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Dehydration of *cis*- and *trans*-2-Phenylcyclohexanols[1]

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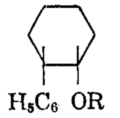
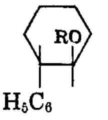
The dehydration of *trans*-2-phenylcyclohexanol by 85% phosphoric acid has been reinvestigated using infrared, ultraviolet, and mass spectrometry to ascertain the composition of the products. Extensive rearrangement occurs to give a product containing *ca.* 14% 1-phenylcyclohexene, 20% unconjugated 3- and 4-phenylcyclohexenes, 17% benzalcyclopentane, 46% unconjugated 1-, 3-, and 4-benzylcyclopentene and 4% 1,3-endoethylene-1,2,3,4-tetrahydronaphthalene. These findings are in substantial agreement with results independently obtained by Schaeffer and Collins,[3] as is the observation that dehydration of *cis*-2-phenylcyclohexanol involves substantially no rearrangement.

Pyrolysis of 2-phenylcyclohexyl methyl sulfite[4] led to 57% 1-phenylcyclohexene and 43% 3-phenylcyclohexene with less than 2% ring contraction product starting with the *cis* isomer. On the other hand, in the case of the *trans* isomer about 21% of the pyrolysis product had suffered ring contraction.

Introduction. It was reported earlier,[5] on the basis of refractive index measurements, that in the dehydration of the 2-phenylcyclohexanols by 85% phosphoric acid, the *cis* isomer (I) gave largely 1-phenylcyclohexene, whereas the *trans* isomer (II) led to 3-phenylcyclohexene. The subsequent preparation, by other means, of pure 3-phenylcyclohexene and measurement of its refractive index,[6,7] however, invalidated the earlier conclusion with respect to the product composition from the *trans* isomer (II). We have therefore reinvestigated the products of the *trans* isomer (II) by analysis with the now readily available tools of ultraviolet and infrared spectroscopy and mass spectrometry. At the same time we reinvestigated briefly the products of dehydration of the *cis* isomer (I) as well as those of the pyrolysis of the 2-phenylcyclohexyl methyl sulfites, III and IV since these products had also been deemed to be mixtures of 1- and 3-phenylcyclohexene on the basis of refractive index only.[4,5]



I, R=H
III, R=OSO_2CH_3



II, R=H
IV, R=OSO_2CH_3

Our results confirm (and, in one minor respect, extend) the findings of Schaeffer and Collins[3]—obtained by the entirely different technique of isotope dilution— that dehydration of *trans*-2-phenylcyclohexanol (II) (but not of the *cis* isomer I) leads to extensive ring contraction. Ring contraction, though to a lesser extent, also occurred in the pyrolysis of the *trans* methyl sulfite IV but not with *cis*-2-phenylcyclohexyl methyl sulfite (III).

Results. Dehydration of *trans*-2-phenylcyclohexanol with 85% phosphoric acid[5] gave a hydrocarbon fraction whose refractive index (1.5493–

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[3] H. J. Schaeffer and C. J. Collins, *J. Am. Chem. Soc.*, **78**, 124 (1956).

[4] G. Berti, *J. Am. Chem. Soc.*, **76**, 1213 (1954).

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

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

[7] A. Berlande, *Compt. rend.*, **213**, 437 (1941).

TABLE I

PROPERTIES OF REFERENCE HYDROCARBONS

Compound	B.P., °C.	Mm.	n_D^{20}	λ, mμ	ϵ_{EtOH}	Ref.
1-Phenylcyclohexene	124–127	14–15	1.5692	—	—	9
	128	16	1.5645 (25°)	247	12,000[a]	10
	82	1	1.5660 (25°)	—	—	11
			1.5690	246	12,120	12
			1.5664 (25°)	248	12,170[b]	13
			1.5692	247	12,940	14
3-Phenylcyclohexene	235	atm.	1.5440 (26°)	—	—	7
	76–79	2	1.5448	—	—	6
			1.5448	—	—	3
			1.5444	253	653	14
			1.5417 (25°)	248	232	13
	118–119	19	1.5449	248	775[b]	[c]
Phenylcyclohexane	105–115	10–15	1.5249	—	—	9
	11–113	13	1.5237 (25°)	—	—	14
	107	13	1.5255[b]	—	—	[c]
Benzalcyclopentane	108–118	8	(1.5518)[d]	—	—	3
	86	1.9	1.5752	248	17,150[b]	[c]
1-Benzylcyclopentene	113–117	18	1.5355–1.5510[e]	—	—	9
	103–107	11	1.5367	—	—	3
	108–109	14	1.5363	248	750[b]	[c]
Benzylcyclopentane			1.5170–1.5245[f]	—	—	9
	70–72	5	1.5200	—	—	15
	103–104	12.5	1.5178[b]	—	—	[c]
1,3-Endoethylene-1,2,3,4-tetrahydronaphthalene (V)	117	25	—	—	—	16
	115	15	—	—	—	17
	108–108.5	13.5	1.5555[b]	248	200[b]	[c]

[a] In cyclohexane. [b] Data used in calculations, see text. [c] This work. [d] Only 66% purity claimed for this sample. [e] At temperatures ranging from 17.5 to 23°. [f] At temperatures ranging from 17 to 21°.

