

## SHORT COMMUNICATIONS

## INFRARED AND ELECTRONIC ABSORPTION SPECTRA OF SOME SUBSTITUTED BENZONITRILES

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THE infrared and Raman spectra of benzonitrile, its mono- and disubstituted derivatives have been studied earlier<sup>1-7</sup>. Ultraviolet absorption spectra of benzonitrile and substituted benzonitriles have also been reported<sup>6-8</sup>. The present communication reports the vibrational analysis of the infrared and electronic absorption spectra of 2,6-, 3,5- dichlorobenzonitriles and 3-chloro-4-methylbenzonitrile (hereafter referred to as compounds I, II and III respectively).

Compounds I, II and III (pure) were obtained from Aldrich Chemical Co., USA. The electronic absorption spectra of the molecules studied were photographed on a Littrow spectrograph using absorption tubes of lengths varying from 40 to 200 cm and the temperature of the vapour varying from  $-10^{\circ}\text{C}$  to  $150^{\circ}\text{C}$ .

The electronic absorption spectra of the molecules studied lie approximately in the region  $\lambda$  3200 Å– $\lambda$  2640 Å and the bands observed are rather sharp and degraded to the red. As the infrared data for the compounds studied are not available, the infrared spectra were recorded on a spectrophotometer (Perkin-Elmer) and calibrated using an error graph.

The infrared and ultraviolet absorption spectra of these compounds were measured and analysed on the basis of  $C_{2v}$  symmetry for compounds I and II and  $C_s$  symmetry for compound III.

The bands of compounds I, II and III correspond to the forbidden electronic transition  ${}^1B_{2u} \leftarrow {}^1A_{1g}$  of benzene and under the reduced symmetry of  $C_{2v}$  of compounds I, II and  $C_s$  of compound III, the transition becomes respectively  ${}^1B_2 \leftarrow {}^1A_1$  and  ${}^1A' \leftarrow {}^1A'$ , which are allowed ones with the transition moment lying in the molecular plane. The fundamental frequencies in the ground and excited states obtained from the analyses are reported in table 1 together with their infrared data and their assignments and also the positions of the O, O bands. The details are being reported separately.

**Table 1** Correlation of the fundamental vibrational frequencies ( $\text{cm}^{-1}$ ) of 2,6-, 3,5- dichlorobenzonitriles and 3-chloro-4-methylbenzonitrile

Compound I			Compound II			Compound III			Wilson number (8)	Assignment
IR	Electronic		IR	Electronic		IR	Electronic			
	GS	ES		GS	ES		GS	ES		
280	284	228	280	276	243	280	282	223	15	$\beta_{\text{C-CN}}$
360	358	284	400	403	346	425	425	301	9a	$\beta_{\text{C-Cl}}$
415	410	365	450	451	421	460	467	421	6a	$\beta_{\text{C-C}}$
640	640	531	665	660	534	1210	—	1125	7b	$\nu_{\text{C-X}}$
720	728	620	720	718	655	700	—	651	7a	$\nu_{\text{C-Cl}}$
790	795	703	810	—	773	820	—	701	1	$\nu_{\text{C-C}}$
1010	—	916	1000	—	935	1000	—	943	12	$\beta_{\text{C-C}}$
1060	—	1013	1100	—	969	1040	—	1023	18a	$\beta_{\text{C-H}}$
1155	—	1141	1120	—	1138	1150	—	1078	18b	$\beta_{\text{C-H}}$
1270	—	1201	1315	—	1226	1305	—	1191	3	$\beta_{\text{C-H}}$
Position of O, O band ( $\text{cm}^{-1}$ )	34021		34265			35334				

IR = infrared; GS = ground state; ES = excited state;  $\beta$  = in-plane bend;  $\nu$  = stretch; X = Cl in compounds I & II and  $\text{CH}_3$  in compound III.

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## OXIDATION STUDIES USING PYRIDINIUM CHLOROCHROMATE ON (+)-3-CARENE DERIVATIVES

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MATSUI *et al*<sup>1</sup> reported that rethronyl esters of ( $\pm$ ) *cis*- and ( $\pm$ ) *trans*-2,2,3-trimethylcyclopropanecarboxylic acids exhibit high insecticidal activity. Therefore, it was expected that the pure optically active isomers of 2,2,3-trimethylcyclopropanecarboxylates, with the 1*R*-*cis* configuration should show enhanced insecticidal activity. For obtaining such esters, the hydroxyaldehyde viz. 2,2-dimethyl-1-(2-methyl-2-hydroxypropyl)-*cis*-1-formylcyclopropane (II) was considered as the suitable starting material.

