

4-Phenyl-5-carboethoxy-6-methyl-3,4-dihydro-2-pyrone. A trace of anhydrous sodium acetate, 6.0 ml. of acetic anhydride, and 0.057 g. (0.205 millimole) 3-phenyl-4-carboethoxy-5-ketocaproic acid were refluxed for 4 hr. under an atmosphere of dry nitrogen. After removal of the acetic anhydride the residue was dissolved in 25 ml. of ether and washed with 2-10 portions of water. The dried ether solution on evaporation yielded 0.051 g. (95.6%) of crystalline 4-phenyl-5-carboethoxy-6-methyl-3,4-dihydro-2-pyrone, m.p. 81.0-81.3 from high boiling petroleum ether.

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Infrared Spectra of Some Cyclic Anhydrides

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The infrared spectrum of an acid anhydride is characterized by a doublet in the 1750-1850 cm^{-1} region² and this doublet most likely arises from their coupling between the carbonyl vibrations in inphase and out of phase modes.³ In general, the 2 bands fall into characteristic regions: The open chain or relatively unstrained cyclic glutaric anhydrides possess the doublet in the 1740-1760 cm^{-1} and 1800-1825 cm^{-1} regions, and the more strained cyclic succinic anhydrides possess the doublet in the 1770-1790 cm^{-1} and 1850-1870 cm^{-1} regions. Furthermore, when this latter series of compounds possesses a conjugated olefinic linkage, the bands shift 20-40 cm^{-1} towards lower frequency. As has been pointed out by Bellamy,² this latter shift places conjugated strained anhydrides in the same region of absorption as unstrained saturated anhydrides and makes structural diagnosis on the basis of infrared absorptions somewhat indefinite.

Jones³ has called attention to the fact that the two bands need not be of equal intensity, but little attention has been paid to the intensity relationship of the two bands in anhydride absorption. Listed in Table I are the results of a limited study of this feature of the spectrum. It is apparent that the intensity features of the bands are of useful diagnostic value. The ratio of the intensities is expressed in terms of optical density ($R = D$ low frequency band/ D high frequency band) and, except for the acyclic materials, this rough measure of intensity is a fair approximation of the more exact integrated intensity values.

As seen from the data in Table I, the intensities

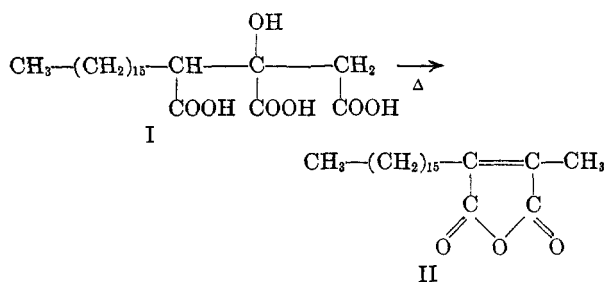
(1) United States Rubber Company Fellow in Chemistry, 1957-1958.

(2) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, J. Wiley and Sons, Inc., New York, 1956, p. 110.

(3) R. N. Jones and C. Sandor, *Techniques of Organic Chemistry*, A. Weissberger, Editor, Interscience Publishing Co., Inc., New York, 1956, Vol. IX, p. 495.

of the two bands do not differ greatly in the acyclic anhydrides. In the unstrained glutaric anhydride, the intensity of the lower frequency band remains about the same, but the intensity of the higher band is greatly diminished and the ratio of intensities increases. In all of the succinic anhydrides, the intensity of the lower frequency band is greater and the intensity of the other band remains about the same order of magnitude as in glutaric anhydride. The ratio of intensities in the succinic series of all of the materials is about the same. For the maleic anhydrides, smaller changes in both bands are found, but the ratio of the intensities increases.

The most striking case is that of methyl hexadecylmaleic anhydride (II), the last entry in the table. This material is a degradation product of the fungal metabolite *agaric acid*, 2-hexadecylcitric acid (I).⁴



The high value of 11.1 for relative band intensities makes it imperative to utilize a very concentrated solution for, otherwise, only the 1757 cm^{-1} band is seen and the presence of a lactone grouping might be indicated. In the case of the two disubstituted maleic anhydrides, a third band of very low intensity lies about 30 cm^{-1} higher than the 1808-1812 cm^{-1} band; perhaps this band is concerned with the anhydride absorption and accounts for the low intensity of the higher frequency band. However, on the basis of the intensity ratio of the maleic anhydrides, a clear differentiation can be made between them and the unstrained cyclic anhydrides absorbing in the same region.

In the succinic and maleic anhydride series, the different effect of substitution is of interest. The band positions in the succinic anhydride series are practically independent of substitution, even though the anhydride is part of a highly strained ring system such as cyclopropane and cyclobutane. Such is not the case in the maleic anhydride series, for the less intense bands shift about 30 cm^{-1} to lower frequency.

