Dehydration of *cis*- and *trans*-2-Benzylcyclopentanols

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The dehydration of *cis*- and *trans*-2-benzylcyclopentanols by 85% phosphoric acid produced an equilibrium mixture of largely unrearranged olefins. Chugaev dehydration produced the expected products of *cis*-elimination. Berti dehydration proceeded preferentially to products of *trans*-elimination on pyrolysis in bulk, but on dilution with silicone oil, a major shift toward *cis*-elimination was observed.

A considerable number of studies of the dehydration of *cis*- and *trans*-2-phenylcyclohexanols and related reactions producing olefin have been reported in recent years.[1] Techniques and procedures developed in these studies encouraged us to investigate the dehydration of the isomeric alcohols, *cis*- (I) and *trans*-2-benzylcyclopentanols (II), especially since the reference hydrocarbons involved would be the same as for the earlier studies.

EXPERIMENTAL

cis-2-Benzylcyclopentanol,[2] b.p. 93–93.5° (0.3 mm.), n^{20}D 1.5409, was prepared from 2-benzylidenecyclopentanone both by Raney nickel hydrogenation of the double bond followed by Meerwein-Ponndorf reduction of the carbonyl group, and by lithium aluminum hydride reduction of the carbonyl group followed by catalytic hydrogenation of the double bond[2]; 3,5-dinitrobenzoate, m.p. 91–92°.[2]

Properties of the reference hydrocarbons are summarized in Table I.

Alcohol dehydrations. A. *With 85% phosphoric acid.* The alcohol was boiled under gentle reflux for 4 hr. with an equal volume of 85% phosphoric acid.[3] After cooling, ether and water were added, the ether layer washed, dried, and distilled from sodium.

B. *By the Berti method.*[6] Two procedures were employed (a) involving pyrolysis in a standard vacuum distillation apparatus and (b) involving addition of several volumes of Dow Corning Silicone Fluid 550, to provide a nonpolar, nonvolatile pyrolysis medium. The methyl sulfite esters were prepared as described earlier;[6] *methyl cis-2-phenylcyclohexyl sulfite*, b.p. 105–106° (0.05 mm.), n^{20}D 1.5320; *trans* isomer, m.p. 47–50°.

The *methyl 2-benzylcyclopentyl sulfites* were so unstable thermally that purification was not possible. The crude products from the *cis*- and *trans*-alcohols contained 12.29 and 12.03% S, respectively. (Calcd. for $C_{13}H_{18}SO_3$: S, 12.61). The *trans*-ester was even less stable than the *cis*.

C. *By the Chugaev procedure. Methyl cis-2-benzylcyclopentyl*

REFERENCE HYDROCARBONS

Compd.[a]	B.P.	Press., Mm.	n^{20}D	ϵ^{248}	ϵ^{262}	Method of Prep.
V[b]	75–76	2	1.5363	720	790	7
VI[c]	69–69.2	2	1.5328	620	760	8
VII	85–86	2	1.5749	17,100	18,200	1
VIII	94–95	2.5	1.5690	12,100	11,500	9
IX	77–78	2.5	1.5447	745	755	1
X	109–111	12	1.5548	210	230	10
XI	72	2.5	1.5179	—	—	1
XII			1.5255	—	—	11

[a] For structures of compounds V–XII, see diagram. [b] The methoxychloromercury derivative was recrystallized from methanol–chloroform, m.p. 120–121°. *Anal.* Calcd. for $C_{13}H_{17}OHgCl$: C, 36.71; H, 4.03; Cl, 8.34. Found: C, 36.92; H, 4.22; Cl, 8.39. [c] The methoxychloromercury derivative failed to crystallize.

trans-2-Benzylcyclopentanol,[2] b.p. 98.5–99° (0.3 mm.), n^{20}D 1.5383, was prepared both by lithium aluminum hydride reduction of 2-benzylidenecyclopentanone or sodium in moist ether reduction of 2-benzylcyclopentanone; 3,5-dinitrobenzoate, m.p. 78–79°.[2]

cis-2-Phenylcyclohexanol,[3] m.p. 40–42° was prepared by hydrogenation of *o*-phenylphenol, the *trans*-isomer, m.p. 55–57°,[4] by reduction of 2-phenylcyclohexanone.[5]

(1) See, *e.g.*, E. L. Eliel, J. W. McCoy, and C. C. Price, *J. Org. Chem.*, **22**, 1533 (1957) for many references; also, J. W. Huffmann and J. E. Engle, *J. Org. Chem.*, **26**, 3116 (1961).

