

TABLE I  
INFRARED SPECTRAL DATA FOR ACID ANHYDRIDE

Compound	Band Positions in $\text{cm.}^{-1}$		$D_H^a$	$D_L^a$	$D_L/D_H$
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)				

<sup>a</sup>  $D_L$  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.

DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF CALIFORNIA  
BERKELEY 4, CALIF.

### Lithium Aluminum Hydride Reduction of Methylcyclohexanones

WILLIAM G. DAUBEN AND RICHARD E. BOZAK<sup>1</sup>

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In an earlier study,<sup>2</sup> 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, Wicker<sup>3</sup> and Hüchel<sup>4</sup> 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 $\text{LiAlH}_4$	% <i>trans</i> at Equilibrium
2-Methylcyclohexanol	70 <sup>a</sup> (64, <sup>b</sup> 82 <sup>c</sup> 60, <sup>d</sup> 59 <sup>e</sup> )	85 <sup>a</sup> (95, <sup>f</sup> 99 <sup>c</sup> 83, <sup>e</sup> ~94 <sup>g</sup> )
3-Methylcyclohexanol	13 <sup>a</sup> (18, <sup>b</sup> 7, <sup>e</sup> <15 <sup>g</sup> )	— (22 <sup>g</sup> )
4-Methylcyclohexanol	84 <sup>a</sup> (81, <sup>b</sup> 82 <sup>c</sup> 75, <sup>d</sup> 80 <sup>g</sup> )	71 <sup>a</sup> (88, <sup>c</sup> 70 <sup>g</sup> )

<sup>a</sup> Present work. <sup>b</sup>D. S. Noyce and D. B. Denney, *J. Am. Chem. Soc.*, **72**, 5743 (1950). <sup>c</sup> See Reference (2). <sup>d</sup> See Reference (3). <sup>e</sup> See Reference (4). <sup>f</sup> R. Cornubert, M. Lafont-Lemoine, and N. Nadjme-Abadi, *Compt. rend.*, **237**, 469 (1953). <sup>g</sup> 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).

from those originally found by us were obtained. With the 4-methyl material, excellent agreement with the recently reported result of Eliel and Ro<sup>5</sup> was obtained. With the 2-methyl material, agreement with the value reported by Hückel<sup>4</sup> last year was obtained and these two values were lower in *trans* content than other reports. Thus, these results with VPC clearly demonstrate that high values of the percentage of the isomer with the lower density were obtained in our earlier work.

It is of interest to look at the present results in terms of the concepts of "product development control" and "steric approach control" in the lithium aluminum hydride reduction.<sup>2</sup> In the case of the 3- and 4-methylcyclohexanols, the amount of stable isomer formed in the reduction is in excess of that found in the equilibrium mixture. As has been pointed out,<sup>2</sup> the relative contributions of the axial and the equatorial approaches in the case of the unhindered ketone (product development control) will depend upon the different energies of the two transition states involved. Since the relative energetics of the two aluminum coordinated species are not known, the equilibrium composition of the alcohols, themselves, serves as a first approximation of the energy difference. However, as already pointed out by Eliel and Ro,<sup>5</sup> in these two cases, this approximation must be on the low side as far as the stable isomer is concerned since any increase in bulk of the oxygen function will serve to increase the amount of the more stable isomer. Thus, the results obtained are in line with expectations derivable from this simplified concept. With regard to the composition of the 2-methylcyclohexanols obtained upon reduction, the presence of more of the less stable isomer than is found in the equilibrium mixture is to be expected on the basis of concurrent functioning of both steric approach control and product development control.

#### EXPERIMENTAL

The reductions were performed as described earlier.<sup>2</sup> The equilibrations also were conducted as previously<sup>2</sup> and approached from each side of the equilibrium mixture. The analyses were performed using an Aerograph Master A-100 Apparatus (Wilkens Instrument and Research, Inc., Walnut Creek, Calif.), equipped with a 10-inch column of 30% glycerol on Chromosorb.<sup>6</sup> The separations were performed at a temperature of  $80 \pm 5^\circ$  with a helium flow rate of  $90 \pm 10$  ml./min. Percentage compositions were obtained from planimeter-determined areas under the separate peaks and the values were reproducible to 1%. Retention times quoted below are taken from the time of injection of sample.

