

CONSTANTS OF SALTS AND ACIDS (Concluded)

Formula	Carbon		Hydrogen		Nitrogen	
	Calcd.	Found	Calcd.	Found	Calcd.	Found
1 C ₁₄ H ₁₀ FNO ₅ ·C ₂₃ H ₂₆ N ₂ O ₄	64.8	65.3	5.2	5.5	6.13	6.06
2 C ₁₄ H ₁₀ FNO ₅ ·C ₂₃ H ₂₆ N ₂ O ₄	6.13	6.60
3 C ₁₄ H ₁₀ FNO ₅	4.81	5.16
4 C ₁₄ H ₁₀ FNO ₅

Racemization of *l*-acid. Initial $\alpha_D -0.36$ in C₂H₅OH—Boiling gave the following α_D readings: fifteen minutes, 0.335; forty-five minutes, 0.25; seventy-five minutes, 0.20; one hundred and thirty-five minutes, 0.17. Calcd. half life period, eighty-six minutes. In boiling glacial acetic acid, rotation was zero in less than twenty minutes. In boiling chloroform, half life period was seventy-two minutes. The acids racemized very slowly in aqueous sodium hydroxide or alcoholic sodium ethylate at room temperature.

Summary

2,3'-Dinitro-6-carboxy-2',6'-dimethoxydiphenyl and 2-nitro-6-carboxy-2'-fluoro-6'-methoxydiphenyl were prepared and resolved. The active forms of the former racemized less readily than those of the latter, showing the fluorine to have less effect in restricting rotation than the methoxy.

URBANA, ILLINOIS

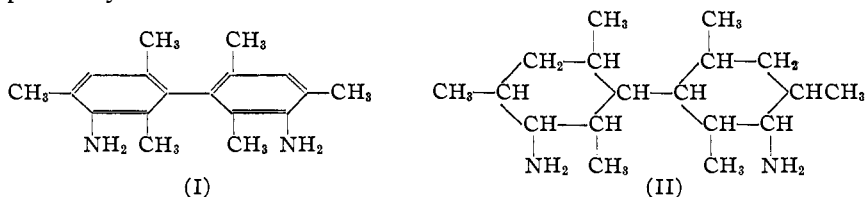
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[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Hydrogenation of Derivatives of Diphenyl

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In connection with the stereochemistry of diphenyl derivatives it would be of interest to ascertain whether or not an optically active dicyclohexyl compound could be obtained by the hydrogenation of an optically active diphenyl compound. For example, if optically active 3,3'-diamino-2,2',-4,4',6,6'-hexamethyldicyclohexyl (II) resulted from the hydrogenation of the corresponding *d*- or *l*-diaminodimesityl (I), then the basis for the optical isomerism of compounds of type I is not some "inherent property" of the parent hydrocarbon.¹



It appears that the most feasible way to discover whether derivatives of dicyclohexyl show optical isomerism based upon molecular asymmetry as

(1) Turner and LeFèvre, *J. Soc. Chem. Ind.*, **45**, 831, 883 (1926); Turner, *Rec. trav. chim.*, **48**, 824 (1929); cf. Richter, *Chem. Rev.*, **10**, 368 (1932).

distinguished from atomic asymmetry, is by such a conversion of optically active diphenyls into dicyclohexyls. This is true because a compound such as II, for example, contains ten asymmetric atoms and the number of isomers is thus too great to make it possible to distinguish readily between those dependent upon molecular and atomic asymmetry.

For the above reasons diaminodimesityl (I) was prepared and resolved.² It was then submitted to the conditions which ordinarily bring about a rapid hydrogenation of a benzenoid ring. When these conditions were found to produce no hydrogenation, the compound was then subjected to such drastic conditions as 350 atmospheres pressure of hydrogen at 225° for many hours in the presence of an equal weight of a very active nickel catalyst. The compound absorbed no hydrogen and was recovered practically unchanged in m.p. (201–202.5°) and molecular rotation after being repeatedly subjected to the drastic conditions described above.

The diethyl and dimethyl esters of 6,6'-dimethoxydiphenic acid were then prepared. The acid corresponding to the esters is readily resolvable but this operation was not carried out since it appeared unnecessary to do so until it had been ascertained whether the *dl* mixture would undergo hydrogenation. The *dl* mixture did not undergo hydrogenation to dicyclohexyl derivatives although repeated treatments with active nickel and hydrogen at 250° and 350 atmospheres in methylcyclohexane as a solvent resulted in the formation of small amounts of liquid products.