(2) J. Mentha and A. P. Phillips, *J. Am. Chem. Soc.*, **78**, 140 (1956).

(3) C. C. Price and J. V. Karabinos, *J. Am. Chem. Soc.*, **62**, 1159 (1940).

(4) E. R. Alexander and A. Mudrak, *J. Am. Chem. Soc.*, **72**, 1810 (1950).

(5) A. C. Cope and C. L. Bumgardner, *J. Am. Chem. Soc.*, **79**, 960 (1957).

(6) G. Berti, *J. Am. Chem. Soc.*, **76**, 1213 (1954).

(7) Y. I. Denisenko, *Ber.*, **69**, 1668 (1936).

(8) By reaction of benzylmagnesium chloride on 3-chlorocyclopentene. *Anal.* Calcd. for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 91.05; H, 9.02.

(9) R. B. Carlin and H. P. Landerl, *J. Am. Chem. Soc.*, **75**, 3969 (1953); R. Y. Mixer and W. G. Young, *J. Am. Chem. Soc.*, **78**, 3379 (1956); J. Weinstock and F. G. Bordwell, *J. Am. Chem. Soc.*, **77**, 6709 (1955).

(10) L. H. Groves and G. A. Swan, *J. Chem. Soc.*, 871 (1951).

(11) From Matheson, Coleman and Bell

TABLE II

DEHYDRATION RESULTS

Dehydration Method	Alcohol	Yield, %	Crude Product B.P.	Mm.	n^{20}D	Analysis V	VI	VII	VIII	IX	X
H_3PO_4	cis-C_5	89	69–90	2.0	1.5490	50–55	15–19	19–20	0	3	4.4
H_3PO_4	trans-	87	70–95	2.2	1.5445	50–55	15–19	15–19	1	4	6.3
Berti[a]	cis-C_5	83	78–82	2.8	1.5373	81–82	15	2.4–3.2	0–0.8	0	0–0.3
Berti[a]	trans-	87	74–80	2.7	1.5367	56–57	38	2.8–4.6	0–1.4	0.8	1.4
Berti[b]	cis-C_5	84	72–78	2.0	1.5350	47–48	49	0–2	0–2	0.4	1.6
Berti[b]	trans-	72	77–79	2.7	1.5402	80–81	9.0	8.2–11.3	0	0	0–2.3
Chugaev	cis-C_5	90	72–74	2.0	1.5341	0–1	95–98	0–2	0–2.5	2.2	0
Chugaev	trans-	87	75–78	2.5	1.5373	88–89	5.0	0.5	4	0	1.6
Berti[b]	cis-C_5	74	80–87	2.5	1.5572	(——2.0——)		0	60–65	37	0
Berti[b]	trans-	70	100–103	4.0	1.5644	(——7.0——)		0.3	85–87	6.0	0
VI + H_3PO_4[c]	—	87	70–85	2.2	1.5395	38	50	7.5	0	2	3

[a] By vacuum distillation neat. [b] By vacuum distillation from silicone oil. [c] 3-Benzylcyclopentene (5 g.) and 85% phosphoric acid were heated under gentle reflux for 1.5 hours.

I   II   III   IV

V   VI   VII   VIII

IX   X   XI   XII
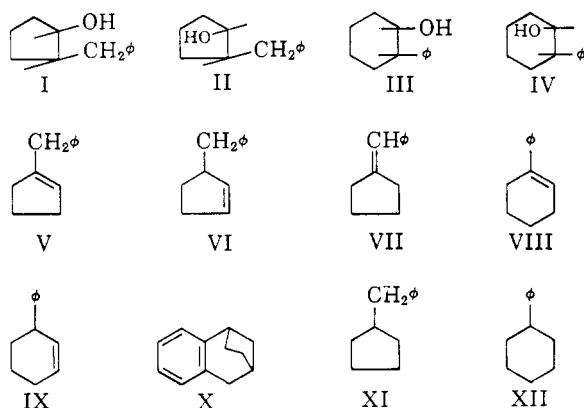
xanthate and the trans-isomer were obtained[12] as red-orange oils in 90–92% yield.