1.5498) was considerably different from that (1.5553) previously observed.[5,8] Estimation of the composition of this material—assuming it to be a binary mixture of 1- and 3-phenylcyclohexane—on the basis of refractive index and ultraviolet extinction coefficient at 252 mμ (*cf.* Table I) led to inconsistent results. Moreover, the infrared spectrum of the dehydration product showed numerous bands not present in either 1- or 3-phenylcyclohexene. On the assumption that part of the material might have suffered ring contraction (*cf.* ref. 15), it was hydrogenated and the infrared spectrum of the hydrogenated material was recorded and compared with the spectra of pure phenylcyclohexane and benzylcyclopentane. Both hydrocarbons were clearly present. Mass spectrometric analysis of the hydrogenated material indicated it to be *ca.* 35% phenylcyclohexane and 65% benzylcyclopentane. Moreover, the presence of benzalcyclopentane in the dehydration product prior to hydrogenation was suggested by the isolation of benzaldehyde from an ozonolysis reaction.

Careful inspection of the mass spectrum of the hydrogenated product disclosed a very large residual peak at mass 129 not present in the mass spectrum of either phenylcyclohexane or benzylcyclopentane. This peak also occurred in the spectrum of the product before hydrogenation. Since 1,3-endoethylene-1,2,3,4-tetrahydronaphthalene (V) is reported to be obtained in the cyclization of the olefin resulting from dehydration of 1-benzylcyclopentanol,[17] and since this hydrocarbon might well have a large mass peak at mass 129, due to loss of

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(8) Calculated from the refractive indices of hydrocarbon standards and the composition of the products reported in ref. 5.

(9) G. Egloff, "Physical Constants of Hydrocarbons," Reinhold Publishing Corp., New York, N. Y., Vol. III (1946), pp. 265, 276.

(10) A. C. Cope, F. S. Fawcett, and G. Munn, *J. Am. Chem. Soc.*, **72**, 3399 (1950).

(11) R. C. Carlin and H. P. Landerl, *J. Am. Chem. Soc.*, **75**, 3969 (1953).

(12) R. T. Arnold and P. N. Richardson, *J. Am. Chem. Soc.*, **76**, 3649 (1954).

(13) J. Weinstock and F. G. Bordwell, *J. Am. Chem. Soc.*, **77**, 6706 (1955).

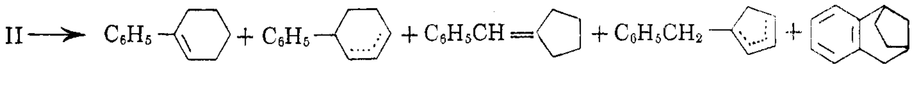
(14) R. Y. Mixer and W. G. Young, *J. Am. Chem. Soc.* **78**, 3379 (1956).

(15) D. V. Nightingale and M. Maienthal, *J. Am. Chem. Soc.*, **72**, 4823 (1950).

(16) W. Baker and W. G. Leeds, *J. Chem. Soc.*, 974 (1948).

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

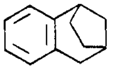
TABLE II



V

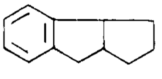
This work:	20%	13%	17%	46%	4%
Ref. 3	21%	15%[a]	*Ca.* 20%	(32%)[b]	[c]

[a] 9% of 3-phenylcyclohexene and 6% of 4-phenylcyclohexene. [b] This figure refers to 1-benzylcyclopentene only. [c] Not analyzed for.



V

the ethylene bridge subsequent to ionization in the mass spectrometer chamber, the presence of V in the dehydration product of II was suspected, especially since phthalic anhydride (in small yield) was isolated from the permanganate oxidation of the product mixture obtained in the dehydration of II. The mass spectrum of a synthetic sample of compound V[16] does, indeed, have an unusually intense peak at mass 129 and mass spectral analysis of the mixture obtained in the dehydration of II followed by hydrogenation showed it to consist of 33.5% phenylcyclohexane, 62.6% benzylcyclopentane, and 3.9% V. Assuming this composition there were still small residual peaks at mass 41 and 65. It is possible that these may be due to very small quantities of other isomers, such as 3,4-benzo[3.3.0]bicyclooctane (VI) but this possibility was not explored further.