As mentioned above, the doublet in the anhydride absorption most likely arises from coupling between carbonyl vibrations. In cyclic anhydrides, the constraint produced by ring closure should increase the angle between the two carbonyl groups, approaching as a limit a colinear arrangement. As this limit is approached, there would be a progressive decrease in intensity of the phase motion because of

(4) H. Thoms and F. Vogelsang, *Ann.*, **357**, 145 (1907).

TABLE I
 INFRARED SPECTRAL DATA FOR ACID ANHYDRIDE

Compound	Band Positions in cm.^{-1}		D_H^a	D_L^a	D_L/D_H
Acetic anhydride	1825	1754	0.150	0.140	0.93
Propionic anhydride	1818	1745	0.190	0.154	0.81
Glutaric anhydride	1812	1764	0.065	0.174	2.7
Succinic anhydride	1866	1792	0.054	0.367	6.8
Cyclobutane-1,2-dicarboxylic acid anhydride	1859	1786	0.042	0.264	6.3
<i>cis</i> -Endomethylenetetrahydrophthalic anhydride	1855	1783	0.048	0.362	7.6
Cyclopropane-1,2-dicarboxylic acid anhydride	1862	1799	0.048	0.402	8.4
Maleic anhydride	1835	1770	0.030	0.268	9.0
2-Methylmaleic anhydride	1832	1764	0.043	0.342	8.0
2,3-Dimethylmaleic anhydride	1812	1757	0.050	0.460	9.2
	(1845)				
2-Methyl-3-hexadecylmaleic Anhydride	1808	1757	0.034	0.378	11.1
	(1835)				

^a D_L is optical density of lower frequency band and D_H is optical density of higher frequency band.

the cancellation of dipole charges. This decrease should be accompanied by an increase in intensity of the out-of-phase motion. Because such a relationship in intensities is found, the higher frequency band of the doublet can be assigned to inphase vibrations.

The spectra were obtained employing a Baird Associates Double Beam Infrared Spectrophotometer using 1.0 mm. sodium chloride cells. All spectra were obtained with $3.0 \times 10^{-3} M$ solutions in carbon tetrachloride.

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Lithium Aluminum Hydride Reduction of Methylcyclohexanones

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In an earlier study,² the composition of the products obtained by lithium aluminum hydride reduction of the isomeric cyclohexanols and of the equilibrium mixture was reported. In this work the ratio of isomers was determined by the density method. Subsequently, Wicker³ and Hüchel⁴ have reinvestigated this same problem and have found results which differ from those first reported. This problem has now been restudied utilizing Vapor Phase Chromatography as the method for analysis and the results obtained together with those re-

ported previously by other workers are given in Table I.

 TABLE I
 ISOMER COMPOSITION OF METHYLCYCLOHEXANOLS

Compound	% <i>trans</i> from LiAlH_4	% <i>trans</i> at Equilibrium
2-Methylcyclohexanol	70 ^a (64, ^b 82 ^c 60, ^d 59 ^e)	85 ^a (95, ^f 99 ^c 83, ^e ~94 ^g)
3-Methylcyclohexanol	13 ^a (18, ^b 7, ^e <15 ^g)	— (22 ^g)
4-Methylcyclohexanol	84 ^a (81, ^b 82 ^c 75, ^d 80 ^g)	71 ^a (88, ^c 70 ^g)

^a Present work. ^bD. S. Noyce and D. B. Denney, *J. Am. Chem. Soc.*, **72**, 5743 (1950). ^c See Reference (2). ^d See Reference (3). ^e See Reference (4). ^f R. Cornubert, M. Lafont-Lemoine, and N. Nadjme-Abadi, *Compt. rend.*, **237**, 469 (1953). ^g E. E. Eliel and R. S. Ro, *J. Am. Chem. Soc.*, **79**, 5992 (1957).

First with regard to the product obtained in the lithium aluminum hydride reduction, the composition of the 4-methylcyclohexanols and the 3-methylcyclohexanols agrees well with that found in all studies. With the 2-methylcyclohexanols where the largest discrepancy existed, the present result is just between the two extremes. In all the results obtained by VPC, two peaks, cleanly separated, were obtained and there was no indication of any other components. Re-examination of some of the samples obtained in our earlier study showed the presence of a third component but it could not be ascertained whether this impurity was actually present in the original mixture or was formed on storage. If, indeed, the former was the case, analysis by density measurement could have readily been affected and yet not detected.

The equilibrium mixtures of the 4-methyl and the 2-methyl-cyclohexanols also were examined with VPC and here again quite different results

- (1) Procter & Gamble Fellow, 1958-1959.
- (2) W. G. Dauben, G. J. Fonken, and D. S. Noyce, *J. Am. Chem. Soc.*, **78**, 2579 (1956).
- (3) K. D. Hardy and R. J. Wicker, *J. Am. Chem. Soc.*, **80**, 640 (1958).
- (4) W. Hüchel and A. Hubele, *Ann.*, **613**, 27 (1958).