

competitive. *E.g.*, whereas palladium promotes quantitative hydrogenolysis of benzyl β -D-glucopyranoside⁵ into glucose and toluene with 1 mole of hydrogen, platinum black in glacial acetic acid promotes the rapid consumption of 3.5 moles of hydrogen. This was interpreted to mean that half of the glucoside cleaved as above after which the toluene changed rapidly into cyclohexane (total, 4H₂), and that the other half simply underwent hydrogenation to cyclohexyl glucopyranoside (total, 3H₂) which was stable toward hydrogenolysis. The cyclohexyl glucoside was not actually isolated in this experiment.

Experimental Section

1- β -Phenyl-1,5-D-anhydroglucitol Tetraacetate.—This compound, originally named β -D-glucopyranosylbenzene tetraacetate, was made by the method of Hurd and Bonner:⁶ mp 155–156°. Its infrared spectrum showed these absorptions: strong at 5.75, 7.25, 7.95–8.15, 9.52, 9.62; medium at 3.41, 3.50, 8.94, 9.15, 10.84, 12.93, 14.19; weak at 6.49 (sh), 6.53, 6.82, 7.09, 7.60, 8.72, 10.20, 11.05, 11.72, 14.50 μ .

1- β -Cyclohexyl-1,5-D-anhydroglucitol Tetraacetate.—To 4.08 g of Ia was added 50 ml of acetic acid containing 5% perchloric acid. This solution was treated for 6 hr with hydrogen in a Parr shaker using 0.25 g of platinum dioxide as catalyst. A colorless oil remained after filtration and evaporation. It was acetylated (Ac₂O 10 ml, AcONa 2 g, 1 hr). After processing, white crystals resulted that were recrystallized from methanol–water: mp 89.5–90.5°; yield, 3.37 g (82%). When this material was kept for 20–30 min at 95° it solidified and now melted sharply at 101–102°. If this melt was cooled quickly, it solidified to a crystalline solid of mp 90–91°. It is dimorphic. The 90–91° form gave $[\alpha]_D^{20}$ –19.3° (*c* 20, CHCl₃); the 101–102° form gave $[\alpha]_D^{20}$ –18.2° (*c* 10, CHCl₃). Its infrared spectrum showed these bands: strong at 3.41, 3.50, 5.75, 7.25, 7.90–8.20, 9.03, 9.40, 9.62; medium at 6.89, 8.74, 10.20, 10.32, 10.98, 11.20; weak at 7.60 (sh), 10.50, 11.50, 11.75, 14.30, 15.50 μ .

Anal. of 90–91° crystals (by H. Beck). Calcd for C₂₆H₃₀O₉ (Iib): C, 58.01; H, 7.29. Found: C, 58.46, 58.62; H, 7.17, 7.26. *Anal.* of 101–102° crystals. Found: C, 58.43, 58.29; H, 7.31, 7.17.

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 (6) C. D. Hurd and W. A. Bonner, *ibid.*, **67**, 1972 (1945).

Decomposition of 3,5-Diphenyl-1-pyrazoline. A Correction

C. G. OVERBERGER, RICHARD E. ZANGARO, AND J-P. ANSELME

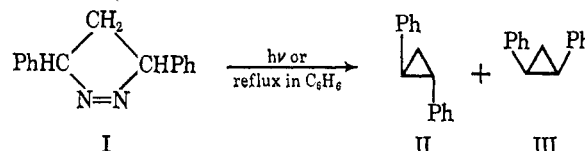
*Department of Chemistry, Polytechnic Institute of Brooklyn,
Brooklyn, New York 11201*

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In previous work,¹ we had reported that *trans*-3,5-diphenyl-1-pyrazoline (I) underwent stereospecific

decomposition with the sole formation of *trans*-1,2-diphenylcyclopropane (II). This conclusion was based on a comparison of refractive indices and nmr spectra with previously published data.² However, it was recently brought to our attention³ that gas chromatographic analysis of the decomposition product indicated that it was composed not only of *trans*-1,2-diphenylcyclopropane (II) but some *cis*-1,2-diphenylcyclopropane (III) as well. This information prompted a re-examination of the reaction in our laboratories.

When I was decomposed at 80° in refluxing benzene, gas chromatographic analysis showed the product to consist of 89% II and 11% III. Photolysis of I gave a product shown by gas chromatographic analysis to be 88% II and 12% III.



Experimental Section

Samples of *cis*- and *trans*-1,2-diphenylcyclopropane were prepared according to the method of Beech, Turnbull, and Wilson⁴ for purposes of comparison. However, the separation of pure isomers was effected by means of preparative vapor phase chromatography instead of repeated vacuum distillation as reported by Curtin.² The apparatus used was an Aerograph Model A-700 (Wilkins Instrument and Research); 20 ft \times $\frac{3}{8}$ in. o.d. aluminum column packed with 20% SE-30 silicone gum rubber on 60–80 mesh Chromosorb-W (DMCS) was used at 185°. A mixture of 90% *trans*- and 10% *cis*-1,2-diphenylcyclopropane was prepared to calibrate an analytical vpc, Perkin-Elmer Model 154D (2 m \times 0.25 in. column packed with silicone grease operated at 185°). The retention times of the *cis* and *trans* isomers in the latter instrument were 16 and 20 min, respectively.

Thermal Decomposition.—A solution of 0.5 g (2.2 mmoles) of freshly recrystallized I in 50 ml of spectroquality benzene was flushed with nitrogen and heated to reflux for 2 hr. The solvent was removed by freeze drying and upon warming to room temperature the product was obtained as an oil. The ratio of *trans*- to *cis*-1,2-diphenylcyclopropane was found to be 89:11.

Photochemical Decomposition.—A solution of 0.5 g (2.2 mmoles) of freshly recrystallized I in 50 ml of spectroquality methanol was flushed with nitrogen and irradiated (Hanovia 450-w high pressure mercury lamp) for 8 hr. The solvent was evaporated, and the product was obtained as an oil. The ratio of *trans*- to *cis*-1,2-diphenylcyclopropane was found to be 88:12.

- (1) C. G. Overberger and J-P. Anselme, *J. Am. Chem. Soc.*, **86**, 658 (1964).
 (2) D. Y. Curtin, *et al.*, *ibid.*, **83**, 4838 (1961); **84**, 863 (1962).
 (3) C. DeBoer and G. S. Hammond, private communication.
 (4) S. G. Beech, J. H. Turnbull, and W. Wilson, *J. Chem. Soc.*, 4686 (1952).