VI

In any case, a synthetic mixture of the above composition (33.5:62.6:3.9) agreed well with the hydrogenation product in refractive index (1.5213 *vs.* 1.5217) and infrared spectrum.

Complete calculation of the composition of the dehydration mixture of II from ultraviolet and refractive index data was unfortunately not feasible, since the data were not sufficiently mathematically independent to allow a sensitive calculation. The approximate benzalcyclopentane content of the mixture was therefore estimated as 17% by comparison of the 11.61μ infrared band of the product mixture with that of synthetic mixtures of varying benzalcyclopentane content. It follows that the benzylcyclopentene content of the mixture must be 46%, since the total benzylcyclopentane after reduction amounts to 63% (*vide supra*). The distribution of the phenylcyclohexene fraction as between conjugated and unconjugated isomer can then be calculated from the ultraviolet data (Table I, marked values) to be 20% 1-phenylcyclohexene and 13% 3-phenylcyclohexene.[18]

It is of interest to compare out data with those of Schaeffer and Collins.[3] Since these investigators have shown that 4-phenylcyclohexene as well as 3-phenylcyclohexene is present in the dehydration mixture of II, and since neither of these isomers would be expected to have strong ultraviolet absorption, it is evident that our purported analysis of 3-phenylcyclohexene (based on UV data) is, in fact, an analysis of unconjugated (combined 3- and 4-)phenylcyclohexene. Similarly, our analysis of benzylcyclopentene (which is based on the difference between total material giving benzylcyclopentane on hydrogenation and benzalcyclopentane as analyzed by infrared) is, in fact, an analysis for total unconjugated (1-, 3-, and 4-)benzylcyclopentene.[19] Taking these facts into account our analysis and that of Schaeffer and Collins[3] are summarized in Table II. It is evident that the two sets of data are in good agreement, except in the case of benzylcyclopentene. However, in this case our figure, as explained above, refers to total benzylcyclopentene whereas that of Schaeffer and Collins[3] refers to 1-benzylcyclopentene only. Since the data of Schaeffer and Collins account for only about 88% of the distilled material, and of the missing 12%, only 4% are accounted for by V, the discrepancy would disappear if the mixture contained about 11 ± 3% of 3- and 4-benzylcyclopentene. In any case, our mass spectral analysis shows convincingly that the dehydration mixture contains 63% of material reducible to benzylcyclopentane.

Dehydration of *cis*-2-phenylcyclohexanol (I) with 85% phosphoric acid gave a hydrocarbon mixture whose refractive index (1.5637–41) was in good agreement with earlier findings (1.5644[5,8]). Hydrogenation of this product led to material which, according to mass spectrometric analysis, contained 97.4% phenylcyclohexane and 2.6% benzylcyclopentane, indicating that very little ring contraction had occurred in the dehydration of I. Schaeffer and Collins[3] report that the dehydration product contains 88% 1-phenylcyclohexene and 2% 3-phenylcyclohexene leaving open the question of the remaining 10% of material. It is

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[18] The infrared spectrum of the product closely resembled that of a synthetic mixture containing 20% 1-phenylcyclohexene, 13% 3-phenylcyclohexene, 17% benzalcyclopentane, 46% 1-benzylcyclopentene, and 4% V.

[19] There is an implicit assumption here that 3- and 4-benzylcyclopentene do not absorb appreciably at 11.61μ, the band used for analyzing benzalcyclopentane. The general consistency of our results, both internally and with those of ref. 3 suggests that this assumption is sound.

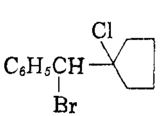
evident that not all this material is a product of ring contraction.

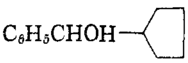
The finding of ring contraction in the dehydration of *trans*-2-phenylcyclohexanol (II) suggested a reexamination of the pyrolysis of *cis*- and *trans*-2-phenylcyclohexyl methyl sulfite (III and IV),[4] since the possibility of ring contraction was not previously considered in the analysis of the products of this reaction. Pyrrolysis of the *cis* isomer (III) gave a hydrocarbon fraction boiling at 115–130°/15 mm. The refractive index of the product (1.5583) was substantially lower than that (1.5625) reported earlier.[4] The discrepancy may be due to the fact that in the previous investigation[4] the reaction product was distilled over sodium at atmospheric pressure, since we were able to show (see Experimental) that 3-phenylcyclohexene, one of the components of the pyrolysis mixture, is not stable under such conditions.[20] Hydrogenation of the pyrolysis product of III gave material which, according to mass spectrometric analysis contained 98.3% phenylcyclohexane and 1.7% benzylcyclopentane, proving substantial absence of ring contraction. The pyrolysis product, according to refractive index and ultraviolet absorption ($\epsilon_{252} = 7{,}140$) contained 57% 1-phenylcyclohexene and 43% 3-phenylcyclohexene. (Calculated for this composition: n_D^{20} 1.5585, ϵ_{252} 7,140; assuming n_D^{20} 1.5692, ϵ_{252} 12,000 for 1-phenylcyclohexene, n_D^{20} 1.5444, ϵ_{252} 700 for 3-phenylcyclohexene.) This finding changes the previous data[4] only qualitatively.

