1.000 g. (2.15 × 10^{-3} mole) of diphenylacetylene dicobalt hexacarbonyl in 20 ml. of methylcyclohexane (b.p. 101°) was refluxed for 31 hours under an atmosphere of nitrogen. Infrared and ultraviolet spectroscopic analyses indicated that 86% of the diphenylacetylene dicobalt hexacarbonyl had been decomposed and that no diphenylacetylene had been formed.

Acknowledgment.—It is a pleasure to acknowledge the assistance of Henry Freiser, of the University of Pittsburgh, in the dipole moment measurements. We wish to thank Morris Mentser, of the Bureau of Mines, for the magnetic susceptibility measurements. We also wish to express our appreciation to John A. Queiser for determining infrared and ultraviolet spectra, to Walter Rosinski and his staff for all macroanalyses, to Anne Svedi for assistance in much of the experimental work, and to Alfred T. Blomquist of Cornell University for a sample of cyclodecyne. This work was supported, in part, by the Air Reduction Chemical Co.

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[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF OAK RIDGE NATIONAL LABORATORY]

Molecular Rearrangements. VI. The Dehydration of *cis*- and of *trans*-2-Phenylcyclohexanol[1]

BY HOWARD J. SCHAEFFER[2] AND CLAIR J. COLLINS

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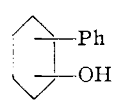
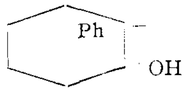
The dehyration of *cis*-2-phenylcyclohexanol-2-C^{14} (Ia) with phosphoric acid has been shown to produce 88% 1-phenylcyclohexene (III) and 2% 3-phenylcyclohexene (IV), in qualitative agreement with the results of Price and Karabinos (ref. 3). When *trans*-2-phenylcyclohexanol-2-C^{14} (IIa) was subjected to the same dehydrating conditions there was produced 21% of 1-phenylcyclohexene (III) but only 9% of 3-phenylcyclohexene (IV). These results are in disagreement with those of previous investigators (ref. 3). In addition to III and IV, the *trans*-alcohol IIa was shown to yield 4-phenylcyclohexene (V), 6%; 1-benzylcyclopentene (VI), 32%, and benzalcyclopentane (VII), approximately 20%. Phenyl migration was shown to occur during the formation of 1-phenylcyclohexene-1,2-C_1^{14} (IIIab) from the *trans*-alcohol IIa. The same mixture of olefins as was produced from the dehydration of the *trans*-alcohol IIa was obtained when labeled 3-phenylcyclohexene (IV) was subjected to the dehydration conditions. These results are discussed, in terms of a mechanism which is consistent with the foregoing observations.

Introduction and Preliminary Results

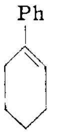
The dehydrations, with phosphoric acid, of *cis*- and of *trans*-2-phenylcyclohexanol (I and II, respectively) were reported in 1940 by Price and Karabinos.[3] The results of this study were interpreted as evidence for the *trans* elimination of the elements of water in such dehydrations, since the *cis*-alcohol was reported to yield chiefly 1-phenylcyclohexene (III) whereas the *trans*-alcohol was said to yield predominantly 3-phenylcyclohexene (IV).



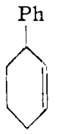
I



II



III



IV

It was suggested[3] that the small amount of isomeric olefin formed in each dehydration was the result either of (a) isomerization of the alcohols I ⇄ II before dehydration, or (b) competitive *cis* elimination of the elements of water from each carbinol.

The Chugaev reactions of the methyl xanthates, and the thermal decompositions of the acetates of I and II were next studied by Alexander and Mudrak,[4] who showed that in each of these reactions *cis* elimination occurred, for the results were the reverse of those reported for the phosphoric acid-catalyzed dehydrations of I and II. Thus, both the acetate and the methyl xanthate of the *cis*-alcohol I yielded primarily 3-phenylcyclohexene (IV), whereas the corresponding *trans* compound yielded principally 1-phenylcyclohexene (III).

