VIBRATIONAL SPECTRA OF METHYL 2, 2-DIMETHYL -3-KETOCYCLOBUTYL ACETATE (I) AND METHYL 2,2-DIMETHYL-3-HYDROXYCYCLOBUTYL ACETATE (II)

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ABSTRACT

The Raman and the infrared spectra of methyl 2, 2-dimethyl 3-ketocyclobutyl acetate and methyl 2, 2-dimethyl-3-hydroxy-cyclobutyl acetate have been studied and the observed frequencies have been analysed in terms of characteristic group freqnencies. The keto ester (I) shows two frequencies in the carbonyl stretching frequency region while the hydroxy ester (II) shows only one. A comparison has been made with the available data for cyclobutane compounds and the possible characteristic frequeneies for these compounds are discussed.

1. INTRODUCTION

During an investigation on some transformation reactions of α-pinene, the keto—(I) and the hydroxy—(II) cyclobutane compounds were obtained. The method of preparation and the properties of these compounds have been reported elsewhere[1]. Since the Raman and the infrared spectra can help in the elucidation of molecular structure, especially in the case of heavy organic molecules, they were recorded and analysed for these compounds. While many infrared investigations are available on the cyclobutane compounds, there are only a few Raman effect studies on these compounds. Lord and Nakagawa[2] analysed the vibrational spectrum of cyclobutane. Kohlrausch and Skrabal[3] reported the Raman spectra of cyclobutane carboxylic acid and its esters. Frei and Gunthard[4] also recorded the vibrational spectra of cyclobutanone and $\alpha, \alpha, \alpha', \alpha'$-$d_4$-cyclobutanone. Durig and Morrissey[5] obtained the vibrational spectra of 2-bromocyclobutanone and 2-bromo 2, 4, 4-trideutero cyclobutanone. In an attempt to locate possible characteristic frequencies for the cyclobutane ring, Ulery and McClenon[6] studied 191 cyclobutane derivatives and suggested some characteristic frequencies.

Recently Conia and his co-workers[7a, b, c] synthesised a large number of bromocyclobutanones and analysed their conformational properties by studying the ultraviolet, infrared and nuclear magnetic resonance spectra of these compounds. In this paper we present the results obtained from a Raman and infrared investigation on the title compounds.

2. EXPERIMENTAL DETAILS AND RESULTS

The Raman Spectra were recorded with a Hilger two prism spectrograph and with the mercury 4358 Å radiation obtained from a Toronto type helical arc as the exciting line. A saturated solution of sodium nitrite was used to cut off the lower wave-length radiations. With a slit width of 0.05 mm and Ilford Astra III plates good spectra were obtained with an exposure time of about twelve hours. The Raman spectra were microphotometered using a Moll microphotometer. The infrared spectra were recorded in the region 400-4000 cm^{-1} with the Carl Zeiss UR-10 automatic recording spectrometer equipped with LiF, NaCl and KBr prisms. The substances were used as neat smears.

Plates I and II give the Raman spectra and the microphotometer tracings of the keto ester (I) and the hydroxyester (II) respectively. The infrared absorption spectra of these two compounds are reproduced in figures 1 and 2 respectively. The Raman shifts (in cm^{-1}, vacuum corrected) along with the visually estimated intensities and the IR absorption frequencies (in cm^{-1}) are given in Table 1. The structures of the two molecules are shown in figure 3.

3. DISCUSSION

Methyl 2, 2-dimethyl-3-ketocyclobutyl acetate and methyl 2, 2-dimetyl-3-hydroxycyclobutyl acetate contain a large number of atoms and functional groups and have no symmetry which can help in the vibrational analysis of the molecule as a whole. Thus we see from Table 1 that a large number of frequencies appear both in the Raman and the infrared spectra of these compounds. Any assignment of these frequencies can therefore only be tentative and with some uncertainties arising particularly in the most active region, namely, 700-1500 cm^{-1}.

3.1. C-H *stretching modes*: Only 3 strong and broad bands occur in the C-H stretching region, both in the Raman and the infrared spectra. There is presumably an overlap between the symmetric stretching modes of the CH_2 groups and the asymmetric stretching modes of the CH_3 groups.