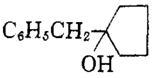
In contrast, hydrogenation of the pyrolysis product of *trans*-2-phenylcyclohexyl methyl sulfite IV gave a product which, according to mass spectrometric analysis, was 78.6% phenylcyclohexane and 21.4% benzylcyclopentane. Here, evidently, ring contraction had taken place (though to a lesser extent than in the phosphoric acid dehydration of alcohol II) and the previous analysis of the pyrolysis product[4] is therefore not valid. A complete analysis of this product was not attempted in the present investigation.

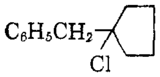
Synthesis of reference hydrocarbons. 1-Phenylcyclohexene, 3-phenylcyclohexene, and 1-benzylcyclopentene were prepared by methods described in the literature,[6,7,21] and the properties of two of the reaction products are shown in Table I to be in good agreement with those reported by other investigators. Considerable difficulties were encountered in the synthesis of benzalcyclopentane. The best sample of benzalcyclopentane obtained in this investigation resulted from the dehalogenation of phenyl(1-chlorocyclopentyl)bromoethane (VII) with zinc; this sample was analytically pure and had n_D^{20} 1.5752; ϵ_{252} 18,400. Successive fractions of this material did not differ in boiling point or refractive index. Slightly impure benzalcyclopentane (n_D^{20} 1.5655) was obtained by the Chugaev reaction of cyclopentyl phenyl carbinol (VIII); this material appeared to contain some sulfur-containing by-products but its infrared spectrum was very similar to that of the material described above.

Other likely procedures failed to yield benzalcyclopentane.[22] Dehydration of 1-benzylcyclopentanol (IX) with iodine and with oxalic acid gave the unconjugated isomer 1-benzylcyclopentene, which was also the major product of the dehydrohalogenation of 1-benzylcyclopentyl chloride (X) with triethanolamine. This preference for formation of the nonconjugated isomer is surprising. It must be due to the preference for an endocyclic bond over an exocyclic one,[23] since dehydration of benzyl diethyl carbinol, $C_6H_5CH_2COH(C_2H_5)_2$ and dehydrohalogenation of the corresponding chloride, $C_6H_5CH_2CCl(C_2H_5)_2$, give the conjugated olefin 1-phenyl-2-ethyl-2-butene, $C_6H_5CH{=}C(C_2H_5)_2$.[24]


VII


VIII


IX


X

Other preparations of benzalcyclopentane which failed are dehydrohalogenation of cyclopentylphenylchloromethane, $C_6H_5CHClC_5H_9$ with boiling pyridine (quaternization appeared to occur), and with boiling aqueous triethanolamine [cyclopentyl phenyl carbinol (VIII) resulted]; dehydration of cyclopentyl phenyl carbinol (VIII) with potassium hydrogen sulfate or phosphoric acid (complex mixtures resulted): and dehydration of 1-benzylcyclopentanol IX with hot solid potassium hydroxide. The latter procedure yielded toluene in almost mole-per-mole yield, apparently as the result of a base-induced cleavage. The other product of the assumed cleavage, cyclopentanone, was probaly resinified by the potassium hydroxide. It is known that treatment of benzyl dimethyl carbinol,

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(20) Berti's crude product had about the same refractive index (1.5580[4]) as our product. Similarly, our pyrolysis product from the *trans*-sulfite IV had n_D^{20} 1.5550, in fair agreement with Berti's product prior to distillation (n_D^{20} 1.5560) but in poor agreement with his distilled product (n_D^{20} 1.5598). H. Pines and M. Kolobielski, *J. Am. Chem. Soc.*, **79**, 1698 (1957) have recently shown that 1-phenylcyclohexene undergoes disproportionation and dehydrogenation when heated above 200° with sodium-benzylsodium.

(21) Y. I. Denisenko, *Ber.*, **69**, 1668 (1936); L. Piaux, *Compt. rend.*, **199**, 1127 (1934).

