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The Dehydration of *trans*-2-Phenylcyclopentanol

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Treatment of *trans*-2-phenylcyclopentanol with 85% phosphoric acid at 90° gave in 22% yield a mixture of 1- and 3-phenylcyclopentene, in which the ratio of 1- to 3-isomer was approximately 1:3. In addition to these olefins, a considerable quantity of high-boiling material was also obtained. This material was exclusively obtained when the reaction was conducted at 150°. It was found to contain a mixture of isomeric dimers resulting from a reaction of the Friedel-Crafts type.

The dehydration of *trans*-2-phenylcyclohexanol with 85% phosphoric acid leads to a mixture of products which include 1-benzylcyclopentene, benzalcyclopentane, 1-phenylcyclohexene, and 4-phenylcyclohexene.[1] The material considered at one time[2] to be the major product, 3-phenylcyclohexene, is also formed, but in very small amount. The ring contraction reaction, whose existence was detected only recently, may be ascribed to steric consequences arising from the fact that the preferred conformation of *trans*-2-phenylcyclohexanol involves an equatorial bonding for both the phenyl and hydroxyl groups.[1,3]

The phosphoric acid dehydration of *trans*-2-phenylcyclopentanol should not be subject to steric influences of this kind, since the cyclopentane ring is nearly planar, and the original considerations of Price and Karabinos[2] should hold. The major product should be 3-phenylcyclopentene rather than 1-phenylcyclopentene. Pure samples of 1- and 3-phenylcyclopentene were used in connection with another problem of this laboratory,[4] and since these samples were available, a separate investigation of the dehydration reaction was undertaken. The starting material was prepared by the action of phenyllithium on cyclopentene oxide, and by analogy with related[5,6] cyclohexene oxide reactions the product was considered to be essentially pure *trans*-2-phenylcyclopentanol. A dehydration reaction was carried out under relatively mild conditions (90°) with 85% phosphoric acid, and the products were separated by distillation to yield (a) a mixture of olefins in 22% yield, (b) a small amount of unchanged alcohol, and (c) a high-boiling residue from which was evaporatively distilled a viscous oil having the composition of a phenylcyclopentene dimer.

The olefin mixture gave analytical data corresponding to a phenylcyclopentene structure, and the infrared absorption spectrum was identical with that of 3-phenylcyclopentene, except for weak bands at 7.48, 7.57, and 10.48 μ. The infrared absorption spectrum of 1-phenylcyclopentene shows strong bands at these wave lengths. The composition of the mixture was determined by three methods. A refractive index plot for mixtures of 1- and 3-phenylcyclopentene in known proportion (values are in Table I) indicated that the reaction mixture contained 22% of 1-phenylcyclopentene. The extinction coefficient at 255 mμ (λ_{max} for 1-phenylcyclopentene) for the mixture was determined and compared with observed values of ϵ_{255} for 1- and 3-phenylcyclopentene (Table II), and by calculation it was found that 27% of the mixture consisted of the conjugated isomer. Extinction coefficient calculations were also made for the sharp infrared absorption peak at 3.27 μ (Table III). This is a stretching band for a =C—H group in a five-membered ring,[4] and from the observed value for the mixture it was calculated that 23% of 1-phenylcyclopentene was present.

In view of the close correspondence obtained through the use of these three physical measurements, the olefin mixture resulting from the phosphoric acid dehydration may be accepted as containing about 25% of 1-phenylcyclopentene. An examination of the C—H stretching absorption

TABLE I

Properties of 1- and 3-Phenylcyclopentene and Mixtures

Compounds	B.p., °C.	mm.	n_D^{21}	% of 1-Phenyl Isomer
1-Phenylcyclopentene	118–121	25	1.5748	100
3-Phenylcyclopentene	97–98	20	1.5390	0
Mixed sample 1			1.5460	23
Mixed sample 2			1.5477	33
Mixed sample 3			1.5491	36
Mixed sample 4			1.5518	49
Reaction product	96–113	19	1.5452	22 (calc'd)

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(4) W. H. Tallent and I. J. Siewers, *Anal. Chem.*, **28**, 953 (1956).

(5) J. W. Cook, C. L. Hewett, and C. A. Lawrence, *J. Chem. Soc.*, 71 (1936).

