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1-PHENYLCYCLOHEXANE-1,2-DIOLS AND THEIR GEOMETRY

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Abstract—*Trans*- and *cis*-1-phenylcyclohexane-1,2-diols, have been prepared and hydrogenated to *trans*- and *cis*-1-cyclohexylcyclohexane-1,2-diols. The infrared absorption spectra leave no doubt as to the geometry of these compounds.

IN a recent publication concerning the preparation of *cis*- and *trans*-1-arylcyclohexane-1,2-diols and their configuration by IR spectroscopy, Davies *et al.* reported[1] that they were unable to obtain such diols with *trans* configuration, notably *trans*-1-phenylcyclohexane-1,2-diol, even though this compound has been described repeatedly in the literature.[2]

The absence of the *trans*-diols from among the compounds examined for intramolecular hydrogen bonding[3] was of distinct disadvantage to drawing the proper structural conclusions and the authors had to make use of a hypothetical spectrum of a *trans*-1-arylcyclohexane-1,2-diol, based on the studies of Schleyer *et al.*[3d] In a prior work of Kleinfelter and Schleyer,[3e] spectral data and interpretation were given regarding the *cis* but again not the *trans* compound.

The present author[4] recently had occasion to prepare *trans*- (and *cis*-) 1-phenylcyclohexane-1,2-diol by following essentially Maan's method[2b] (see Experimental) and to study their high resolution I.R. absorption spectra in the 3 μ region.

The data obtained with these compounds as well as with the 1-cyclohexylcyclohexane-1,2-diols derived from them by hydrogenation leave no doubt as to the geometry of the *trans*-compound, which also follows from the findings (e.g., lack of ketal formation) of the authors cited in Ref 2.

The spectrum of *trans*-1-phenylcyclohexane-1,2-diol (as taken in 0·005 molar carbon tetrachloride solution) shows only one diffuse band in the 3 μ region, with a maximum at 3602 cm^{-1}. Obviously, this band represents the unresolved O—H stretching frequencies of the tertiary and secondary hydroxyl groups, which would be expected to appear in the position characteristic of the "phenyl-bound" hydroxyl groups of the α- and β- phenylethanols (at 3600 and 3610 cm^{-1}, respectively[3c]) or, by closer analogy, of 1-phenylcyclohexanol and *cis*-2-phenylcyclohexanol (at 3604 and 3596 cm^{-1} respectively[4]). Since the spectrum excludes the presence of any

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[1] M. T. Davies, D. F. Dobson, D. F. Hayman, G. B. Jackman, M. G. Lester, V. Petrow, O. Stevenson and A. A. Webb, *Tetrahedron* **18**, 751 (1962).

[2a] J. Böeseken, *Ber. Dtsch. Chem. Ges.* **56**, 2409 (1923), *Rec. Trav. Chim.* **47**, 683 (1928).

[b] C. J. Maan, *Rec. Trav. Chim.* **48**, 332 (1929), *Liebegs Ann*, **467**, 232 (1928).

[c] R. Filler, B. R. Camara and S. M. Naqui, *J. Amer. Chem. Soc.* **81**, 658 (1959).

[3a] L. P. Kuhn, *J. Amer. Chem. Soc.* **74**, 2492 (1952), *Ibid.* **76**, 4323 (1954).

[b] A. R. H. Cole and P. R. Jefferies, *J. Chem. Soc.* 4391 (1956).

[c] A. W. Baker and A. T. Shulgin, *J. Amer. Chem. Soc.* **80**, 5358 (1958).

[d] P. von R. Schleyer, D. S. Trifan and R. Bacskai, *J. Amer. Chem. Soc.* **80**, 6691 (1958).

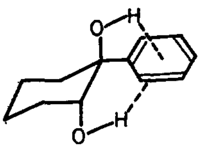
[e] D. C. Kleinfelter and P. von R. Schleyer, *J. Amer. Chem. Soc.* **83**, 2329 (1961).

[4] E. Galántay; Untersuchungen in der Phenylcyclodecan-Reihe (Ph.D. thesis) Prom. Nr. 2966 (1959); Eidgenössische Technische Hochschule, Zürich, Switzerland; copies available on request from above institution.

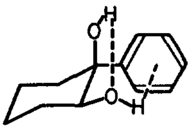
—O—H · · · O— hydrogen bonds or free hydroxyl groups, the compound must exist, predominantly if not exclusively, in the conformation shown in I.

Here we like to draw attention to a simple method, which, in addition to providing conclusive confirmation of the configuration of *trans*-1-phenylcyclohexane-1,2-diol, can be employed whenever it is desirable to eliminate complications due to hydroxyl-to-phenyl or similar hydrogen bonds in the interpretation of absorption spectra in the 3 μ region. It has been found,[4] that the phenyl group in these compounds can be easily hydrogenated to the cyclohexyl group without hydrogenolysis of the tertiary (benzylic) hydroxyl group by using a rhodium-on-alumina catalyst in aqueous suspension, at room temperature and atmospheric pressure.

