (vide infra).

All of the intense peaks in the spectra of I and II represent lower molecular weight

#### Fragmentation of organic compounds on electron-impact-V

		Peak intensities						
m/e	Compound	(1)	(II)	(III)	(IV)	(V)	(VI)	(VII)
39		60	41	66	58	51	33	35
40		9	6	12	10	10	6	6
41		93	68	100	90	76	55	60
42		40	7	21	20	10	7	7
43		72	17	80	28	85	38	44
51		20	9	20	18	16	12	16
53		20	10	24	21	16	16	21
54		16	3	9	14	7	4	5
55		55	26	58	57	34	25	36
56		100	20	92	100	100	20	20
57		31	28	16	22	20	2	4
65		9	13	21	19	15	6	9
67		12	11	18	13	9	5	9
69		45	100	50	60	92	100	100
70		53	28	29	33	21	40	3
71		4	3	8	2	4	12	18
75		8	6	8	10	5	4	5
77		6	6	11	12	7	9	13
81		11	2	10	8	6	5	4
83		16	20	7	7	7	11	2
87		10	2	8	4	6	3	5
89		6	5	14	8	7	4	9
98		9	20	53	69	10	48	70
102		9	4	17		5	<u> </u>	
109		6	4	4	16	3	2	2
111		4	3	3	10	2		_
123		5	3	23	6	14	3	7
124				27	5	3		_
125				10	2	7		3
126				16	3	2		
137			1		11	_		_
165			2		1	1	_	1
179			1	<u> </u>				
194		0.1	0.2	2	0.3	0.2	0.2	0.3

TABLE 2A. PARTIAL\* MASS SPECTRA OF 1,1-DICHLOROCYCLOPROPANES

\* Only those peaks are listed which are at least 10% as intense as the base peak or are of special interest. The latter consist of the parent peaks, various low intensity peaks relevant to the discussion of fragmentation mechanisms and peaks of moderate intensities included for comparison purposes.

hydrocarbon ions. These ions do not appear to be generated by simple cleavage of the molecular ion; simple cleavage of II would produce an abundant ion at m/e 57 if this were the case. The peak at m/e 57 is weak, however, and the base peak occurs at m/e 69. The ion represented by this peak may result from cleavage of the m/e 98 ion.



		Peak intensities						
m/e	Compound	(VIII)	(IX)	(X)	(XI)	(XII)	(XIII)	(XIV)
39		20	77	80	52	40	51	47
40		4	11	11	7	6	8	6
41		36	97	100	66	58	74	51
42		2	48	42	100	39	9	42
43		6	96	45	31	47	<b>5</b> 2	56
51		6	25	28	19	15	16	20
53		5	26	26	18	13	17	26
55			60	46	21	14	24	83
56		3	74	63	26	100	100	53
57		100	13	20	6	26	20	7
63		2	10	14	8	6	8	10
65		4	30	32	19	11	14	16
67		3	24	15	11	9	12	9
69			36	26	10	6	46	72
70			12	18	6		4	16
71		3	7	7				12
75			30	20	14	8	8	13
77		4	18	20	17	15	16	19
79		2	10	13	11	12	13	11
81			10	28	13	6	8	5
83		—	10	6	4	3	8	10
84			13		4	3	2	100
85			12	2	4	2	3	10
ð/ 90			13	12	9	6	6	7
01		2	17	18	16	8	8	16
91		2	14	20	0 27	3	8 2	10
102			14	20	10	4	2	-
102			1	9 Q	16	22	24	-
105			-	2	10		34 11	2
109			9	30	55	26	11	0
110			100	6	13	5	2	5
111			13	28	36	17	39	3
112			65	4	8	3	4	3
114			10		2	_		
116		Acces 100	16	4	2	_		
123		4	24	12	10	16	23	9
124			11	78	6	3		_
125		2	11	8	5	9	14	5
126			6	48	2			
137			2	13	_	2	2	
138			2	6	42	23	24	
151					8	4	3	
152				6				
194		0.1	0.6	2	1			0.3

TABLE 2B. PARTIAL\* MASS SPECTRA OF 1,1-DICHLOROCYCLOPROPANES

\* See Table 2A for criteria used to select data included in this table.