All of the resources of this Laboratory with respect to technique and equipment and all the experience in the use of nickel as a catalyst for hydrogenation have been of no avail for the hydrogenation of these two derivatives of diphenyl. Various types and preparations of nickel catalyst of known activity, various temperatures, pressures, solvents, time and ratios of catalyst to organic compound, etc., have alike yielded negative results.

In contrast with these *d* and *dl* compounds, 3,3'-dimethyl- and 4,4'-dimethyldiphenyl were readily hydrogenated to the corresponding dicyclohexyls. Diethyl diphenate was successfully hydrogenated to a mixture of isomeric 2,2'-dicarbethoxydicyclohexyls. 4,4'-Dihydroxydiphenyl was converted in a fair yield to the corresponding dicyclohexyl. Fluorenone which may also be regarded as a substituted diphenyl was also readily hydrogenated to dodecahydrofluorene. Dimesityl (a hexamethyldiphenyl) was previously hydrogenated to the corresponding hexamethyldicyclohexyl.³ Among the many compounds which have been subjected to the conditions for catalytic hydrogenation in this Laboratory a few such as benzidene and 3,3'-diaminodiphenyl have not been successfully hydrogenated because of condensation or decomposition, but only the *d*- and *dl*-diphenyl derivatives referred to above have failed to react.

(2) Adams and Moyer, *THIS JOURNAL*, **51**, 630 (1929).

(3) Adkins, Zartman and Cramer, *ibid.*, **53**, 1425 (1931).

It is possible that the same factors which prevent the rotation of the rings with respect to each other in resolvable derivatives of diphenyl, also prevent the reaction (adsorption) of the benzenoid ring by the catalyst, and so inhibit the first step in the catalytic hydrogenation of the former.

Experimental Part

The 3,3'- and 4,4'-dimethyldiphenyl⁴ (18 g.) were quantitatively hydrogenated in five to six hours in methylcyclohexane at 200°, 100 atm., with 4 g. of ammonium carbonate type nickel catalyst to the corresponding 3,3'-dimethyldicyclohexyl, b. p. 254–256° (740 mm.)⁵ and 4,4'-dimethyldicyclohexyl, b. p. 119–121° (10 mm.)⁶. The 4,4'-dihydroxydiphenyl⁷ (19 g.) was hydrogenated in twelve hours in ethanol at 200°, 100 atm., with two applications of catalyst of 5 g. each to 4,4'-dihydroxydicyclohexyl, m. p. 204–207° (78% yield), and 4-hydroxydicyclohexyl, m. p. 94–98° (22% yield). *Anal.* Calcd. for C₁₂H₂₂O₂: C, 72.67; H, 11.19. Found: C, 73.08; H, 11.25. *Anal.* Calcd. for C₁₂H₂₂O: C, 79.04; H, 12.17. Found: C, 78.75; H, 12.16.⁸

The 4,4'-dimethoxydiphenyl⁴ when subjected to hydrogenation as for the dihydroxy compound gave a 50% yield of 4-methoxydicyclohexyl, b. p. 120–121° (7 mm.), d_{25}^{25} 0.9394; n_D^{25} 1.4772, MR'_D, calcd. 58.86; found, 59.03. *Anal.* Calcd. for C₁₃H₂₄O: C, 79.51; H, 12.33. Found: C, 79.34; H, 12.29.

Diethyl diphenate (16 g.) in methylcyclohexane was hydrogenated twice at 200°, 100–165 atmospheres with 5 g. of a nickel catalyst. The product (13 g.) b. p. 167–170° (3 mm.) was a liquid n_D^{25} 1.4769, from which upon standing for twenty-four hours at 15° 3 g. of crystals separated. After recrystallization from ethanol, the solid had a m. p. of 84–85° and was presumably *trans* 2,2'-dicarboethoxydicyclohexyl. *Anal.* Calcd. for C₁₈H₃₀O₄: C, 69.68; H, 9.68. Found: C, 69.44; H, 9.54. The liquid and presumably *cis* isomer was then fractionated and 5.9 g. of a colorless viscous liquid b. p. 155–158° (1–2 mm.) was obtained: d_{24}^{24} 1.0438; n_D^{24} 1.4774; MR'_D calcd. 84.23; found, 83.99. *Anal.* Found: C, 70.05; H, 9.61.