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TABLE II

ULTRAVIOLET ABSORPTION SPECTRA DATA

Compounds	$\epsilon_{255} \times 10^{-3}$	% of 1-Phenyl Isomer
1-Phenylcyclopentene	10.71	100
3-Phenylcyclopentene	0.43	0
Reaction product	3.17	27 (calc'd)

TABLE III

INFRARED ABSORPTION SPECTRA DATA

Compounds	$\epsilon_{3.27}{}^{a}$ μ	% of 1-Phenyl Isomer
1-Phenylcyclopentene	37.7	100
3-Phenylcyclopentene	53.7	0
Reaction product	50.0	23 (calc'd)

[a] See Experimental Section for details.

bands in a high-resolution infrared spectrophotometer gave no indication of the presence of a four-membered ring isomer;[4] the rather unlikely possibility that a ring contraction occurred in this reaction was therefore eliminated. The preparation of the 1-phenylcyclopentene used as a reference compound involved the dehydration of 1-phenylcyclopentanol under conditions essentially identical to those employed to obtain the mixture of olefins from *trans*-2-phenylcyclopentanol. The fact that an 81% yield of 1-phenylcyclopentene was obtained in the former reaction is sufficient proof that it does not rearrange or polymerize under these conditions. Therefore, from the composition of the mixture of olefins produced, it may be concluded that the original arguments of Price and Karabinos[2] hold for the dehydration of *trans*-2-phenylcyclopentanol, and that the ring contraction observed for the six-membered analog is correctly ascribed to conformational relationships.

When the dehydration was carried out at 150°, no olefinic material boiling in the proper range was obtained. Instead, the chief product was a high-boiling viscous oil from which was separated by evaporative distillation a sample that gave analytical data corresponding to the phenylcyclopentene dimer. The fact that this sample absorbed 0.97 mole-equivalent of hydrogen when catalytically reduced indicated that the dimer was probably a Friedel-Crafts product resulting from the addition of the aromatic ring of one phenylcyclopentene molecule to the olefinic bond of a second molecule. The hydrogenated sample was subjected to strong oxidation conditions with potassium permanganate, and the organic acids were separated into an acetone-soluble and an acetone-insoluble fraction. The two fractions were found by paper chromatographic analysis and paper electrophoresis studies to contain benzoic acid and a mixture of phthalic acids, respectively (Tables IV and V). The phthalic acid mixture corresponded most closely in its properties to a mixture of isophthalic and terephthalic acids. The ultraviolet absorption spectra of authentic samples of these two acids were compared with that of the oxidation product mixture, and calculations from these spectra indicated that the mixed acids consisted of 28% isophthalic acid and 72% terephthalic acid. A mixture of this composition was made from authentic specimens, and the ultraviolet absorption spectrum of the "synthetic" mixture was compared with that of the mixed oxidation products. The results are in Figure 1; the "synthetic" and isolated mixtures gave almost identical ultraviolet spectra.

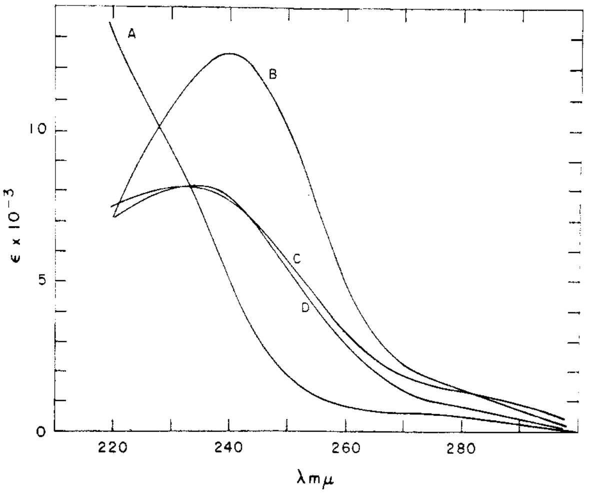


FIGURE 1. ULTRAVIOLET ABSORPTION SPECTRA. A, isophthalic acid; B, terephthalic acid; C, acetone-insoluble acid mixture from dimer oxidation; D, "synthetic" mixture of isophthalic acid (28.6%) and terephthalic acid (71.4%). All spectra were taken in 0.1% sodium hydroxide solution.