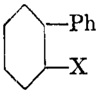
(22) Difficulties in the preparation of benzalcyclopentane are also reported in ref. 3.

(23) *Cf.* H. C. Brown, *J. Org. Chem.*, **22**, 439 (1957).

(24) A. Klages, *Ber.*, **37**, 1724 (1904); K. Auwers and F. Eisenlohr, *J. prakt. Chem.*, [2] **82**, 94 (1910). Unfortunately the structural evidence for the product is not convincing. See also J. M. Lamberti and P. H. Wise, *J. Am. Chem. Soc.*, **75**, 4787 (1953).

TABLE III

ELIMINATION FROM 2-PHENYL-SUBSTITUTED CYCLOHEXYL COMPOUNDS

X in 	Stereo-isomer	Method	1-Phenyl[a]	Products % 3-Phenyl[a]	Ring Contr.	Ref.
OH	*cis*	H_3PO_4	88[3]	2[3]	3[b]	3, *b*
OH	*trans*	H_3PO_4	17,[b] 21[3]	9[c]	63[b]	3, *b*
OAc	*cis*	Pyrol.	7	93	0	6
OAc	*trans*	Pyrol.	86.5	13.5	0	6
OCS_2CH_3	*cis*	Pyrol.	0–4	96–100	0	6
OCS_2CH_3	*trans*	Pyrol.	88	12	0	6
OSO_2CH_3	*cis*	Pyrol.	57	43	<2	[b]
OSO_2CH_3	*trans*	Pyrol.	[d]	[d]	21	[b]
NH_2	*trans*	HNO_2	~0	~0	~100	15
$N^+(CH_3)_3$	*cis*	OH, Δ	100	0	0	12
$N^+(CH_3)_3$	*trans*	OH, Δ	100	0	0	12, 13
$O \leftarrow N(CH_3)_2$	*cis*	Pyrol.	9	91	0	26
$O \leftarrow N(CH_3)_2$	*trans*	Pyrol.	85	15	0	26

[a] -cyclohexene. [b] This work. [c] Also 6% 4-phenylcyclohexene.[3] [d] Combined yield of phenylcyclohexenes: 79%.

$C_6H_5CH_2COH(CH_3)_2$ with hot potassium hydroxide yields toluene and acetone.[25]

Discussion. The mechanism of dehydration of *trans*-2-phenylcyclohexanol (II) with phosphoric acid has been adequately presented by Schaeffer and Collins[3] who were able, by radiochemical means, to ascertain the extent of phenyl migration in this reaction. The results of several recent studies of elimination from 2-phenyl-substituted cyclohexyl compounds are summarized in Table III.

The reactions may be divided into four classes, *viz.:* (1) Reactions which proceed stereospecifically (or nearly so) with *cis* elimination; in this class are the pyrolysis of acetate,[6] xanthates,[6] tertiary amine oxides,[26] and the *trans* isomer of 2-phenylcyclohexyltrimethylammonium hydroxide.[12,13] Where two products of *cis* elimination are possible, the conjugated 1-phenylcyclohexene is preferred over the unconjugated 3-phenylcyclohexene by a ratio of about 85–88 to 12–15. (2) Reactions which appear to be stereospecific with *trans* elimination; the acid-catalyzed dehydration of *cis*-2-phenylcyclohexanol seems to be in this category, since it gives *ca.* 88% of the conjugated 1-phenylcyclohexene.[3] (3) Reactions of low stereospecificity but not involving ring contraction, such as the pyrolysis of *cis*-2-phenylcyclohexyl methyl sulfite. (4) Reactions involving ring contractions. Here are found the pyrolysis of *trans*-2-phenylcyclohexyl methyl sulfite, the acid-catalyzed dehydration of *trans*-2-phenylcyclohexanol and the reaction of *trans*-2-phenylcyclohexylamine with nitrous acid,[15] with the extent of ring contraction increasing in the order given. These data suggest that as the ionic character of the transition state increases (from what may be essentially an ion pair in the pyrolysis of the sulfite[4,27] to an almost free solvated carbonium ion in the nitrous acid reaction), the amount of ring contraction also increases. The large amount (43%) of unconjugated product (3-phenylcyclohexene) resulting in the pyrolysis of *cis*-2-phenylcyclohexyl methyl sulfite may also be explained on the basis of an ion-pair mechanism, since the methyl sulfite part of the ion pair may have a tendency to abstract an adjacent proton on the same side of the molecule (*i.e.*, *cis*) and in the *cis* isomer, a hydrogen *cis* to the methyl sulfite group is available only at position 3 (*cf.* Fig. 1).

