

Conformational Analysis

IV. *trans*-2,4-Dimethyloxetane and *cis*-2,3-*trans*-4-TrimethyloxetaneKALEVI PIHLAJA, KATRIINA
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Our previous reports have been concerned with 1,3-dioxanes^{1,2} and their existence in skew-boat form.³ Virtanen *et al.*^{4,5} reported the NMR spectra and mass spectra of some mono- and geminally disubstituted oxetanes, but very little is known about vicinally alkyl-substituted oxetanes.^{6,7} Hence the aim of this study was to prepare some new 2,4- and 2,3,4-methyl-substituted oxetanes and compare their NMR and mass spectra with those of the mono- and geminally disubstituted oxetanes.

2,4-Dimethyloxetane. The reaction of 2,4-pentanediol (Fluka AG) with acetyl chloride in the presence of anhydrous calcium chloride was carried out by the method of Meltzer and King.⁸ The yield of chloroacetate, b.p. 66–88°C at 11 torr, was 76%. Dropwise addition of 21.4 g of the crude chloroacetate to a vigorously stirred mixture of 55 g of potassium hydroxide and 17 ml of water at 140–160°C when repeated three times gave 4.5 g of a product which boiled at 76–91°C.⁹ The crude product was run through a Perkin-Elmer F 21 preparative gas chromatograph equipped with a column containing 5% Carbowax 20 M on Chromosorb G (60/80 mesh). The sample contained mainly *trans*-2,4-dimethyloxetane, but also some of the *cis* form was present as an impurity, the n_D^{25} was 1.4100.

2,3,4-Trimethyloxetane. The chloroacetate of 3-methyl-2,4-pentanediol (Fluka AG) was obtained in 81% yield.⁸ 5 g portions of the chloroester were added dropwise to the following mixtures at 140–150°C:

A. 8.2 g KOH+8.2 g NaOH+1 ml H₂O;
B. 15 g KOH+5 ml H₂O; C. 16 g KOH+4 ml H₂O; D. 15 g KOH+6 ml H₂O.

The combined products were dried and distilled from sodium. The fractionation yielded a small amount of a product boiling at 80–82°C. This was purified further by running it through a preparative gas chromatograph, after which a relatively pure sample of *cis*-

2,3-*trans*-4-trimethyloxetane was obtained. Its n_D^{25} was 1.3942.

2,2,4-Trimethyloxetane. Attempts to prepare this compound either via the chloroester starting from 2-methyl-2,4-pentanediol or by pyrolysis of 4,4,6-trimethyl-2-oxo-1,3-dioxane^{8,9} were not successful.

NMR spectra were recorded for solutions which contained 50 μ l of the substrate in 450 μ l of carbon tetrachloride or benzene on a Perkin-Elmer R 10 spectrometer working at 60 MHz. Tetramethylsilane was the internal standard.

Mass spectra were recorded on a Perkin-Elmer M 270 analytical mass spectrometer using ionizing energies of 10, 30, and 70 eV. The pressure and temperature of the ion chamber were 10⁻⁶ atm and 120°C. The mass spectrum of *cis*-2,4-dimethyloxetane could also be recorded at 70 eV owing to the slightly different retention times of the *cis* and *trans* forms of this oxetane in the 1% silicone column connected to the inlet system of the mass spectrometer.

NMR data are shown in Table 1 and mass spectral fragmentation patterns in Table 2.

Jokisaari *et al.*⁴ reported recently a fully analysis of the PMR spectrum of 2-phenyloxetane. Fig. 1 presents the formulae and the vicinal coupling constants for this compound and for *trans*-2,4-dimethyl- and *cis*-2,3-*trans*-4-trimethyloxetane. It is seen that the coupling constants of *cis*-2,3-*trans*-4-trimethyloxetane agree closely with the corresponding coupling constants of 2-phenyloxetane. Similarly, when the symmetry of *trans*-2,4-dimethyloxetane which leads to the magnetic equivalence of the H₃ and H₃* protons, the H₂ and H₄ protons and the two methyl groups is taken into account, the average of the two different coupling constants of this compound, 6.92 Hz, is just half the sum of the relevant coupling constants of the phenyl derivative. Also the chemical shift data are in good agreement with those reported for other oxetanes (Table 1).⁴

The mass spectra of *cis*- and *trans*-2,4-dimethyl- and *cis*-2,3-*trans*-4-trimethyloxetanes contain peaks due to the molecular ions, although these peaks are not very strong. The mass spectra of mono-alkyl- and geminally dialkyl-substituted oxetanes recorded by Virtanen *et al.*⁵ also contained either relatively weak or no peaks due to molecular ions.

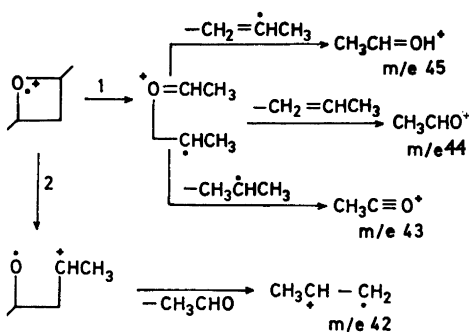
The most abundant ion in the 70 eV spectrum of *cis*-2,4-dimethyloxetane corresponds to the fragment CH₂CH=OH⁺,

Table 1. NMR shifts in Hz from internal TMS standard and coupling constants of *trans*-2,4-dimethyl- and *cis*-2,3,*trans*-4-trimethyloxetanes at 33.2°C. The solutions contained 50 μ l of the substrate in 450 μ l of solvent.