The difficulties of determining the yields and identities of liquid, isomeric olefins are indicated by Alexander and Mudrak,[4] who measured the refractive indices of the redistilled products from each reaction for this purpose. These authors point out that the yields calculated by Price and Karabinos[3] are based upon an incorrect refractive index for 3-phenylcyclohexene, but state that the general conclusions[3] concerning the acid-catalyzed dehydrations of I and II remain valid.[5]

By the use of the carbon-14 dilution technique,[6] a method not available to Price and Karabinos[3] at the time of their experiments, it should be possible, by employing carbon-14 labeled reactants, to gain accurate information concerning the yields of olefins III and IV upon dehydration of *cis*-2-phenylcyclohexanol (Ia) and *trans*-2-phenylcyclohexanol (IIa). It should be possible also to determine whether the small amount of 1-phenylcyclohexene (IIIab) obtained upon dehydration of alcohol IIa is the consequence of *cis* elimination of the elements of water, or of participation of the phenyl group during removal of the hydroxyl ion. This latter possibility has been speculated upon by Cram.[5] Thus, in the dehydration of *trans*-2-

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[1] This paper was presented at the 128th meeting of the American Chemical Society, Minneapolis, Sept., 1955, and is based upon work performed under Contract Number W-7405-eng-26 for the Atomic Energy Commission at Oak Ridge National Laboratory; previous paper, C. J. Collins, THIS JOURNAL, **77**, 5517 (1955).

[2] Graduate Fellow of the Oak Ridge Institute of Nuclear Studies from the University of Florida, Gainesville. This paper is taken from the Ph.D. dissertation of H. J. Schaeffer. Senior advisor, University of Florida, Professor W. M. Lauter.

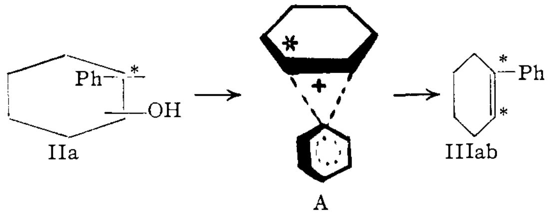
[3] C. C. Price and J. V. Karabinos, THIS JOURNAL, **62**, 1159 (1940).

[4] E. R. Alexander and A. Mudrak, *ibid.*, **72**, 1810 (1950).

[5] See, however, D. J. Cram, *ibid.*, **74**, 2137 (1952), footnote 2.

[6] R. H. Mayor and C. J. Collins, *ibid.*, **73**, 471 (1951).

phenylcyclohexanol-2-C^{14} (IIa) the contribution of such an intermediate ion[5] as A, for example, should



lead to the formation of 1-phenylcyclohexene-1,2-C_1^{14} (IIIab) in which the radioactive carbon is equally divided between the 1- and 2-positions of the cyclohexene ring.

We have repeated the experiments of Price and Karabinos[3] employing *cis*-2-phenylcyclohexanol-2-C^{14} (Ia) and *trans*-2-phenylcyclohexanol-2-C^{14} (IIa), and have determined the yields, for the dehydration of each alcohol, of olefins III and IV. In addition, for the dehydration of IIa, three further olefins have been identified as products, and the extent of phenyl participation in the formation of 1-phenylcyclohexene (IIIab) has been determined. On the basis of our experiments, it has been necessary to modify certain conclusions of the previous investigators.[3] The experimental methods employed, the results of these experiments, and the conclusions drawn from the present work are discussed in the following sections.

Yields of 1-Phenylcyclohexene (IIIa) and 3-Phenylcyclohexene (IVa) on Dehydration of Alcohols Ia and IIa.—The dehydrations of the *cis*- and the *trans*-alcohols Ia and IIa each labeled with carbon-14 in the 2-position were carried out by heating under reflux for four hours equal weights of the appropriate alcohol and 85% phosphoric acid. The mixture from dehydration of each alcohol was analyzed for olefins IIIa and IVa by means of the radioactivity dilution technique,[6] which is described in detail (as are the synthetic procedures), later in this paper. The results of these experiments are given in Table I, and are compared with those of Price and Karabinos.[3]

Although the results of the dehydration of the *cis*-alcohol Ia are in qualitative agreement with those of Price and Karabinos,[3] the results of dehydration of the *trans* compound IIa are in disagreement. Thus, in our hands, the *trans*-alcohol underwent dehydration to produce more 1-phenylcyclohexene (IIIa) than the 3-isomer IVa in the ratio of 2:1. In addition, the two olefins IIIa and IVa previously reported as the sole products of these reactions, account for only 30% of the material yield in the dehydration of the *trans*-alcohol IIa.