3.2. *The* C=O *stretching modes*: The keto ester (I) has two frequencies (at ~ 1740 and $\sim 1780\ \mathrm{cm}^{-1}$) both in the Raman and the infrared. In cyclobutanone and in bromocyclobutanone the C=O frequency occurs at

TABLE 1

Observed Raman and Infrared Frequencies of the keto-(I) and the hydroxy-(II) esters.

keto ester Frequency cm^{-1}		Hydroxy ester Frequency cm^{-1}		Assignment
Raman	Infrared	Raman	Infrared	
174 (3)*		190 (2)*		
247 (0)		221 (2)		
275 (1)				
303 (2)		304 (2)		C – C – C bending
373 (3)		375 (4)		C = O (keto) bending
		462 (2)	462 (w)	
495 (0)			535 (w)	
547 (1)	540 (vw)	547 (2)	555 (w)	
595 (0)	595 (w)		595 (w, br)	
	627 (m)			
	635 (sh)	645 (2)	645 (w)	
655 (4)	652 (w)			
693 (7)	690 (w)	706 (5)	702 (w)	Ring vibration
730 (1)		748 (2)		
	770 (w)			
	792 (vw)	789 (2)	792 (w)	
			810 (w)	
836 (3)	842 (vw)		845 (w)	
859 (3)	865 (w)	850 (2)	865 (w)	Ring vibration
	882 (w)	878 (3)	888 (w)	
900 (3)				
		912 (4)	923 (w)	Ring vibration
		938 (1)	942 (w)	
957 (6)			965 (w)	
996 (6)	1004 (m)	992 (4)	1005 (s)	CH_3 rocking
			1020 (sh)	
	1023 (m)			
			1045 (s)	

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* Numbers in brackets give the visually estimated intensities for the Raman lines.
vs : Very Strong, s : Strong, sh : Shoulder, m : Medium, w : Weak, vw : Very Weak, br : broad.

TABLE 1—(*contd.*)

keto ester Frequency cm^{-1}		Hydroxy ester Frequency cm^{-1}		Assignment
Raman	Infrared	Raman	Infrared	
1058 (1)		1051 (4)	1061 (s)	C-OH bending
	1074 (s)			
	1082 (sh)		1105 (s)	
	1120 (w)	1133 (3)	1135 (s)	
1138 (1)				
	1150 (w)	1158 (3)		
	1181 (s)		1182 (s)	
1203 (2)	1202 (s)		1202 (s)	C-H bending
1235 (2)	1242 (w)	1223 (3)	1232 (s)	CH_2 twisting
		1248 (3)		
1270 (2)	1272 (s)		1265 (s, br)	CH_2 twisting
1318 (1)	1327 (s)		1320 (s)	CH_3 bending
1365 (0)		1374 (1)	1372 (s)	*gem* dimethyl bending
	1388 (s)		1385 (sh)	
1398 (1)	1405 (w)			
1417 (0)	1428 (vw)		1424 (m)	
1444 (7)	1445 (s)	1447 (6)	1445 (s)	CH_2 bending
1464 (7)	1474 (m)	1462 (6)	1471 (m)	CH_3 bending
		1645 (1)	1650 (w)	O−H bending
1738 (4)	1745 (vs)	1735 (3)	1740 (vs, br)	C=O stretching (ester)
1778 (7)	1785 (vs)			C=O stretching (ketone)
2870 (5)	2875 (m)	2870 (5)	2874 (m)	C−H stretching
2923 (10)	2935 (s)	2915 (8)	2935 (sh)	C−H stretching
2974 (10)	2968 (s)	2958 (10)	2965 (vs)	C−H stretching
			~3450 (s, br)	O−H stretching

~1780cm^{-1}. Hence it is to be concluded that the higher frequency (*i.e.*, 1780 cm^{-1}) is the one corresponding to the keto group and the other frequency (*i.e.*, 1740 cm^{-1}) is due to the ester C=O. The hydroxy ester (II) shows only one frequency both in the infrared and the Raman (at ~ 1740 cm^{-1}).