*2-Methylcyclohexanols.* At  $88^\circ$  and 90 ml./min. flow rate, the retention time for the *cis* isomer was 8.0 min. and for the *trans*-isomer was 15.4 min. The retention time for starting ketone at  $80^\circ$  and 100 ml./min. flow rate was 4.5 min.

(5) E. E. Eliel and R. S. Ro, *J. Am. Chem. Soc.*, **79**, 5992 (1957).

(6) The use of glycerol columns for separation of isomeric cyclohexanols was reported by R. Komers, K. Kochloeff, and V. Bazant, *Chem. & Ind. (London)*, 1405 (1958).

*3-Methylcyclohexanols.* At  $81^\circ$  and 92 ml./min. flow rate, the retention times were 14.0 min. for the *trans* and 20.2 min. for the *cis*. Under ketone conditions, the starting material had an 8 min. retention time.

*4-Methylcyclohexanols.* Under the conditions used for the 3-methyl isomer, the retention time for the *cis* isomer was 14.6 min. and for the *trans* isomer was 21.3 min.

DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF CALIFORNIA  
BERKELEY 4, CALIF.

### 5-Amino-3-chloropyridazine<sup>1</sup>

EDGAR A. STECK<sup>2</sup>

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3,6-Dichloropyridazine undergoes reaction with ammonia to produce I, 6-amino-3-chloropyridazine (m.p.  $213\text{--}214^\circ$  dec.), as is well known.<sup>3,4</sup> It was of interest to determine whether the same compound resulted when sodium amide was caused to act on the dichloro compound. Rearrangements have frequently occurred when sodium amide has been used (*cf.*, *inter alia*, refs. 5,6). The aminochloro compound which was obtained in 64% yield melted at  $141.5\text{--}142^\circ$ , and was clearly not I. This has been assigned the structure of the rearrangement product, II, *viz.*, 5-amino-3-chloropyridazine. Present circumstances have precluded dehalogenation of II to 4-aminopyridazine, which was prepared by Kuraishi<sup>7</sup> subsequent to the completion of this work.



#### EXPERIMENTAL

A vigorously stirred solution of 14.9 g. (0.1 mole) of 3,6-dichloropyridazine in 150 ml. of xylene was treated with 12.0 g. (0.3 mole) of sodium amide and refluxed for 10 hr. To the brown mixture there was added an excess of aqueous hydrochloric acid. The layers were filtered and separated. The organic layer was extracted further with 6*N* hydrochloric acid, and the acidic extracts were concentrated prior to basification. A light tan solid (9.5 g., m.p.  $135\text{--}138^\circ$ ) was obtained; four crystallizations from benzene-hexane mixture

(1) Pyridazines IV. Previous contribution: E. A. Steck, R. P. Brundage, and L. T. Fletcher, *J. Am. Chem. Soc.*, **76**, 4454 (1954).

(2) Present address: McNeil Laboratories, Philadelphia, Pa.

(3) E. A. Steck, R. P. Brundage, and L. T. Fletcher, *J. Am. Chem. Soc.*, **76**, 3225 (1954).

(4) J. Druey, Kd. Meier, and K. Eichenberger, *Helv. Chim. Acta*, **37**, 121 (1954).

(5) R. Levine and W. C. Fernelius, *Chem. Revs.*, **54**, 483 (1954).

(6) J. D. Roberts, H. E. Simmons, Jr., L. A. Carlsmith, and C. W. Vaughan, *J. Am. Chem. Soc.*, **75**, 3290 (1953).

(7) T. Kuraishi, *Pharmaceutical Bulletin (Japan)*, **4**, 137 (1956).