Molecular weight determinations of the oil from the dehydration of IIa suggested that this product was a mixture of monomers of the same approximate molecular weight as the olfins IIIa and IVa. The ease of oxidation of this mixture with permanganate suggested the presence of unsaturation.

Our attack on the problem, therefore, was to (1) synthesize a number of olefins isomeric with III and IV, which we suspected by reason of our ability to justify them mechanistically might be present in this mixture; (2) add a weighed amount of each purified olefin to a separate aliquot of the mixture obtained on dehydration of II; (3) reisolate the olefin after homogenizing the solution; (4) convert this olefin to a solid derivative and purify to constant radioactivity content; (5) calculate, from the foregoing data, the yield of the particular olefin.

TABLE I

YIELDS OF 1-PHENYLCYCLOHEXENE (III) AND OF 3-PHENYLCYCLOHEXENE (IV) UPON PHOSPHORIC ACID DEHYDRATION OF *cis*-2-PHENYLCYCLOHEXANOL (Ia) AND OF *trans*-2-PHENYLCYCLOHEXANOL (IIa)

		Yield, %			
Expt.	Reactant	Of III		Of IV	
1	*cis*-Alcohol Ia	88		2.4	
Ref. 3	*cis*-Alcohol I	56–62		9–17	
2	*trans*-Alcohol IIa	18.8	Av. 21.0		
3	*trans*-Alcohol IIa	20.8		9.6	Av. 9.3
4	*trans*-Alcohol IIa	23.4		9.0	
Ref. 3	*trans*-Alcohol II	10–18		59–68	

Additional Methods and Results

Synthetic and Degradative Methods.—The syntheses of *cis*- and *trans*-2-phenylcyclohexanol-2-C^{14} (Ia and IIa) were accomplished as shown in Chart I, the carbon-14 being introduced in the preparation of pimelonitrile-1,7-C_2^{14}. The radiochemical structures of the products were established by oxidation of 1-phenylcyclohexene-1-C^{14}, of 2-phenylcyclohexanone-2-C^{14} and of Ia and IIa to benzoic acid. The benzoic acid fractions obtained from these oxidations possessed lower molar radioactivities than the compounds oxidized by about 2–3%. These results indicate that the alcohols Ia and IIa are discretely labeled with carbon-14 in the 2-position at least to the extent of 97–98%. The lower radioactivity assays of the benzoic acid fractions are caused in all probability by isotope effects occurring during the oxidation of these compounds.

1-Phenylcyclohexene-1-C^{14} (IIIa) was prepared as indicated in Chart I. The degradation of IIIa and the conversion of it to a derivative suitable for radioactivity assay were accomplished in three ways: (a) oxidation of the olefin with potassium permanganate to δ-benzoylvaleric acid (VIII), (b) preparation of the solid 1-phenylcyclohexene nitrosochloride (X), and (c) preparation of 2-phenyl-2-cyclohexenone oxime (XI), followed by oxidation of these derivatives to benzoic acid.

3-Phenylcyclohexene (IV) labeled with carbon-14 was prepared by a modification of the Berlande[7a,b]