# Fragmentation of organic compounds on electron-impact---V

		Peak intensities						
m/e	Compound	(XV)	(XVI)	(XVII)	(XVIII)	(XIX)	(XX)	(XXI)
36		24	42	20	12	24	30	34
38		17	24	16	13	15	22	22
39		84	100	78	88	63	100	98
40		13	16	14	13	10	15	14
41		81	93	85	100	68	98	100
42		9	27	8	14	7	13	13
43		13	30	100	33	13	22	30
50		9	17	9	9	8	13	17
51		25	46	24	27	22	37	48
52		8	15	8	8	6	12	15
53		31	57	26	32	72	53	62
55		38	93	12	26	20	41	60
56		21	10	26	16	4	9	10
57		38	9	15	10	100	8	11
63		15	28	11	11	10	18	22
65		34	47	25	43	20	28	34
66		12	10	7	9	4	9	9
67		34	43	19	34	15	30	50
69		77	20	11	17	6	20	25
70		6	74	2	2	15	8	8
75		12	18	13	20	6	15	16
77		43	72	36	39	22	62	70
78		9	16	8	7	6	14	15
79		23	54	63	39	25	53	42
80		4	9	9	6	6	10	9
81		20	68	31	29	30	70	64
84		100	2	7	34	2	2	3
89		11	41	8	18	6	22	30
91		31	62	14	13	34	38	55
92		5	10	2	2	6	7	10
93		40	62	4	10	11	34	63
94		6	9	_	2	2	9	10
95		15	22	2	4	4	19	35
101		5	10	6	10	2	2	2
102		12	10	30	28	2	4	5
103		14	12	23	38	5	42	20
104		07	5	11	12	2	) 19	24
105		12	11	12	12	0	10	24
107		13	40	12	20	40	20 6	20 6
111		~ ~	13	4	12	3	3	2
112			13		12		2	
112		6	5	12	6	3	9	4
116		5	11	24	11	2	9	9
117		4	13	10	6	5	52	22
119			4	2	ž	2	16	8
123		15	72	23	30	36	68	70
124		_		10	20	3	15	14
125		3	21	2	5		6	11
126				5	12		6	5
129		15	40		4	—	6	24

TABLE 2C. PARTIAL\* MASS SPECTRA OF 1,1-DICHLOROCYCLOPROPANES

	Peak intensities											
m/e	Compound	(XV)	(XVI)	(XVII)	(XVIII)	(XIX)	(XX)	(XXI)				
130		26	4				9	2				
131		7	13		2		•	12				
137		10	3	25	88	2	4	3				
138		4		6	8							
139		7	2	16	56		3	2				
143		3	11	6		31	16	7				
151				2	2		20					
158		11	41	14	9	8	27	51				
159		_	14		8		23	34				
160		4	14	5		3	7	19				
161							7	11				
165			11					14				
167			7					9				
194			3	0.2	3	0.4	1	2				

TABLE 2C (Continued)

\* See Table 2A for criteria used to select data included in this table.

This fragmentation could also involve migration of a methyl group in place of the hydrogen atom. In view of the numerous modes of fragmentation of the lower molecular weight hydrocarbon ions possible, fragmentation processes leading to these ions generally will not be discussed in this paper.

1,1-Dichloro-2,2-dialkylcyclopropanes. Compounds III to VII all produce a moderately abundant ion at m/e 98. The formation of this ion is probably more favorable here than in the case of I and II because a more highly substituted olefin is produced.<sup>13</sup> The chlorine-containing species produced in this fragmentation carries little or none of the positive charge.

$$\begin{array}{c} \begin{array}{c} C_{1} \\ H \\ R_{1}R_{2}C \\ C \\ R_{3} \end{array} \end{array} \xrightarrow{-CH_{2}CCl_{2}} \left[ R_{1}R_{2}C = CHR_{3} \right]^{+} \\ (III), (IV), (V), (VI), (VII) \end{array}$$

Compounds III to VII also undergo cleavage with loss of the larger alkyl group to produce chlorine-containing ions in low abundance. The ions appear at m/e 123 in the spectra of III, V, VI, VII, and VIII and at m/e 137 in the spectrum of IV. A hydro-carbon ion produced by the loss of hydrogen chloride plus a chlorine atom also appears at m/e 123 in the spectra of III to VII; however, the chlorine-containing ions produced by  $\alpha$ -cleavage carry at least 40 per cent of the ion current at this mass number.



