The two fluorinated tertiary alcohols examined in this study, $(CH_3)_2(CF_3)COH$ and $(CF_3)_2(CH_3)COH$, have their fragmentation patterns summarized in Table IV. The base peak for both compounds occurs at m/e 43, which would correspond to the acetyl ion $CH_3C{\equiv}O^+$. In the case of $(CH_3)_2(CF_3)COH$ this assignment is not unequivocal because of the possible formation of the rearrangement ion, $C_3H_7^+$. Unfortunately the peak at m/e 44 is too high to permit a choice on the basis of isotope ratios. The ions corresponding to loss of CF_3 from the molecule ion are prominent in both spectra. This ion accounts for 11.4% of the total ionization in $(CH_3)_2COH(CF_3)$ and is the second most abundant. For this compound the acetyl ion could form from an intermediate acetone molecule ion. This latter ion could result from α cleavage of CF_3 and simultaneous loss of the hydroxyl H. This seems unlikely as the characteristic acetone molecule ion is missing in the alcohol spectrum. A more probable explanation of acetyl formation would involve loss of CF_3 and CH_4 to form the ion directly. Similar considerations would apply to formation of the acetyl ion in $(CH_3)COH(CF_3)_2$. Here its formation *via* decomposition of an intermediate 1,1,1-trifluoroacetone molecule ion seems unlikely after consideration of the fragmentation pattern[8] of 1,1,1-trifluoroacetone. In both alcohols loss of CF_3 rather than CH_3 predominates, especially in (CH_3)-$COH(CF_3)_2$ where the ratio of the corresponding peak heights is about 20:1.

TABLE IV
$(R_1)(R_2)(CH_3)COH$, PER CENT OF TOTAL IONIZATION ($\%\Sigma_{13}$) OF SELECTED FRAGMENTS

Fragment[c]	$R_1 = CH_3$[a] $R_2 = CF_3$	CF_3[b] CF_3
Mol ion		
M—H[d]		
M—H_2O	0.1	
M—HF		
M—CH_3	5.6	0.4
M—CF_3	11.4	7.3
$C_3H_3F_4^+$		2.3
$C_3H_3F_2^+$	0.2	2.2
CF_3^+	1.9	8.0
CHF_2O^+	0.3	3.3
CH_3CFOH^+	4.9	6.4
HCF_2^+	0.7	2.8
CH_3CO^+	*22.7*[e]	*32.1*
$C_3H_7^+$		
$CHCO^+$	4.6	0.3
$C_3H_5^+$		
$C_3H_3^+$	2.5	
CF^+	9.0	2.3
CH_2OH^+		
$C_2H_5^+$	3.1	1.4
COH^+		
$C_2H_3^+$	2.6	1.1
CH_3^+	7.1	4.1
Max %[f]	2.1	2.5

[a] See footnote *a*, Table II. [b] See footnote *b*, Table II. [c] See footnote *b*, Table I. [d] Ion formed by loss of hydrogen atom. [e] Italic percentages correspond to base peaks. [f] See footnote *f*, Table I.

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Hydrogenation of a Benzylic Ether without Hydrogenolysis. 1-β-Cyclohexyl-1,5-D-anhydroglucitol

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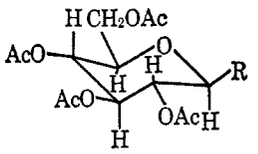
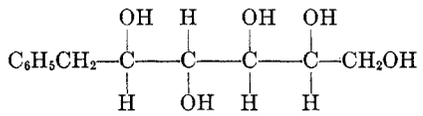
Benzylic groups are frequently characterized by the readiness with which they undergo hydrogenolysis. The topic has been reviewed by W. H. Hartung and R. Simonoff.[1] An example using a cyclic ether in this category is 2-phenyltetrahydropyran, which changes into 5-phenyl-1-pentanol[2] when hydrogenated with a palladium catalyst. A carbohydrate example is the cleavage of methyl 4,6-*O*-benzylidene-α-D-glucoside by hydrogen and platinum into toluene and methyl α-D-glucopyranoside.[3]



Ia, $R = C_6H_5$
b, $R = C_6H_{11}$

In view of this evidence, we expected a rather facile hydrogenolysis of 1-β-phenyl-1,5-D-anhydroglucitol tetraacetate (Ia) into the tetraacetate of L-gulo-6-phenyl-1,2,3,4,5-hexanepentol



Actually, however, none was obtained. With a palladium catalyst there was no reaction. With a platinum catalyst there was hydrogenation to 1-β-cyclohexyl-1,5-D-anhydroglucitol tetraacetate (Ib) in 82% yield. If any hydrogenolysis occurred concurrently, the product was in too small amounts to identify. That hydrogenation of Ia can occur without any significant amount of hydrogenolytic cleavage is a noteworthy observation in view of the benzylic ether structure.

The structure of Ib was supported by elemental analysis and by its infrared spectrum which lacked peaks characteristic of an aromatic ring in the 6.2–6.8-μ region.

An acidic medium was used with the platinum catalyst, namely, acetic acid containing perchloric acid. It is known[4] that acids increase the effectiveness of platinum to hydrogenate the aromatic ring. In the carbohydrate area, it is known also that the hydrogenation and hydrogenolysis reactions are sometimes

(1) *Org. Reactions*, **7**, 263 (1953).
(2) R. H. Baker, K. Cornell, and M. Cron, *J. Am. Chem. Soc.*, **70**, 1490 (1948).
(3) K. Freudenberg, H. Toepffer, and C. Andersen, *Ber.*, **61**, 1750 (1928).
(4) J. Brown, H. Durand, and C. S. Marvel, *J. Am. Chem. Soc.*, **58**, 1594 (1936).

competitive. *E.g.*, whereas palladium promotes quantitative hydrogenolysis of benzyl β-D-glucopyranoside[5] 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, $4H_2$), and that the other half simply underwent hydrogenation to cyclohexyl glucopyranoside (total, $3H_2$) 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 (Ac_2O 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 [α] −19.3° (*c* 20, $CHCl_3$); the 101–102° form gave [α] −18.2° (*c* 10, $CHCl_3$). 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 $C_{20}H_{30}O_9$ (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.

(5) N. K. Richtmyer, *J. Am. Chem. Soc.*, **56**, 1633 (1934).
(6) C. D. Hurd and W. A. Bonner, *ibid.*, **67**, 1972 (1945).

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

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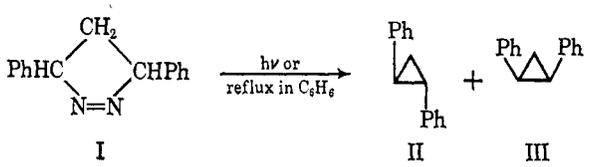
In previous work,[1] we had reported that *trans*-3,5-diphenyl-1-pyrazoline (I) underwent stereospecific decomposition with the sole formation of *trans*-1,2-diphenylcyclopropane (II). This conclusion was based on a comparison of refractive indices and nmr spectra with previously published data.[2] However, it was recently brought to our attention[3] 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 reexamination 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.



I II III

Experimental Section

Samples of *cis*- and *trans*-1,2-diphenylcyclopropane were prepared according to the method of Beech, Turnbull, and Wilson[4] 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 (Wilkens Instrument and Research); 20 ft × 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 × 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).