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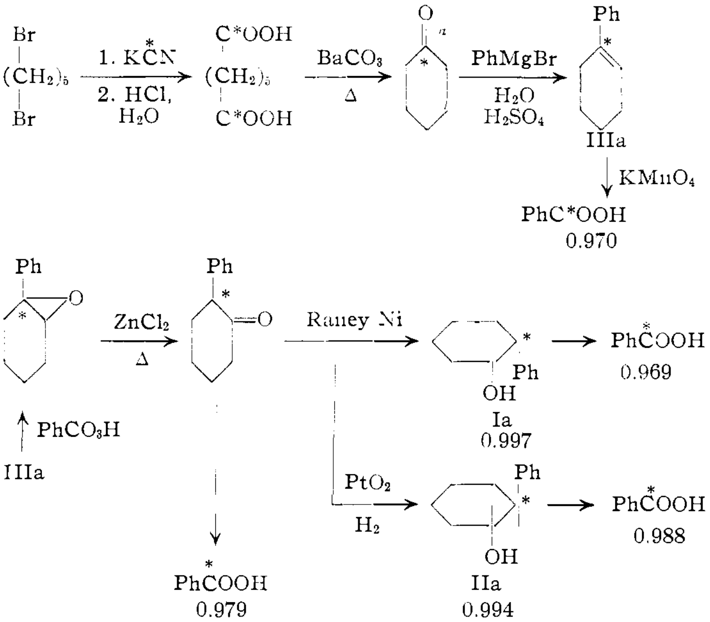
(7) (a) A. Berlande, *Bull. soc. chim.*, [V] **9**, 644 (1942). (b) In this paper Roman numerals have been used to designate the names of the various compounds where repetition of their names would be cumbersome. In the case of radioactive compounds, letters have been appended to the Roman numerals to indicate the position of labeling. Thus, IIa represents *trans*-2-phenylcyclohexanol-2-C^{14} discretely labeled in the 2-position whereas IIIab represents a mixture of 1-phenylcyclohexene-1,2-C_1^{14} labeled at both the 1- and 2-positions.

In the tables, radioactive 3-phenylcyclohexene has been labeled IVa although the amount of carbon-14 adjacent to the phenyl group is only 26% of the total radioactivity. In the synthesis of radioactive 3-phenylcyclohexene an allylic rearrangement probably occurs so that the carbon-14 is distributed among the 1-, 2- and 3-positions in the ratio of 1:2:1. For an example of this type of rearrangement in symmetrical molecules, see R. F. Nystrom and J. C. Leak, THIS JOURNAL, **75**, 3039 (1953).

CHART I



[a] The molar radioactivity of this compound was taken as 1.000. The molar radioactivities of the other compounds listed in this chart are expressed as fractions of the original radioactivity of cyclohexanone-1-C^{14}.

method. Owing to the fact that the position of labeling was unimportant for the isomerization and stability experiments, the radiochemical structure of 3-phenylcyclohexene was not proven exhaustively. It was shown, however, that 26% of the carbon-14 in the cyclohexene nucleus was adjacent to the phenyl group (Table VI). In order to obtain a solid derivative suitable for radioactivity assay, 3-phenylcyclohexene was converted to the solid methoxychloromercury derivative XII, which was also oxidized to benzoic acid.

The synthesis of 4-phenylcyclohexene V was accomplished by the method of Konigsberger and Salmon.[8] This compound was converted to the solid β-phenyladipic acid upon oxidation with chromium trioxide.

1-Benzylcyclopentene (VI) was prepared as described by Denisenko and co-workers.[9,10] This compound was converted to its solid nitrosochloride and the radioactivity content of VI was determined by assay of this derivative.

Benzalcyclopentane (VII) was synthesized by a two-step reaction with benzylcyclopentene (VI) as the starting material. Anhydrous hydrogen bromide was added to VI to give 1-bromo-1-benzylcyclopentane which upon dehydrohalogenation with methanolic potassium hydroxide formed benzalcyclopentane (VII). Benzalcyclopentane is a difficult compound to prepare in pure form since (a) surprisingly, the double bond apparently is more stable in the unconjugated position (compound VI), and (b) most preparations of this material by the present authors contained appreciable amounts of a material, probably an oxidation product, which was difficult to remove (see Experimental section). This compound was degraded by ozonolysis to benzaldehyde whose 2,4-dinitrophenylhydrazone was assayed for radioactivity. This latter assay was taken as a measure of the radioactivity content of olefin VII obtained as a dehydration product of IIa.

In order to ensure that the derivatives of the olefins were radiochemically pure, it was necessary to prepare the various derivatives from mixtures of non-radioactive and radioactive olefins whose radioactivity content was known and determine that no contamination had occurred. For example (see the Experimental section), the radiochemical purity of derivative VIII of 1-phenyl-cyclohexene was determined by oxidizing a mixture of 1-phenylcyclohexene-1-C^{14} (IIIa) and 3-phenylcyclohexene (IV) to δ-benzoylvaleric acid (VIII). A 1% decrease in radioactivity was observed, the same decrease observed upon oxidation of pure IIIa, and most probably caused by an isotope effect. This showed that there was no dilution of the radioactivity by an oxidation product of IV.