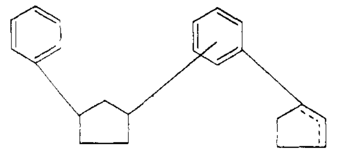
TABLE IV

PAPER CHROMATOGRAPHIC DATA

Acid	Rf Values A[a]	B[b]	C[c]
Benzoic	0.93	0.91	0.94
Mixture I[d]	0.91	0.89	0.93
Phthalic	0.76	0.83	0.88
Isophthalic	0.87	0.88	0.92
Terephthalic	0.85	0.87	0.90
Mixture II[e]	0.86	0.88	0.91
Trimesic	0.81	0.85	
Succinic	0.70	0.83	0.78
Oxalic			0.25
Malonic	0.36		0.71

[a] *n*-Butyl alcohol, acetic acid, water (4:1:1). [b] *tert*-Butyl alcohol, acetic acid, water (2:1:1). [c] *sec*-Butyl alcohol, formic acid, water (15:3:2). [d] Acetone-soluble oxidation product. [e] Acetone-insoluble oxidation product.

From these data, it was concluded that the reaction leading to a dimeric structure was one of the Friedel-Crafts type, in which steric hindrance prevented reaction in the *o*-position. The reaction occurred in approximately 3:7 ratio for *m*:*p* addition; and as a result of evidence presented above concerning the stability of 1-phenylcyclopentene, it was assumed that the 3-position of the cyclopentane ring was involved. The structure of the dimers may therefore be represented by:



In addition to *m,p*-isomerism, the olefinic bond of the dimer might be expected to occur in one or both of the two positions indicated in the formula. It was assumed that the conjugated and non-conjugated isomers would have ultraviolet spectra similar to those of 1- and 3-phenylcyclopentene, respectively. On this basis it was calculated that the mixture contained 58% of conjugated isomers. Continued exposure to the reaction conditions would presumably increase the amount of conjugated isomers, and this estimate should therefore be taken only as an indication that complete conversion to a conjugated system does not occur in phosphoric acid at 150° during a four hour period.

TABLE V

PAPER ELECTROPHORESIS DATA

Acid	Cm. Moved[a]
Benzoic	7.5
Mixture I[b]	7.7
Phthalic	10.3
Isophthalic	10.2
Terephthalic	10.4
Mixture II[c]	10.4
Trimesic	12.2

[a] Conditions: 0.1 *N* ammonium acetate buffer, *p*H 8.7, 5–6 ma., 5.0 v./cm., four hours. The data given are corrected for electroösmosis. [b] Acetone-soluble oxidation product. [c] Acetone-insoluble oxidation product.

In the case of both the phenylcyclopentenes and the mixture of isomeric dimers it has been assumed that the double bond was not in a 4-phenylcyclopentene position. This assumption may not be completely justified, in view of the isolation of a small amount (6%) of 4-phenylcyclohexene from the dehydration of *trans*-2-phenylcyclohexanol.[1] The presence of a few percent of 4-phenylcyclopentene in the olefin fraction isolated in this work might have escaped detection.

The literature contains several examples of dehydrations of substituted cyclopentanols, but none are directly comparable to these experiments. The dehydration-decarboxylation of methyl 2-phenyl-3-hydroxycyclopentanecarboxylate in boiling 50% hydrochloric acid gave 42% of 1-phenylcyclopentene as the sole isolated product,[7] but in the absence of stereochemical assignments for the substituents it is not possible to determine the course of the dehydration. The phthalic anhydride dehydration of two stereoisomers of 2-methyl-5-isopropylcyclopentanol gave the same product, 1-methyl-3-isopropylcyclopentene, and this was interpreted by the author as meaning that the alkyl groups were *cis* in each stereoisomer.[8] From a study of the acid-catalyzed dehydration of the two racemic forms of 2-isopropylcyclopentanol, Vavon and Barbier[9] concluded that the rate of dehydration was much greater for the *cis* isomer, but the position of the double bond in the isopropylcyclopentene products was not determined. Vapor-phase dehydrations with aluminum oxide catalysts have been reported for 2-methylcyclopentanol, to give predominantly 1-methylcyclopentene[10] along with some of the 3-methyl isomer, and for 2,2,4- and 2,4,4-trimethylcyclopentanol, to give 3,3,5-trimethylcyclopentene (from both alcohols), 1,4,4-trimethylcyclopentene (from the 2,4,4-isomer), and 1,2,4-trimethylcyclopentene (from the 2,2,4-isomer).[11] A related vapor-phase dehydration over alumina, that of 1,2-diethylcyclohexanol to give 1-ethyl-2-ethylidenecyclohexanol, was recently described by Karabinos.[12]