The only abundant ion in the spectrum of VIII occurs at m/e 57. It is generated by simple cleavage of the molecule and demonstrates that the t-butyl group stabilizes a positive charge more effectively than the dichlorocyclopropyl group.

1,1-Dichloro-2,3-dialkylcyclopropanes. Compounds IX, X, and XI exhibit dramatically different mass spectra from II. The most abundant ion in the spectrum of of IX occurs at m/e 110. Analogous ions appear at m/e 124 and m/e 138 in the spectra



of X and XI. Cleavage with elimination of the lower molecular weight alkyl group is not a favorable process; the expected peak at m/e 166 is not detectable in the spectrum of IX while the peak at m/e 152 is only eight per cent as intense as the peak at m/e 124 in the spectrum of X.



Other moderately abundant chlorine-containing ions occur at m/e 109, 123 and 137 in the spectra of IX and X and at m/e 109, 123 and 151 in the spectrum of XI. These ions may be produced by  $\alpha$ -cleavage of the molecular ion or by  $\beta$ - or  $\gamma$ -cleavage of the rearranged fragment. An alternative mode of formation of an ion at m/e 123 occurs by the loss of hydrogen chloride plus a chlorine atom 33 to 50% of the time in the spectra of IX to XI.

The presence of a point of branching at the carbon atom attached to the cyclopropyl ring in 1,1-dichloro-2,3-dialkylcyclopropanes leads to a significant decrease in the abundance of chlorine-containing ions in the mass spectrum. The most abundant ions produced from XII, XIII, and XIV are hydrocarbon ions, probably produced in the same manner as the m/e 98 in the spectrum of II. The expected ion at m/e 138 is present in low abundance in the spectra of XII and XIII, but the characteristic ion at m/e 110 is virtually absent in the spectrum of XIV.





1,1-Dichloro-2,2,3-trialkylcyclopropanes. Compounds XV to XIX display less characteristic fragmentation patterns than the compounds discussed to this point since numerous abundant ions are produced. Many of the fragments result from the loss of various combinations of hydrogen chloride, chlorine atoms and alkyl radicals. The mass spectra of XV and XVI do display the expected intense peaks at m/e 84 (C<sub>6</sub>H<sub>12</sub>) and 70 (C<sub>5</sub>H<sub>10</sub>), respectively, but these peaks do not dominate the spectra.



The corresponding dichloroolefin ions are present in very low abundance. The spectra of XVII and XVIII are more difficult to rationalize. Peaks appear at m/e 152, 124, 70 or 42, but their intensities are low. In addition, the loss of a butyl group from XVIII produces a very abundant ion whereas this is not observed in the spectrum of XVII. Compound XIX exhibits a strong peak at m/e 57 (C<sub>4</sub>H<sub>9</sub>), demonstrating again that the t-butyl group competes effectively with the dichlorocyclopropyl group in directing the fragmentation process.



1,1-Dichloro-2,2,3,3-tetraalkylcyclopropanes. The spectra of XX and XXI are dominated by ions generated by the simple cleavage of the molecule. Compound XX exhibits mass peaks at m/e 159 [M - Cl], m/e 158 [M - HCl], m/e 151 [M - C<sub>3</sub>H<sub>7</sub>], m/e 143 [M - HCl - CH<sub>3</sub>] and m/e 123 [M - HCl - Cl] while XXI exhibits peaks at m/e 165 [M - C<sub>2</sub>H<sub>5</sub>], m/e 158 [M - HCl], m/e 143 [M - HCl - CH<sub>3</sub>], m/e 128 [M - HCl], m/e 143 [M - HCl - CH<sub>3</sub>], m/e 129 [M - HCl - C<sub>2</sub>H<sub>5</sub>] and m/e 123 [M - HCl - Cl].

#### Identification of isomeric octenes

It is apparent that the mass spectra of 1,1-dichlorocyclopropane derivatives yield significant information concerning the location of the carbon-carbon double bond in octenes of known carbon skeleton if the degree of branching is not high.

The most significant correlation can be deduced from the most characteristic reaction exhibited by the various isomers.