Identification of Further Products in the Dehydration of *trans*-2-Phenylcyclohexanol-2-C^{14} (IIa).—In order to determine which compounds, other than IIIa and IVa, were formed as a result of the dehydration of *trans*-2-phenylcyclohexanol, this reaction was repeated using labeled IIa, and the product was divided into several aliquots. To each aliquot a different one of the non-radioactive olefins, 1-phenylcyclohexene (III), 3-phenylcyclohexene (IV), 4-phenylcyclohexene (V), 1-benzylcyclopentene (VI) and benzalcyclopentane (VII) was added. Each of the aliquots was usually subjected to some initial physical method for separating the compound which had been added (and which now was mixed with the radioactive olefin of identical structure which has been formed on dehydration). After this initial partial purification, the liquid compound in question was converted to its appropriate solid derivative. After repeated crystallization of this derivative until its radioactivity content was constant between crystallizations, the yield could be determined with high accuracy. The results of these experiments are given in Table II, together with those results included previously in Table I. The total material yield of these products is about 90%, leaving 10% of the reaction mixture unaccounted for. It is possible, therefore, that one or more unknown products of this reaction may require future identification.

Effect of Dehydrating Conditions on 1- and 3-Phenylcyclohexenes (III and IV).—The stability of 1-phenylcyclohexene (III) was determined by subjecting equal weights of the olefin III and phosphoric acid to the dehydration conditions. The experiments were performed in two ways: (a) by refluxing equal weights of non-radioactive 1-

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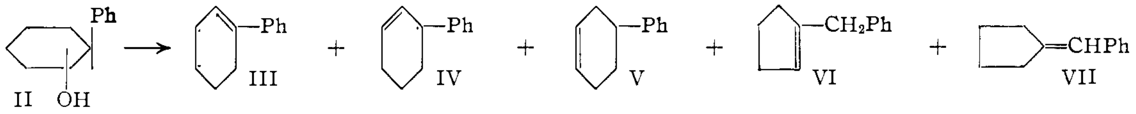
[8] C. Konigsberger and G. Salmon, *J. Polymer Sci.*, 1, 353 (1946).

[9] Ya. I. Denisenko, *Ber.*, **69B**, 1668 (1936).

[10] Ya. I. Denisenko and V. M. Kotel'nikoma, *J. Gen. Chem. (U.S.S.R.)*, **7**, 1357 (1937).

TABLE II

PRODUCTS FORMED UPON DEHYDRATION OF *trans*-2-PHENYLCYCLOHEXANOL (IIa)



Expt.	III	IV	V	VI	VII
2	18.8%				
3	20.8	9.6%			
4	23.4	9.0	6.0%	31.6%	
5			5.7	32.5	*ca.* 20%
Average	21.0	9.3	5.8	32	

phenylcyclohexene and phosphoric acid for 4 hours, diluting with a known weight of 1-phenylcyclohexene-1-C^{14}, and oxidizing the mixture to δ-benzoylvaleric acid (VIII); and (b) by the reverse of the above procedure, that is, by subjecting 1-phenylcyclohexene-1-C^{14} (IIIa) to the dehydrating conditions and diluting with 1-phenylcyclohexene before preparing the derivative. From each of these experiments, the loss of 1-phenylcyclohexene under the dehydration conditions was calculated.

The stability of a mixture of 1-phenylcyclohexene-1-C^{14} (IIIa) and non-radioactive 3-phenylcyclohexene (IV) was next examined. In this case it was necessary to prepare two derivatives of 1-phenylcyclohexene (III). One derivative of III was prepared from an undiluted aliquot of the olefins and the other was prepared from a diluted aliquot. With these two assays both the loss of 1-phenylcyclohexene (III) and the isomerization of 3-phenylcyclohexene (IV) to 1-phenylcyclohexene (III) were then calculated.