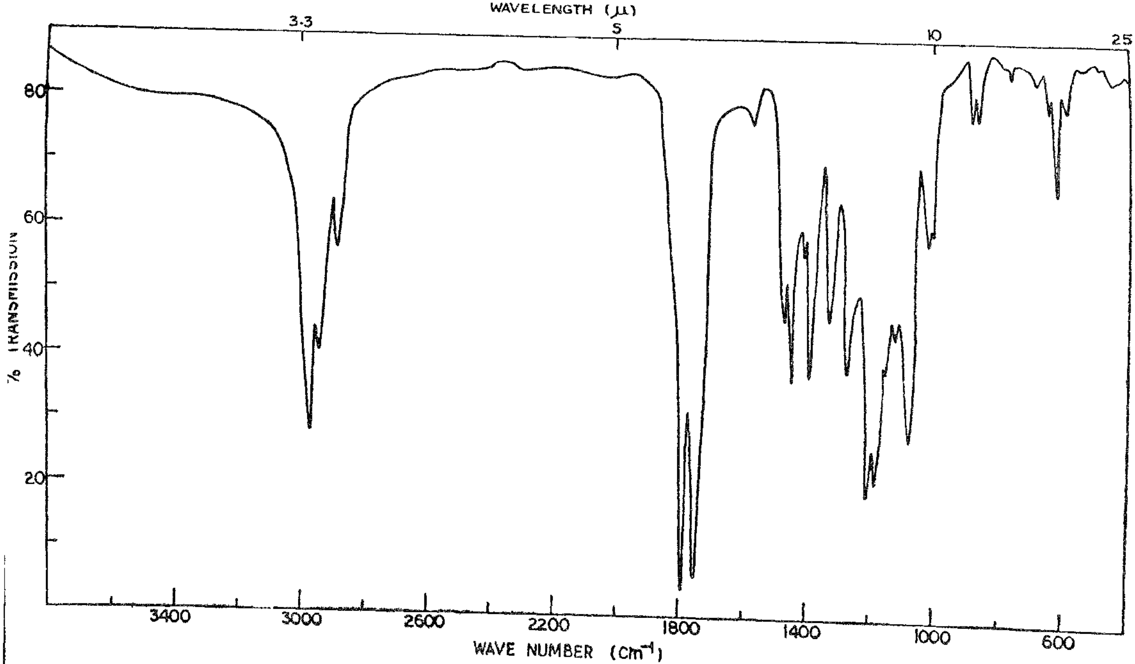


FIG. 1

The IR Absorption Spectrum of the keto-ester (I)