Many attempts have been made to hydrogenate benzidine but none of them have been successful (although considerable quantities of hydrogen were absorbed) because of the liberation of ammonia and the formation of high molecular weight compounds. In ethanol a 26% yield of N-tetraethylbenzidine (m. p. 85°) was obtained⁹ while in methylcyclohexane a small yield of 4-aminodicyclohexyl was isolated.¹⁰ The 3,3'-dinitrodiphenyl (25 g.) in ethanol was hydrogenated in a few minutes at 100 atmospheres, 100°, with 4 g. of nickel catalyst. The corresponding 3,3'-diaminodiphenyl was formed almost quantitatively.¹¹

The 6,6'-dimethoxydiphenic acid was prepared by the same method with two exceptions as that used by Kenner and Turner.¹² The 2-nitro-3-methoxybenzoic acid was reduced with hydrogen and Adams platinum oxide catalyst in acetic acid instead of with ferrous ammonium sulfate, and the yields were thereby almost doubled over those reported by Kenner and Turner. The resulting aminomethoxybenzoic acid was converted to the corresponding diphenic acid, by the method described for the preparation

(4) Gardner and Borgstrom, *THIS JOURNAL*, **51**, 3376 (1929).

(5) Kursanoff, *J. Russ. Phys.-Chem. Soc.*, **34**, 224 (1902); *Chem. Centr.*, 1228 (1902).

(6) Tschitschibabin and Jeigasins, *J. Russ. Phys.-Chem. Soc.*, **46**, 812 (1914); *Chem. Centr.*, 875 (1915).

(7) Hunter and Woollett, *THIS JOURNAL*, **43**, 149 (1921).

(8) Schrauth, *Ber.*, **56**, 1905 (1923), reported m. p. for the *cis* 83°, for the *trans* 105°.

(9) Hoffman, *Ann.*, **115**, 366 (1860).

(10) Kursanoff, *ibid.*, **318**, 324 (1901).

(11) Brunner, *Ber.*, **20**, 1028 (1887).

(12) Kenner and Turner, *J. Chem. Soc.*, 2340 (1928).

of diphenic acid by Huntress.¹³ It is important that the diazotization be carried out at 35–37° and that the coupling reaction take place in the presence of a stirrer so designed that the surface as well as the body of the reaction mixture is thoroughly agitated. The yield of acid from the coupling reaction was 85% and after purification with zinc and acetic acid the m. p. (with decomposition) was 295–298°.

Summary

A number of derivatives of diphenyl have been subjected to the conditions for catalytic hydrogenation to the corresponding dicyclohexyls. Reaction ensued with all the compounds except the two which possessed the structure necessary for molecular asymmetry and they resisted hydrogenation even under very drastic conditions.

(13) Huntress, "Organic Syntheses," John Wiley and Sons, New York, 1927, Vol. VII, p. 30.

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The Influence of Branched Chains on Optical Activity. The Configuration of Methyl-tertiary-butylcarbinol

BY PHILIP G. STEVENS

In a recent paper¹ it was shown that in an homologous series of secondary carbinols, a change of a propyl to an isopropyl group caused a shift of the optical rotation in the opposite direction from that of the propyl carbinol. In the case of methylisopropylcarbinol, the shift was insufficient to change the sign of rotation; but with the other members, ethyl-, propyl- and butylisopropylcarbinols, the shift was accompanied by a reversal of the sign of rotation. It can be seen that if a branched chain (isopropyl group) directly attached to the asymmetric carbon atom causes a shift of the rotation in the opposite direction, a further branching of the chain (tertiary-butyl group) might cause an even greater shift, possibly sufficient to invert the sign of rotation even of the first member of the series.

The correlation of methyl-tertiary-butylcarbinol was therefore undertaken in order to complete the study of the effect of the branched chain on the optical rotation. The only sure method of correlation is by direct chemical means as in the case of methylisopropylcarbinol. The case of methyl-tertiary-butylcarbinol is however a much more difficult one, and up to the present time no direct chemical method has been found.

The only recourse therefore is correlation by means of Freudenberg's Displacement Rule. Freudenberg² has already assigned dextro methyl-tertiary-butylcarbinol as related to the other dextro carbinols. This tentative correlation, however, rests solely upon the rotation of the phthalate,

(1) Stevens, *THIS JOURNAL*, **54**, 3732 (1932).

(2) Freudenberg, "Stereochemie," 1932, p. 696.