Anal. Calcd. for $C_{14}H_{18}S_2O$: S, 24.1. Found: S, 23.4 (cis), 23.6 (trans).

For the cis isomer, decomposition began at 170° and was complete in 2.5 hr. at 200°. For the trans isomer, decomposition began at 140° and was complete after 2 hr. at 175°. The products were collected and redistilled at reduced pressure from sodium.

Analysis of products. In addition to the yields and physical properties reported in Table II, the dehydration mixtures were submitted to a number of analytical procedures, including bromine titration in acetic acid,[13] ultraviolet absorption at 248 and 252 mμ, infrared absorption at 9.65 and 10.36 (V) and 7.36 μ (VI), competitive epoxidation, gas chromatography before and after hydrogenation, and mass spectrometry after hydrogenation.[1]

Competitive epoxidation was carried out on 0.03 mole of olefin mixture in 100 ml. of thiophene-free benzene at 7° with an equimolar amount of perbenzoic acid.[14] Aliquots were withdrawn for peroxide determination. The second-order rate constants for the reference hydrocarbons are summarized in Table III.

From these rate data and the extent of epoxidation occurring in 60 min. at 7° for known mixtures as well as reaction products, it is possible to estimate the ratio of V and VI for those mixtures consisting principally (over 90%) of these two hydrocarbons.

(12) F. G. Bordwell and P. S. Landis, J. Am. Chem. Soc., 80, 2450 (1958).

(13) K. Uhrig and H. Levin, Ind. and Eng. Chem., Anal. Ed., 13, 90 (1941).

(14) See, e.g., I. M. Kolthoff and T. S. Lee, J. Poly. Sci., 2, 206 (1947).

TABLE III

SECOND-ORDER RATE CONSTANTS FOR EPOXIDATION OF REFERENCE HYDROCARBONS AT 7°

Compound	Average k_2 (mole^{-1}, min.$^{-1}$)
1-Benzylcyclopentene (V)	7.37
3-Benzylcyclopentene (VI)	0.708[a]
Benzylidenecyclopentane (VII)	1.96
1-Phenylcyclohexene (VIII)	1.98
3-Phenylcyclohexene (IX)	0.215

[a] A value of 1.63 was observed at 30°.

1-Benzylcyclopentene oxide was also prepared on a 2-g. scale in 65% yield, b.p. 94–96° (2.5 mm.), n^{20}D 1.5291. The 3-isomer had b.p. 98–99° (2.5 mm.), n^{20}D 1.5324.

Anal. Calcd. for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.95; H, 8.19 (1-isomer); C, 83.17; H, 8.33 (3-isomer).

Gas chromatography in a column of 375 theoretical plates packed with Carbowax 20M on chromosorb was not successful in separating V from VI, VII from VIII or IX from X, but gave excellent separations of these pairs from each other. The hydrogenated mixtures were readily and quantitatively resolved into X, XI, and XII. The relative retention times of the reference hydrocarbons is indicated in Table IV.

TABLE IV

RETENTION VOLUMES[a] OF REFERENCE HYDROCARBONS

Compound	Retention Time (min.)	Retention Volume (ml.)	Retention Volume (relative to V)
V	6.0	480	1.00
VI	6.0	480	1.00
VII	10.6	848	1.77
VIII	10.6	848	1.77
IX	7.5	600	1.25
X	7.5	600	1.25
XI	5.5	440	—
XII	6.25	500	—

[a] Calculated for two meter 25% alkaline Carbowax 20M column, detector, and bath at 200°.

A sample of analytical results for the product of Berti dehydration of cis-2-benzylcyclopentanol is summarized in Table V.