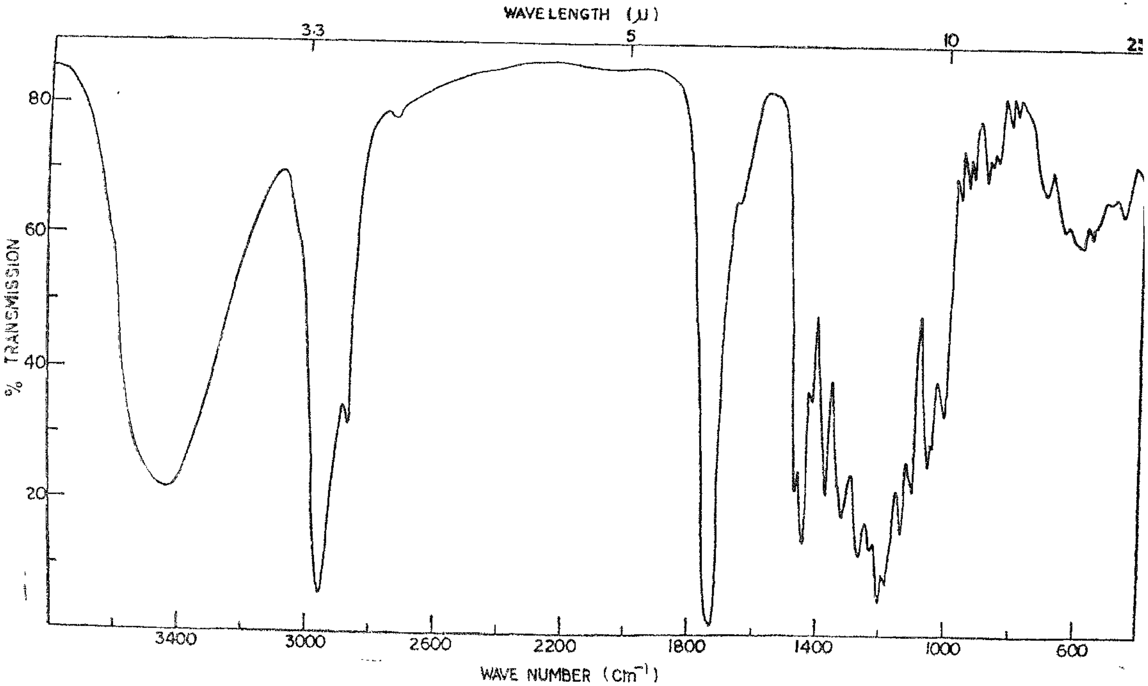


FIG. 2

The IR Absorption Spectrum of hydroxy-ester (II)

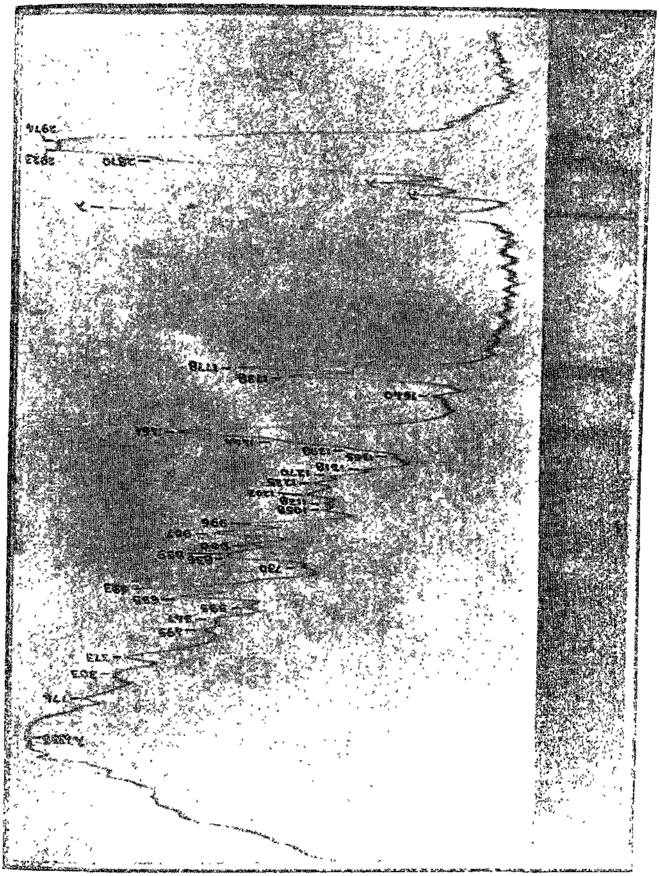


PLATE I

Raman Spectrum of Keto-Ester (I) and its Microphotometer Record

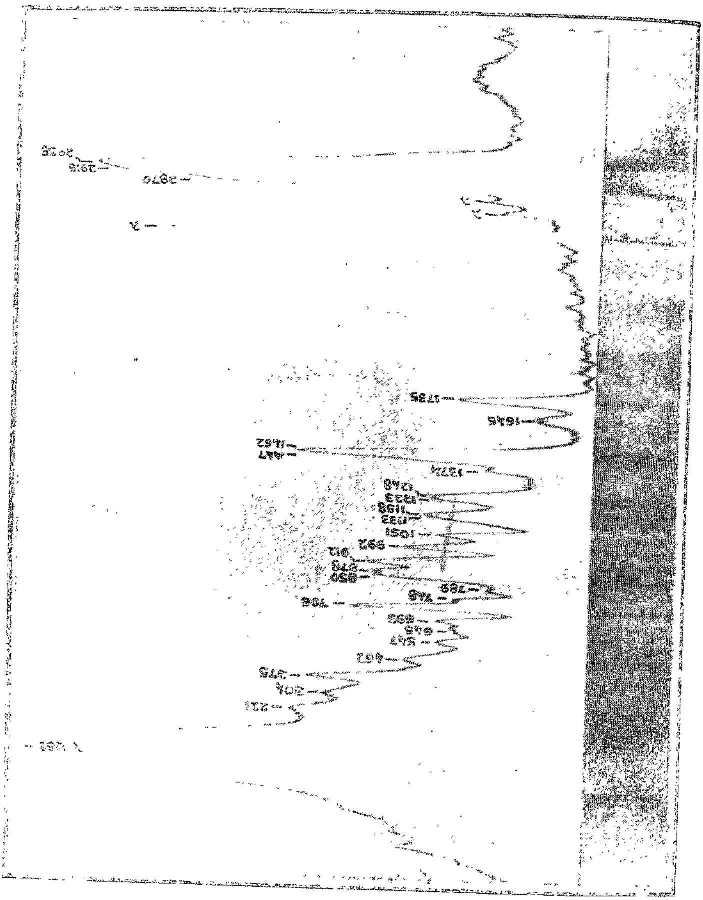
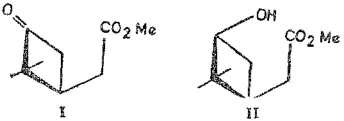