	Solvent	H ₂	H ₃	H ₄	2-Me	3-Me	4-Me	J ₂₃	J ₃₄	J _{Me}
<i>trans</i> -2,4-Dimethyl-oxetane (average spectrum)	CCl ₄	283.3	136.9	283.3	81.7	—	81.7	6.92	6.92	6.19
	C ₆ H ₆	278.5	121.2	278.5	74.85	—	74.85	6.78	6.78	6.19
<i>cis</i> -2,3, <i>trans</i> -4-Tri-methyloxetane	CCl ₄	257	152.5	285	79	62.5	73	5.6 ^d	7.8 ^d	6.2 ^a 7.5 ^b 6.6 ^c

^a ²J_{Me}. ^b ³J_{Me}. ^c ⁴J_{Me}. ^d ± 0.2 Hz.

which may be formed by route (1). The same path may also yield the fragments



m/e 44 and *m/e* 43. Ring cleavage by carbon-oxygen bond fission and loss of acetaldehyde gives the fragment C₃H₆⁺, *m/e* 42. All other fragments (relative intensities > 5 %) are produced in the above decompositions or by secondary processes.

The most abundant peak lies at *m/e* 45 also in the 10 eV mass spectrum of *trans*-2,4-dimethyloxetane, the other fragments being *m/e* 71 (M⁺ - CH₃, 12 %), *m/e* 68 (M⁺ - C₂H₄, 13 %), *m/e* 43 (CH₃C≡O⁺, 11.5 %) and *m/e* 42 (C₃H₆⁺, 8 %). All of these ions except *m/e* 68 are due to ring cleavages by routes (1) and (2).

The fact that the fragment C₃H₆⁺ *m/e* 42 is the most abundant ion in the 30 and 70 eV mass spectra of *trans*-2,4-dimethyloxetane shows that decomposition by carbon-oxygen bond scission is favored. All the other fragments can again be ex-

plained on the basis of path (1) or secondary processes. The relatively abundant fragment CHO⁺ (*m/e* 29) is formed from the (M⁺ - CH₃) fragment by path (1).

The most abundant peak in the 10 eV mass spectrum of *cis*-2,3,*trans*-4-trimethyloxetane corresponds to the fragment C₄H₈⁺ (*m/e* 56) formed by path (2). The only other abundant ion in the 10 eV spectrum of this compound is obviously due to C₃H₇O⁺ (*m/e* 59).

The most abundant fragment in the 30 and 70 eV mass spectra of the trimethyl derivative is the ion C₄H₈⁺ (*m/e* 56) (route 2) which in turn yields the fragment C₃H₆⁺ (*m/e* 41) by loss of a methyl group. The peaks at *m/e* 45, 44, and 43 are again due to the decomposition of the ring by route (1). The relatively abundant ion at *m/e* 29 may be due to the formation of C₂H₅⁺ or CHO⁺ fragments, the latter being formed from the (M - CH₃)⁺ fragment by route (1).

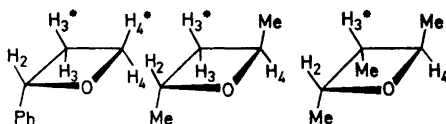
Generally, the observed fragmentation patterns are in close agreement with those reported earlier for oxetanes and other cyclic ethers.⁵

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Table 2. Mass spectral fragmentation patterns of *trans*-2,4-dimethyloxetane and *cis*-2,3,*trans*-4-trimethyloxetane at 10, 30, and 70 eV and that of *cis*-2,4-dimethyloxetane at 70 eV.

<i>m/e</i>	Relative intensity						
	<i>cis</i> -2,4 70 eV	10 eV	<i>trans</i> -2,4		10 eV	<i>cis</i> -2,3, <i>trans</i> -4	
	70 eV	30 eV	70 eV	30 eV	70 eV	30 eV	70 eV
15	2	—	4	10	—	2	6
27	9	—	14	19	—	6	16
28	—	—	5	6	—	12	15
29	4	—	9	11	—	13	17
39	10	—	10	18	—	7	13
40	2	—	10	11	—	3	4
41	12	—	44	49	—	62.5	68
42	11	8	100	100	—	7.5	9
43	18	12	44.5	44.5	—	17	21
44	2	1	5.5	4.5	—	3	4
45	100	100	89	63	—	7	7
55	—	—	—	—	—	10	11
56	—	—	—	—	100	100	100
57	—	—	—	—	—	8.5	8
59	—	—	—	—	39	6	7
68	2	13	2	2	—	—	—
71	3	12	8	6	—	2	3
81	—	—	—	—	14	—	—
86 (M ⁺)	—	6	2	2	—	—	—
100 (M ⁺)	—	—	—	—	2	1	0.5



J_{23}	7.31 Hz	$J_{23} = J_{3^*4} = J_1$	$J_{23}^* = 7.8$ Hz
J_{23}^*	7.79 Hz	$J_{23}^* = J_{34} = J_2$	$J_{3^*4} = 5.6$ Hz
J_{34}	9.15 Hz	$(J_1 + J_2)/2 = 6.92$ Hz	
J_{34}^*	7.74 Hz	$J_1 = 5.6$ Hz	
J_{43}^*	5.62 Hz	$J_2 = 8.2$ Hz	
$J_{3^*4}^*$	8.19 Hz		

Fig. 1. Formulae and vicinal coupling constants of 2-phenyl-, *trans*-2,4-dimethyl- and *cis*-2,3,*trans*-4-trimethyloxetanes.

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