Thus, *trans*-1-phenylcyclohexane-1,2-diol on hydrogenation gave the known[2a] *trans*-1-cyclohexylcyclohexane-1,2-diol, which, as expected (the bulk of phenyl and cyclohexyl groups and thus their preference for equatorial position on the cyclohexane chair conformation can be regarded as roughly the same) shows only one unresolved band at 3623 cm^{-1} for the two "free" hydroxyl groups, both in axial positions. The situation is entirely analogous to the well studied case of *trans*-1-isopropylcyclohexane-1,2-diol.[3b]



I *trans*-1-phenylcyclohexane-1,2-diol



II *cis*-1-phenylcyclohexane-1,2-diol

Our data regarding *cis*-1-phenylcyclohexane-1,2-diol[4] are in fair agreement with those reported.[1,3e] The spectrum of this compound exhibited two sharp bands at 3549 and 3586 cm^{-1} and only a weak, diffuse band at 3623 cm^{-1}. This finding is best reconciled[3e,4] with II as the predominant conformation. The weak band at 3623 cm^{-1} probably reflects the presence of another conformation with a free secondary hydroxyl group.

Similarly, *cis*-1-phenylcyclohexane-1,2-diol can be quantitatively hydrogenated to the known[2a] *cis*-1-cyclohexylcyclohexane-1,2-diol, which again shows an easily interpretable I.R. absorption spectrum, analogous to that of *cis*-1-isopropylcyclohexane-1,2-diol[3b] (bands at 3577 and 2623 cm^{-1}).

EXPERIMENTAL

The IR absorption spectra were determined on 0·005 molar carbon tetrachloride solutions by means of a Double Pass Monochromator (The Perkin Elmer Corporation) with lithium fluoride prism. M.p. are corrected.

cis- and trans-1-Phenylcyclohexane-1,2-diols: An emulsion of 7·20 g undistilled[2c] 1-phenyl-1,2-epoxydocyclohexane in 72 ml 0·05 N H_2SO_4 was shaken for 4½ hr at room temp, then extracted with chloroform. The washed ($NaHCO_3$) and dried extract gave on evaporation 7·62 g partially crystalline residue, which was taken up in 175 ml anhydrous acetone and after addition of 0·20 g conc H_2SO_4 and 20 g anhydrous sodium sulphate, was allowed to stand at room temp. After 24 hr, 20 g calcium carbonate was added and the mixture stirred for a further 24 hr. Evaporation of the filtered solution gave 9·2 g residue which, after addition of some $NaHCO_3$ solution, was steam distilled.

Ether extraction of the distillate yielded 4·55 g light oil, which was refluxed for 30 min with a mixture of 50 ml ethanol, 25 ml water and 0·35 ml 2 N HCl. Chloroform extraction yielded the crude *cis* diol (3·29 g, m.p. 90–95°), which was purified by 2 recrystallizations from chloroform–hexane and vacuum sublimation; m.p. 94·5–95°, reported[2a] 95°.

The residue of the steam distillation was extracted with chloroform and ether to obtain 1·63 g crystals with m.p. 93–95°. After 3 recrystallizations from chloroform–hexane the pure *trans*-diol melted at 97·7–98·2°, reported[2a] 98·5°. A mixed m.p. of the *cis* and *trans* diols, gave a depression of at least 25°.

cis-*Cyclohexylcyclohexane*-1,2-*diol:* A suspension of 264·1 mg *cis*-1-phenylcyclohexane-1,2-diol and 607·0 mg rhodium-on-alumina catalyst (Baker) in 15 ml water was stirred in a hydrogen atmosphere (19·5°/723 mm). After uptake of 103 ml gas, enough ether was added to dissolve all organic material. Evaporation of the centrifuged clear solution gave 265 mg of the pure diol; m.p. 126–127°, reported[2a] 122–123°. For the spectroscopical work, the diol was sublimed at 115°/0·005 mm.

trans-*Cyclohexylcyclohexane*-1,2-*diol.* A suspension of 202·3 mg *trans*-1-phenylcyclohexane-1,2-diol and 120 mg rhodium-on-alumina catalyst in 15 ml water was hydrogenated as above, the theoretical amount of gas being consumed in 5 hr. The crude product (205·1 mg) m.p. 110–127°, after 2 recrystallizations from chloroform–hexane followed by vacuum sublimation yielded pure *trans*-diol, m.p. 142–143°; reported[2a], 142°.

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