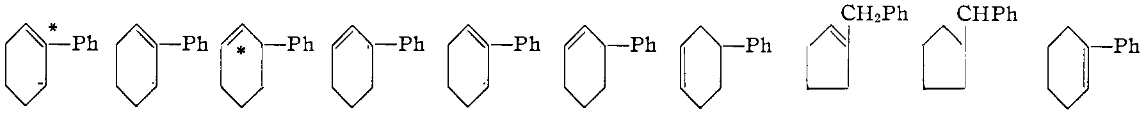
In order to test the stability of 3-phenylcyclohexene (IV), the radioactive olefin IV was heated with phosphoric acid under the same conditions used for dehydrating alcohols Ia and IIa. With the aid of the dilution technique the presence as well as the yields of each of the olefins III, IV, V, VI and VII were determined. It is to be noted that a mixture of the same five isomeric olefins was obtained from the isomerization of radioactive 3-phenylcyclohexene (IV) as was obtained from the dehydration of *trans*-2-phenylcyclohexanol-2-C^{14} (IIa). All of these stability experiments are summarized in Table III.

That the isomerization of 3-phenylcyclohexene (IV) is not measurably reversible was demonstrated in two ways: (a) by subjecting a mixture of 1-phenylcyclohexene-1-C^{14} (IIIa) and non-radioactive 3-phenylcyclohexene (IV) to the dehydrating conditions, diluting with 3-phenylcyclohexene (IV), and preparing the methoxychloromercury derivative XII of 3-phenylcyclohexene; and (b) by refluxing equal weights of non-radioactive benzalcyclopentane (VII) and phosphoric acid for 4 hours, diluting with radioactive 3-phenylcyclohexene (IV) and preparing the same derivative XII. Thus, it was found that neither 1-phenylcyclohexene (IIIa) nor benzalcyclopentane (VII) is isomerized to 3-phenylcyclohexene (see Table VI).

Determination of Phenyl Migration in Reactions Yielding 1-Phenylcyclohexene (III).—*cis*-2-Phenylcyclohexanol-2-C^{14} (IIa) was dehydrated with phosphoric acid as described previously (see Tables I and II) to yield 87.7% of 1-phenylcyclohexene (IIIa). No phenyl migration occurred during this reaction since the benzoic acid obtained on oxidation of IIIa so prepared contained only 2.6% less radioactivity than the parent alcohol Ia, the same decrease of radioactivity observed on oxidation of both the discretely labeled alcohol and the discretely labeled olefin IIIa to benzoic acid, and explainable on the basis of an isotope effect (Chart II). Dehydration of *trans*-2-phenylcyclohexanol-2-C^{14} (IIa) afforded 1-phenylcyclohexene (IIIab) which was oxidized to benzoic acid containing an average of 24.4% less carbon-14 than the parent alcohol (see Chart II). Radioactive 3-phenylcyclohexene (IV)[7b] was isomerized under the de-

TABLE III

ISOMERIZATION PRODUCTS OF 1-PHENYLCYCLOHEXENE AND OF 3-PHENYLCYCLOHEXENE IN REFLUXING PHOSPHORIC ACID



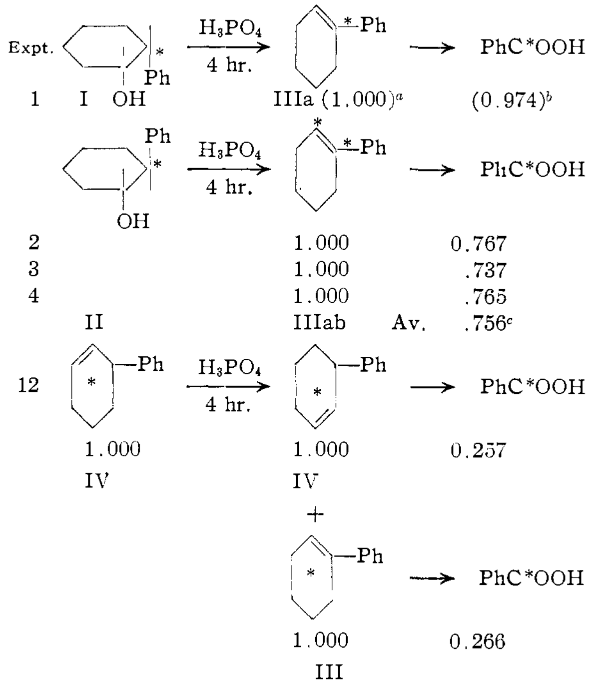
Expt.	Mole % reactant				Isomerization of IV to form, %					Loss of, %
6	0.548	..	..	0.452	12.4[b]	..	..	..	..	6.6[c]
7	0.476	..	..	0.524	12.3[b]	...	..	..	..	7.9[c]
8	..	1.00	..	...	...	...	..	..	..	18.3
9	1.00	..	..	...	...	...	..	..	..	11.4
10	...	..	..	1.00	11.2	...	..	..	..	..
11	...	..	1.00	...	17.2	58.6[a]	11.5	5.9	*ca.* 3	..
12	...	..	1.00	...	6.8	76.2[a]	..	..	..	..