EXPERIMENTAL[13]

trans-2-Phenylcyclopentanol. To 1 l. of a 0.73 *N* solution of perbenzoic acid in chloroform,[14] chilled in ice, there was added 45.0 g. of cyclopentene. This solution was held for one week at 0–5°. The solution then was washed with 10% sodium hydroxide and water, dried, and distilled to yield 14.3 g. (25%) of cyclopentene oxide, b.p. 99–99.5° (757 mm.), n_D^{25} 1.4350 (reported[15] b.p. 100–101°, n_D^{23} 1.4321).

A solution of phenyllithium was prepared from 2.5 g. of lithium shavings and 27 g. of bromobenzene in 200 ml. of ether. The cyclopentene oxide (14.3 g.) was added dropwise to this solution while it was stirred vigorously. The mixture was heated under reflux for 3.5 hours, and the product was isolated in the usual way after the addition of water. Distillation gave 9.6 g. (40%) of *trans*-2-phenylcyclopentanol, b.p. 110–113° (2 mm.), n_D^{25} 1.5478.

Anal. Calc'd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.38; H, 8.82.

The *phenylurethan* was prepared; m.p. 82–83° (Kofler stage) after recrystallization from hexane.

Anal. Calc'd $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81; N, 4.98. Found: C, 77.03; H, 6.73; N, 4.85.

Dehydration reaction. A mixture of 5.0 g. of *trans*-2-phenylcyclopentanol and 5.0 ml. of 85% phosphoric acid was stirred and heated at 90° for 4 hours. An equal volume of water was added, and the products were extracted with benzene. The benzene solution was washed with water and distilled. There was obtained 1.0 g. (22%) of an olefin mixture, b.p. 96–113° (19 mm.), n_D^{21} 1.5452.

Anal. Calc'd for $C_{11}H_{12}$: C, 91.61; H, 8.39; Found: C, 91.35; H, 8.36.

Further distillation at 1 mm. gave 0.8 g. of unreacted

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starting material. The viscous residue was subjected to evaporative distillation to give a small quantity of $C_{22}H_{24}$ isomers. In a second experiment the dehydration reaction was carried out at 150° for 4 hours with the same quantities of reactants. No distillate was obtained when the products of this reaction were heated to 233° at 1 mm.; evaporative distillation at 140° (1–2 μ) gave a small quantity of a clear viscous oil. The Rast molecular weight was found to be 286 (calc'd for $C_{22}H_{24}$, 288).

Anal. Calc'd for $C_{22}H_{24}$: C, 91.61; H, 8.39. Found: C, 91.37; H, 8.17.

Hydrogenation of the dimer fraction. The hydrogenation of 126 mg. of the mixed dimeric products was carried out at room temperature and atmospheric pressure in ethanol with a 10% palladium-carbon catalyst. The reduction required 0.97 mole-equivalent of hydrogen and was complete in 35 minutes. The catalyst was removed by filtration, and the solvent was evaporated to yield a viscous oil which was not characterized. It was subjected immediately to oxidation.

Oxidation of $C_{22}H_{26}$ fraction. The hydrogenated dimer fraction was suspended in water (5 ml.). The mixture was heated at 95–100° and stirred for 9 hours during which time small portions of potassium permanganate were added periodically (a total of 1.5 g. was used). The manganese dioxide was removed by filtration, and the solution was washed with ether. The aqueous mixture was acidified to *p*H 1 with hydrochloric acid, and the organic acids were removed by continuous extraction with chloroform. The total yield of organic acids was 42 mg.; this was triturated with acetone to yield two fractions: Mixture I, an acetone-soluble fraction, and Mixture II, an acetone-insoluble fraction.