Pyridinium chlorochromate<sup>2</sup> (PCC) is considered as one of the best mild oxidizing agents for selective oxidation of primary alcohols to aldehydes in high yields. The diol (III), obtainable from (+)-3-carene (I) was subjected to PCC oxidation in the hope of getting the desired hydroxyaldehyde (II). Contrary to our expectation a mixture of two lactones was obtained as the major product of the reaction.

These have been separated by column chromatography over silicic acid. Fractions eluted with

petroleum ether containing 65% chloroform gave a solid, purified by crystallization from petroleum ether (36%), m.p. 82–83° [ $\alpha$ ]<sub>D</sub><sup>25</sup> – 78° (C, 2.0, CHCl<sub>3</sub>) identified as (–) *cis*-dihydrochrysanthemolactone (V) by comparison of spectral properties with those reported in the literature<sup>3</sup>.

Elution of column with chloroform containing 20% ethyl acetate furnished a TLC pure liquid (18%) identified as the hydroxylactone (VII), \*C<sub>10</sub>H<sub>18</sub>O<sub>3</sub>, M<sup>+</sup> 186, [ $\alpha$ ]<sub>D</sub><sup>25</sup> – 48° (C, 1.7, CHCl<sub>3</sub>) by spectral properties described below: \*\*IR: 3521 (OH), 1752 ( $\gamma$ -lactone); PMR: 1.26 (9H, *s*, methyls of hydroxyisopropyl and one of the methyls at C<sub>4</sub>), 1.4 (5H, *s*, overlapping a multiplet, another methyl at C<sub>4</sub> and CH<sub>2</sub> at C<sub>5</sub>), 2.2–2.5 (3H, *m*, CH<sub>2</sub> at C<sub>2</sub> and methine proton at C<sub>3</sub>), 3.06 (1H, *brs*, exchangeable with D<sub>2</sub>O, OH proton).

The assignment of structure to hydroxylactone (VII) was further confirmed by its conversion to the known (–) pyrocine<sup>4</sup>. Thus, dehydration of hydroxylactone (VII) by PTS in refluxing benzene afforded a crystalline solid (85%), C<sub>10</sub>H<sub>16</sub>O<sub>2</sub>, M<sup>+</sup> 168, m.p. 84–85°; [ $\alpha$ ]<sub>D</sub><sup>26</sup> – 66° (C, 1.8, CHCl<sub>3</sub>) identified as (–) pyrocine (VIII) on the basis of following spectral data; IR: 1770 ( $\gamma$ -lactone), 840 (CH=C<); PMR: 1.21, 1.36 (3H each, *s* each, methyls at C<sub>4</sub>), 1.7, 1.76 (3H each, *s* each, vinyl methyls), 2.26, 2.43 (1H each, *d* each, J = 5 Hz each, methylene protons at C<sub>2</sub>), 2.96 (1H, *m*, methine proton at C<sub>3</sub>) and 5.0 (1H, *d*, J = 9 Hz, olefinic proton).

However, PCC oxidation of diol (III) under buffer conditions (2 equivalents of sodium acetate) afforded in addition to the above two lactones (V and VII) the expected hydroxyaldehyde (II) but in low yield (13%) as a thick liquid, C<sub>10</sub>H<sub>18</sub>O<sub>2</sub>, M<sup>+</sup> 170, identified by spectral data; IR: 3509 (OH), 2740, 1695 (CHO); PMR: 0.75 (1H, *m*, C<sub>3</sub> cyclopropane proton), 1.0, 1.1 (3H each, *s* each, *gem*-dimethyl), 1.2 (8H, *brs*, methyls of hydroxy isopropyl and CH<sub>2</sub> at C<sub>3</sub>), 1.6 (1H, *m*, C<sub>1</sub> cyclopropane proton), 2.96 (1H, *brs*, exchangeable with D<sub>2</sub>O, OH proton) and 9.3 (1H, *d*, J = 6 Hz, aldehyde proton).

The tertiary alcohol (XIV) was considered as a suitable intermediate, since it was expected to give, on dehydration followed by oxidation of the resulting olefin, the required 2,2,3-trimethylcyclopropanecarboxylic acid. However, the Huang-Minlon reduction of (II) to (XIV) did not proceed satisfactorily.

\* Satisfactory elemental analysis have been obtained for all the compounds reported.

\*\* IR bands expressed in  $\nu$  (cm<sup>-1</sup>) and PMR chemical shifts in  $\delta$  (ppm) scale with TMS as internal standard.