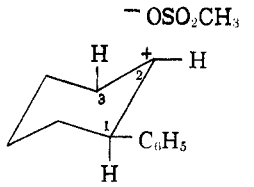


FIGURE 1

EXPERIMENTAL[28]

cis-2-Phenylcyclohexanol (I), m.p. 40–42° (lit.[4] 40–42°) was prepared by Raney nickel hydrogenation of *o*-phenylphenol at 100–110° and 2000–2200 p.s.i.[5]

trans-2-Phenylcyclohexanol (II). Equilibration of commercial mixed 2-phenylcyclohexanol with aluminum isopropoxide[29] was found to be a more convenient route to this isomer than the previously published procedure.[6] Mixed 2-phenylcyclohexanol (417 g., Matheson, Co., Inc.) was equilibrated by boiling with 2700 ml. of anhydrous isopropyl alcohol containing 167 g. aluminum isopropoxide and 9 ml. acetone at reflux for 90 hr. After 2 l. of solvent was distilled, the residue was poured into 3.5 l. of water containing 300 ml. hydrochloric acid. The organic layer was separated, the aqueous layer extracted with ether, and the combined

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(25) D. Sontag, *Ann. chim.*, [11] **1**, 384 (1934).

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

(27) C. C. Price and G. Berti, *J. Am. Chem. Soc.*, **76**, 1207, 1211 (1954).

(28) Elementary analyses by Micro-Tech Laboratories, Skokie, Ill. Infrared analyses by Mr. D. Sweeney on a Perkin-Elmer Model 21 double-beam instrument and by Mr. Rolland Ro on a Baird double-beam instrument. Mass spectra by Mr. George W. Young on a Consolidated Model 21-103A mass spectrometer.

(29) *Cf.* W. G. Dauben, G. J. Fonken and D. S. Noyce, *J. Am. Chem. Soc.*, **78**, 2579 (1956). We thank Professor Dauben for communicating this method to us in advance of publication.

TABLE IV

Physical Data on Product Mixtures from Dehydration of *cis*- and *trans*-2-Phenylcyclohexanols

Expt. No.	Alcohol Dehydrated	Dehydration Method	Yield, %	Boiling Range, °C.	Press., Mm.	n_D^{20}	ϵ_{252}	ϵ_{248}
1	*cis*	H_3PO_4	88	115–130	16	1.5641	9400	10,000
2	*cis*	H_3PO_4	89	115–130	16	1.5637	—	—
3	*trans*	H_3PO_4	85	105–117	12	1.5493	5880	5,830
4	*trans*	H_3PO_4	87	109–121	13	1.5498	5990	—
5	*cis*	Berti[4]	90	115–130	15	1.5583	7140	7480
6	*trans*	Berti[4]	80	116–132	15	1.5550	6950	7040

organic material washed with dilute acid and water, dried, and distilled. After two recrystallizations the *trans*-alcohol melted at 56–57° (lit.[6] 56–57.5°).

Dehydration by phosphoric acid. The procedure was that reported earlier,[5] involving gentle boiling under reflux with an equal volume of phosphoric acid for 4 hr. After dilution with water, extraction with ether, washing with water and drying, the olefin mixtures were distilled through a modified Claisen flask and then redistilled at reduced pressure from sodium. The properties of the products are summarized in Table IV.

Ozonization of 7.9 g. of the dehydration product from the *trans*-alcohol and phosphoric acid followed by distillation gave 0.5 g. of material boiling below 105° (13 mm.), which gave a precipitate with 2,4-dinitrophenylhydrazine. The hydrazone, after recrystallization from ethanol, had a melting point of 237–238°, undepressed on admixture with authentic benzaldehyde 2,4-dinitrophenylhydrazone. None of the cyclopentanone derivative could be isolated, even by alumina chromatography, although the procedure used readily separated a synthetic mixture of the dinitrophenylhydrazones of cyclopentanone and benzaldehyde.

Oxidation of 5 g. of the same mixture of olefins by boiling with aqueous potassium permanganate, followed by filtration and precipitation with acid yielded 2.1 g. of mixed acids, m.p. 120–180°. This was redissolved in a minimum amount of 10% potassium hydroxide. Reacidification precipitated *benzoic acid*, m.p. 119–121°. Continuous extraction of the mother liquor with ether gave 250 mg. of acid. After repeated sublimation and bicarbonate washing, *phthalic anhydride*, m.p. 129–130°, was obtained. Its identity was confirmed by mixed melting point and infrared spectra.