TABLE V

Per Cent of Compounds V through X in the Product
Mixture from Berti Dehydration of
cis-2-Benzylcyclopentanol

%						Method
V	VI	VII	VIII	IX	X	
		2.4				Ultraviolet
65–85	10–15					Infrared
		15.0				Epoxidation
(———99.8———)	(———0———)	0.3				G. C.[a]
(———96.8———)	(—3.2—)	(———0———)				G. C.

[a] Gas chromatography of the hydrogenated product mixture.

DISCUSSION

The composition of dehydration mixtures summarized in Table II permits several major conclusions. In regard to the phosphoric acid dehydration, the new results with 2-benzylcyclopentanols differ from the earlier results with 2-phenylcyclohexanols[1,3,15] in several major respects. Firstly, in the former, neither cis nor trans isomers produced any significant carbon skeleton rearrangement, in contrast to the cis-C_6 isomer (III) for which the major products involved ring contraction.[1,15] Secondly, in contrast to C_6 isomers, the C_5 isomers gave almost complete equilibration of the double bond (Compounds V, VI, and VII, Table II). This ready equilibration was shown to be possible by refluxing VI with phosphoric acid (see Table II).

The Chugaev dehydrations gave almost exclusively the products of cis elimination. For the cis isomer (I), this is almost entirely the Δ^3-olefin, VI. For the trans isomer (II), where cis elimination in both directions is possible, the Δ^1-olefin predominates to about the same degree as for the case of IV.[1]

For the Berti dehydrations, i.e., pyrolysis of the methyl sulfite esters in bulk, the elimination occurred principally in the trans-sense. Since we had earlier suggested[1] that, in the polar sulfite ester medium some degree of ionic character might be possible for the process, it seemed of interest to ascertain the effect of an inert nonpolar diluent. Silicone oil was found suitable for this purpose and, as predicted, the composition of the products for
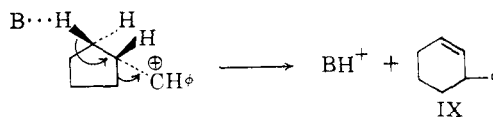
(15) H. J. Schaeffer and C. J. Collins, J. Am. Chem. Soc., 78, 124 (1956)

both the five- and six-membered rings shifted appreciably toward those isomers formed by cis elimination. One might represent the transitions occurring for the two processes in the following manner.
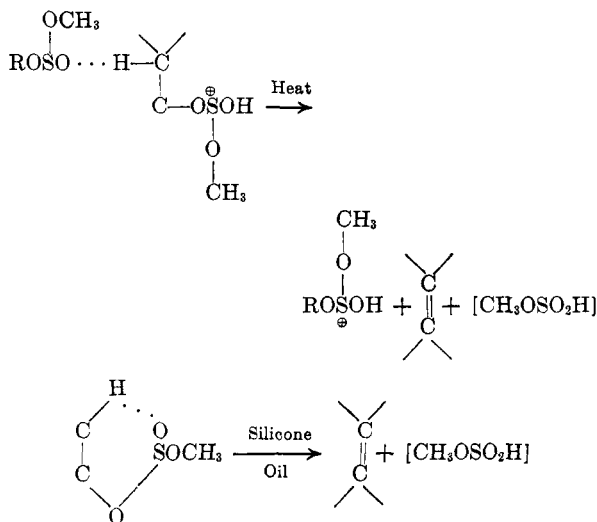
This shift to less carbonium ion character is also indicated by the appreciable decrease in ring contraction for pyrolysis of trans-2-phenylcyclohexyl methyl sulfite in silicone oil (7.3%, Table II) compared to bulk (21%[1]).

One minor point which seems of interest is the formation of the less stable 3-phenylcyclohexene (IX) as the product of ring expansion in the phosphoric acid dehydration of I or II, or isomerization of VI. This suggests firstly that, under conditions where the double bond equilibrates rapidly in the C_5 ring, it is much less labile in the C_6 ring. Secondly, the preferred formation of the less stable isomer suggests that there must be a preferred mechanism for its formation. We speculate that this might involve the following concerted transformation involving removal of a proton from the protonation product of VII.