PLATE II

Raman Spectrum of Hydroxy-Ester II and its Microphotometer Record



I II

FIG. 3

The structure of methyl 2, 2—dimethyl-3 ketocyclobutyl acetate (I) and methyl 2, 2—dimethyl-3—hydroxycyclobutyl acetate (II)

3.3. CH_3, CH_2 *deformation frequencies* : The bending frequencies for these groups normally occur in the range 1440-1480 cm^{-1}. In this range there are two strong bands both in the infrared and the Raman *viz.*, at 1445 cm^{-1} and 1465 cm^{-1}. The former is likely to be due to the CH_2 bending and the latter due to the CH_3 bending[8]. In addition, there occurs at ~1390 cm^{-1} a strong band in the infrared only which is likely to be due to *gem.* dimethyl group[8]. The rocking, twisting and wagging modes of the CH_2 and CH_3 groups are very sensitive to the nature and the types of the neighbouring bonds. Hence it is difficult to say exactly where these frequencies occur. Ulery and McClennon[6] suggest that the frequency at 1235 cm^{-1} may be characteristic of the CH_2 twist in the ring. Since in the present case the molecules contain a large number of CH_2 and CH_3 groups, it is possible that there is considerable interaction between the various groups leading to a splitting and/or a change in the frequency values.

3.4. *Ring vibrations* : In the cyclobutane molecule, Lord and Nakagawa[2] assign the frequencies at 898, 926 and 1001 cm^{-1} to the ring vibrations. In cyclobutanone[4] the frequencies at 675, 850, 958 and 1124 cm^{-1} are assigned to the ring vibrations, while in bromocyclobutanone Durig *et al*[5] identify these as occurring at 686, 892, 892, 964, 1029 and 1063 cm^{-1}. Ulery and McClenon[6] suggest the frequency at 750 cm^{-1} to be characteristic of the inplane bending of the cyclobutane ring. All these authors agree that the ring breathing vibration occurring at ~940–980 cm^{-1} is strongly Raman active and is characteristic of the cyclobutane ring. However, in heavily substituted molecules it is very difficult to identify and distinguish the ring vibrations from those of the twisting, rocking and wagging modes of the CH_2 groups.

3.5. *Other low frequency vibrations* : In the Raman spectra of the keto and the hydroxy esters, in the present case, there occur two strong vibrations at 303 and 373 cm^{-1}. The keto $C=O$ bending frequency in cyclobutanone and bromocyclobutanone occurs at 403 cm^{-1} and 379 cm^{-1} respectively and is strong. Hence in the present case the frequency occurring at 373 cm^{-1} is to be identified with the keto $C=O$ bending and the one that occurs at 303 cm^{-1} is probably a C-C-C deformation frequency.

4. CONCLUSION

The Raman and the infrared spectra of methyl 2, 2-dimethyl-3-ketocyclobutyl acetate and methyl 2, 2-dimethyl-3-hydroxycyclobutyl acetate were recorded and the observed frequencies were interpreted. A comparison with the available data for the cyclobutane compounds has been made and the possible characteristic frequencies for these compounds were discussed.

5. ACKNOWLEDGEMENT

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