Berti dehydration.[4] The alcohols were converted to their methyl sulfite esters by treatment with methyl chlorosulfinite in pyridine and ether at −5°. The crude esters, *cis*-2-phenylcyclohexyl methyl sulfite (94%), n_D^{20} 1.5320 (lit.[4] 1.5313), and *trans*-2-phenylcyclohexyl methyl sulfite (89%), m.p. 46–48° (lit.[4] m.p. 48–50°), were pyrolyzed without purification and the olefins produced redistilled *in vacuo* over sodium to give material with properties as reported in Table III.

1-Phenylcyclohexene was prepared by heating 1-phenylcyclohexanol (from cyclohexanone and phenylmagnesium bromide), m.p. 60–61° (lit.[11] 62°) with an equal weight of potassium acid sulfate at 140–150° for 0.5 hr. The olefin was twice redistilled. Diagnostic infrared bands[30] were found at 9.44, 10.86, 12.44, 13.48, and 15.27μ (lit.[14] 10.86, 12.42, and 13.44μ).

3-Phenylcyclohexene was prepared both by the Chugaev procedure from *cis*-2-phenylcyclohexanol[6] (b.p. 118–119°/19 mm., n_D^{20} 1.5449) and by reaction of 3-bromocyclohexene[31] with phenylmagnesium bromide[7] (b.p. 114.5–115°/15 mm., n_D^{20} 1.5450). To obtain the low refractive index observed, which agrees with that reported by Alexander and Mudrak[6] and Schaeffer and Collins,[3] it appears important to distill at diminished pressure. Berlande[7] and Berti,[4] who distilled at atmospheric pressure, obtained material of somewhat higher refractive index, possibly due to thermal isomerization. The diagnostic infrared bands[30] of 3-phenylcyclohexene are at 11.23, 11.37, 12.70, 13.86, and 14.88μ (lit.[14] 11.17, 11.33, 12.67, 13.79, and 14.81μ).

1-Benzylcyclopentene (*A*) 1-Benzylcyclopentanol (IX, from cyclopentanone and benzylmagnesium chloride[3]), m.p. 59.5–61° (lit.[3] 58–60°) was dehydrated by heating with oxalic acid.[21] The material boiled at 108–109°/14 mm. and had n_D^{20} 1.5363. The material absorbed in the infrared at 9.32, 9.70, and 10.40μ. Diagnostic bands of benzalcyclopentane (see below) were absent. The same material, b.p. 102–104°/11.5 mm., n_D^{20} 1.5360, was obtained by dehydration of IX with iodine. (*B*) The carbinol IX was converted to the corresponding chloride by shaking with concentrated hydrochloric acid. Dehydrohalogenation with triethanolamine gave material boiling at 103–120°/12 mm., n_D^{20} 1.5362–1.5484. The infrared spectrum indicated that this material was principally 1-benzylcyclopentene.

Benzalcyclopentane (*A*) Crude 1-chloro-1-benzylcyclopentane (X, 208 g.) was brominated in boiling carbon tetrachloride by adding bromine dropwise under illumination by a tungsten projector lamp. The residue of crude α-(1-chlorocyclopentyl)benzyl bromide (VII) left after distillation of the solvent was added dropwise to a well stirred slurry of 150 g. of zinc powder in 1 l. of boiling ethanol. The exothermic reaction required occasional cooling. After addition was completed, another 50 g. of zinc was added and the mixture stirred for 8 hr. Dilution with an equal volume of saturated aqueous calcium chloride, extraction with ether, washing with water, drying and distillation gave 110 g. (65% from 1-benzylcyclopentanol) of crude olefin, b.p. 115–119°/12 mm.

Attempted distillation from sodium at 14 mm. appeared to lead to rearrangement to benzylcyclopentene, since the distillate had n_D^{20} 1.5360. However, distillation over sodium at 1.9 mm. gave material of constant boiling point (86°) and refractive index (n_D^{20} 1.5752).

Anal. Calcd. for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 90.94; H, 8.94.

The sample crystallized when cooled to −20°.

(*B*) Cyclopentylphenylcarbinol (VIII) was prepared in poor yield by the reaction of cyclopentylmagnesium bromide with benzaldehyde.[15] Much benzyl alcohol and cyclopentene were formed also. The desired carbinol boiled at 142–143.5°/13 mm., n_D^{20} 1.5412 (lit.[15] b.p. 110–112°/5 mm., n_D^{20} 1.5412). Application of the Chugaev procedure to this carbinol gave somewhat impure benzalcyclopentane, b.p. 122–123°/14.5 mm., n_D^{20} 1.5655 which did not crystallize at −20° and contained some sulfurous by-product. Nevertheless, the infrared spectrum of this sample was very similar to that of the sample from the above dehalogenation reactions. Diagnostic bands in the infrared are found at 9.84, 10.99, and 11.61μ.