The distribution of positive charge between the olefinic hydrocarbons and the chlorine-containing olefins produced by the characteristic fragmentation reaction discussed above is a function of the degree of substitution of the two molecules. When the number of alkyl groups attached to the vinylic carbon atoms of the chlorine containing olefin produced in the fragmentation is equal to the number attached to the vinylic carbon atom of the olefinic hydrocarbon fragment, the chlorine-containing olefin carries most of the positive charge. When the number of alkyl groups attached to the vinylic carbon atoms of the olefinic hydrocarbon fragment is larger, however, it carries most of the positive charge. The detailed correlations which have been established for the specific octenes studies can be summarized as follows:

Monoalkylethylene derivatives. No peaks of significant intensity appear beyond m/e 98. The peak at m/e 98 is small if the olefin is linear; if there is an alkyl group attached to the allylic carbon atom of the parent olefin, the peak at m/e 98 becomes moderately intense (intensity is less than 25% of the base peak).

Unsymmetrical dialkylethylene derivatives. A strong peak occurs at m/e 98 which is at least 40% as intense as the base peak unless additional branching occurs at carbon

atoms further removed from the carbon-carbon double bond than the allylic carbon atom. In the latter case, a weak peak occurs at m/e 98.

Symmetrical dialkylethylene derivatives. Strong peaks which represent dichloroolefin molecular ions are produced at m/e (95 + R), where R is the mass of the smallest alkyl group attached to a vinylic carbon atom, if the parent olefin is linear. If an alkyl group is attached to the allylic carbon atom, however, the peak representing the chlorine-containing olefin ions decreases substantially in intensity and an intense peak appears which represents a hydrocarbon ion with m/e (R + 13), where R is the mass of the branched alkyl group.

Trialkylethylene derivatives. A moderately strong peak representing a hydrocarbon ion is produced at m/e ( $R_1 + R_2 + 12$ ), where  $R_1$  and  $R_2$  represent the masses of the two alkyl groups attached to the same vinyl carbon atom *if* at least one of these two alkyl groups is larger than methyl. If both groups are methyl, no highly characteristic peaks are produced, although the large number of peaks would suggest the compound is a tri- or tetra-substituted ethylene.

Tetraalkylethylene derivatives. The large number of intense peaks would suggest that the original compound is a tri- or tetra-substituted olefin. If other points of branching are not present, the substituents (R) could be identified by the [M - R] fragments, where R is the mass of the alkyl group attached to the vinylic carbon atoms in the parent olefin.

## CONCLUSION

On the basis of the work carried out on isomeric octenes, it appears that the location of the carbon-carbon double bond in olefins of known carbon skeleton and moderate molecular weight can be determined from the mass spectrum of the corresponding 1,1-dichlorocyclopropane derivative if the degree of branching is small. The identification of the olefin becomes more difficult, however, as the degree of branching increases and in many cases, it would not be possible to arrive at an unambiguous structure on the basis of mass spectra data alone.

### EXPERIMENTAL

General. The olefins were obtained from Chemical Samples Company or Phillips Petroleum Company in a purity of 99% or higher. Distillations were carried out in a Nester Faust Annuler Teflon Spinning Band Distillation Column, Model No. NFT 50. The n.m.r. spectra were obtained on neat liquids on a Varian A-60 spectrometer. The low resolution mass spectra were recorded on a Consolidated Electrodynamics Corp. Model 21-103C spectrometer at 70 eV and the samples were introduced through an inlet at 200°C into the ion source at 275°C. The high resolution mass spectra were recorded on a Consolidated Electrodynamics Corporation Model 21-110B mass spectrometer.

Preparation of compounds. All of the compounds were prepared by the reaction of the appropriate olefin with chloroform and potassium t-butoxide according to the procedure given by Doering and Henderson.<sup>14</sup> The yields of distilled products were 5 to 62% and gave satisfactory elemental analyses. (Calculated for  $C_9H_{16}Cl_2$ : C, 55·4; H, 8·3; Cl, 36·3. Found (Average Values): C, 55·2; H, 8·3; Cl, 36·5. The n.m.r. spectra of the products were consistent with their expected structures and indicated that no isomerization occurred during the synthesis.

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