Paper chromatography of acid fractions. Mixture II and reference compounds, with the exception of benzoic acid, were employed at a concentration of 10 mg. of acid per ml. of 1% sodium hydroxide solution. For benzoic acid and mixture I acetone solutions (10 mg./ml.) were preferred. One drop of each solution was spotted on each strip. The solvent systems are indicated in Table IV; the paper was Whatman I, and the ascending method was used. The acids were detected with an indicator. This was prepared from a 0.04% solution of Bromcresol Green in 95% ethanol by adjusting to a blue-green color with 1% sodium hydroxide solution. The acids appear as yellow areas, while sodium hydroxide appears as a blue area (R_f values of 0.24–0.30, 0.60–0.62, and 0.22–0.23 respectively, for columns A, B, and C in Table IV). This general method for the chromatography of salts is based on the poorly understood phenomenon of salt hydrolysis during paper chromatography.[16,17,18]

Paper electrophoresis of acid fractions. The apparatus was a variation of a hanging-paper design. Compounds were spotted at 1.5-cm. intervals along a center line on a Whatman 1 paper strip 42 cm. long and 26.5 cm. wide. This strip then was draped over a glass rod with the ends dipping 1 cm. into electrode compartments filled with 0.1 *N* ammonium acetate buffer, *p*H 8.7. The strip was allowed to wet by capillary action. Electrophoresis then was carried out at 200 v. and 5–6 ma. for 4 hours. The positions of the aromatic acids were established by scanning for ultraviolet absorption with a densitometer (Photovolt Model 525) and a mercury light source. The values in Table V are for maximum density. Urea was used as a neutral reference compound for the determination of electroösmosis. It was detected as a yellow spot by spraying the appropriate portion of the strip after electrophoresis with a 0.5% solution of *p*-dimethylaminobenzaldehyde in 1.0 *N* hydrochloric acid.

Spectroscopy. Comparisons of infrared spectra were made with a Perkin-Elmer Model 21 spectrophotometer and liquid samples. Ultraviolet measurements were made in ethanol with a Cary Model 11 MS Spectrophotometer. A study of the C—H stretching bands of 1- and 3-phenylcyclopentene, and of the olefin fraction boiling at 96–113° (19 mm.), was carried out on a Beckman IR-3 spectrophotometer. For the data in Table III, concentrations of 0.337, 0.336, and 0.338 mole/liter respectively for these three compounds in carbon tetrachloride were used, with a 0.4-mm. cell and the same slit width in each case. Details of this method for studying individual C—H bonds may be found in another paper.[4]

Reference compounds. Phenylcyclopentanol was prepared by the action of phenylmagnesium bromide on cyclopentanone following the general procedure described by Zelinsky.[19] It was dehydrated by stirring with an equal volume of 85% phosphoric acid for 4 hours at 90°. This gave *1-phenylcyclopentene* in 30% over-all yield from cyclopentanone. The yield from 1-phenylcyclopentanol was 81%. The physical properties given in Table I are in good agreement with values reported in the literature. The ultraviolet absorption spectrum of the product (λ_{max} 255 mμ, ϵ_{max} 10.7 × 10^3) is interesting in view of the recent studies of Overberger and Tanner[20] concerning the effect of α- and β-alkyl substituents on the ultraviolet absorption spectrum of styrene. Apparently cyclization nullifies some of the steric influence of an α-substituent. The ultraviolet absorption spectrum of 1-phenylcyclohexene[21] (λ_{max} 248, ϵ_{max} 12.2 × 10^3) shows a similar effect.

3-Bromocyclopentene was prepared by action of N-bromosuccinimide on the olefin. It was converted to 3-phenylcyclopentene by reaction with phenylmagnesium bromide. The procedure used was analogous to that of reported[22,23] preparations in which 3-chlorocyclopentene was the starting material. In the present synthesis the product was obtained in 16% over-all yield from cyclopentene. Its physical properties (see Table I) were in good agreement with the reported values. The ultraviolet absorption spectrum showed much fine structure and was qualitatively and quantitatively very similar to that of phenylcyclopentane.[4]

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