1,3-Endoethylene-1,2,3,4-tetrahydronaphthalene (V) was pre-

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(30) By "diagnostic infrared bands" are meant absorption bands which occur in the given compound but not in any of its isomers looked for in the product mixture.

(31) K. Ziegler, A. Spaeth, E. Schaaf, W. Schumann, and E. Winkelmann, *Ann.*, 551, 80 (1942).

pared from benzene and cyclopentene-1-carboxylic acid[32] as described in the literature.[16] The material boiled at 108–108.[illegible]°/13.5 mm. and had n_{D}^{20} 1.5555. Diagnostic infrared peaks are found at 9.05, 9.45, 9.62, 10.20, 10.35, 10.56, 12.95, and 13.86μ.

Benzylcyclopentane was prepared by hydrogenation of benzylcyclopentene over Raney nickel catalyst at 44 p.s.i. and room temperature; b.p. 103–104°/12.5 mm., n_{D}^{20} 1.5178. The compound has a sharp absorption peak at 9.69μ and lesser peaks at 9.27 and 11.04μ.

Phenylcyclohexane was purified by fractionation of commercial material (Eastman) through a 24-inch helix-packed column, b.p. 107°/13 mm., n_{D}^{20} 1.5255. Diagnostic infrared peaks are found at 9.35, 9.94, 10.03, 11.29, and 11.58μ.

Hydrogenation of reaction products. The reaction products of runs 2, 4, 5, and 6 (Table III) were hydrogenated over Raney nickel at 32–45 p.s.i. at room temperature. The hydrogenated products had the following properties:

Run 4. B.p. 104–105°/13 mm., n_{D}^{20} 1.5217.
Run 5. B.p. 111–113°/15 mm., n_{D}^{20} 1.5261.
Run 6. B.p. 107–108°/14 mm., n_{D}^{20} 1.5240.

The distilled hydrogenation products were analyzed mass spectrometrically,[33] using the 92-peak for benzylcyclopentane (B), 104 for phenylcyclohexane (P) and (in run 4) 129 for 1,3-endoethylene-1,2,3,4-tetrahydronaphthalene (V). The results were as follows:

Run 2. 2.6% B, 97.4% P.
Run 4. 62.6% B, 33.5% P, 3.9% V (n_{D}^{20} calcd.[34] 1.5218. Found: 1.5217).
Run 5. 1.7% B, 98.3% P (n_{D}^{20} calcd.:[34] 1.5254. Found: 1.5261).
Run 6. 21.4% B, 78.6% P (n_{D}^{20} calcd.:[34] 1.5239. Found: 1.5240).

The infrared spectrum of the hydrogenation product of run 4 was compared with that of a synthetic mixture of the indicated composition and there was good agreement in the relative intensity of the peaks.

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[32] Prepared by Mr. Anthony T. Tu by saponification of the ester obtained according to the method developed by the Rev. Conrad Pillar in these laboratories and described by R. L. Kronenthal and E. I. Becker, *J. Am. Chem. Soc.*, **79**, 1095 (1957).

[33] For a brief review with references see: E. L. Eliel, Th. J. Prosser and G. W. Young, *J. Chem. Ed.*, **34**, 72 (1957).

[34] Using the marked values in Table I.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS UNIVERSITY]

Correlation of Ultraviolet Absorption Spectra with Structure of α,β-Unsaturated Acids and Derivatives[1]

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A correlation between the structure and ultraviolet absorption spectra of α,β-unsaturated acids and derivatives has been developed from data found in the literature. For alicyclic and acyclic types each added alkyl substituent at the olefinic double bond produces a bathochromic shift of *ca.* 8–10 mμ. For alicyclic acids a 5-mμ shift is obtained with any exocyclic double bond and each endocyclic double bond in a five- or seven-membered ring. Other structural features which affect the value of the absorption maximum in these compounds are discussed briefly, including hetero atom substitution at the olefinic double bond and extended conjugation. Examples of the utility of the correlation with respect to structure elucidation are presented.

The position and intensity of the ultraviolet region K-band absorption have been found valuable as an aid to structure elucidation, in particular for such compounds as α,β-unsaturated ketones,[3,4] aldehydes,[5] nitroölefins[6] and conjugated dienes.[3c,4] However, no summary correlation between structure and ultraviolet absorption maxima of α,β-unsaturated acids and derivatives has appeared, although their characteristic absorption region (205–230 mμ) is well recognized. Certain workers have noted, in limited series of compounds, the bathochromic displacements produced by increasing substitution at the olefinic double bond,[7–11] and the correlation between ultraviolet absorption and structure in a small group of alicyclic acids.[11,12] The present paper correlates the available ultraviolet spectra of α,β-unsaturated acids and deriva-

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