[a] This figure represents the 3-phenylcyclohexene remaining after isomerization. [b] Av. 12.35. [c] Av. 7.3.

hydration conditions to 1-phenylcyclohexene (III) and subsequent oxidation of III to benzoic acid indicated that phenyl migration had not occurred.

CHART II

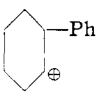
DETERMINATION OF PHENYL MIGRATION IN 1-PHENYLCYCLOHEXENE [III]



[a] The molar radioactivity of product III is actually less than that of I, II or IV, owing to the use of carrier technique in which a known weight of non-radioactive olefin was added to an aliquot from the reaction mixture to facilitate preparation of a solid derivative. This procedure will be fully explained in the Experimental section. [b] The figure was obtained by dividing the molar radioactivity of the benzoic acid by that of IIIa. [c] This corresponds to a *net* phenyl migration of 24%, neglecting the small error introduced by the oxidative isotope effect.

Discussion

From Tables I, II and III it is apparent that the mechanism of dehydration of the *cis-* and *trans*-2-phenylcyclohexanols (I and II) is more complicated than had been previously thought.[3] The implications of these data are as follows: 1. From the fact that Ia and IIa yield the products III–VII in widely differing amounts, we may conclude that these two alcohols do not produce, upon dehydration, a common classical carbonium ion intermediate B. At least one of these alcohols and possibly both must, therefore, undergo dehydration *via* concerted processes.



B

2. If a bridged ion (or its equivalent) were the only intermediate in the formation of 1-phenylcyclohexene (III) from the *trans* alcohol IIa, it is obvious that the radioactivity should be distributed equally between the 1- and the 2-positions of the cyclohexene ring. That the observed phenyl migration is only 24%, however, is readily explainable by reason of the two paths of formation of 1-phenylcyclohexene during the dehydration of IIa. Let us consider that portion of the 1-phenylcyclohexene (IIIab) which is formed by participation of the phenyl group during dehydration, and assume that it has a 50:50 distribution of radioactivity between the 1- and the 2-positions. We have shown experimentally that the portion which is formed by the isomerization of 3-phenylcyclohexene yields unrearranged 1-phenylcyclohexene IIIa. With a knowledge of the total yield of 1-phenylcyclohexene (III) from the dehydration of *trans*-2-phenylcyclohexanol-2-C^{14} (IIa), it is possible to calculate the fraction of radioactivity which should be observed to be lost from the 1-position of the olefin IIIa and IIIab, if we assume that the extent of isomerization of IV → III during this reaction is the same as that observed when labeled IV is placed under similar conditions. Given in Table IV (column 2) are the data for the observed losses of radioactivity in the 1-position of 1-phenylcyclohexene (IIIa and IIIab) during dehydration experiments 2, 3 and 4 (Chart II). The average yield of III in these experiments was 21% (see Tables I and II). From Table III, the yields of III in experiments 6, 7, 10, 11 and 12 have been employed to calculate the percentages given in column 4 of Table IV.

TABLE IV

THE OBSERVED AND CALCULATED PERCENTAGE LOSS OF RADIOACTIVITY IN THE BENZOIC ACID OBTAINED FROM 1-PHENYLCYCLOHEXENE UPON DEHYDRATION OF *trans*-2-PHENYLCYCLOHEXANOL-2-C^{14}

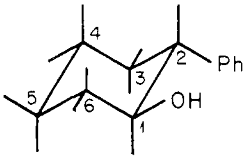
Expt.	Obsd. C^{14} loss, %	Expt.	Calcd. C^{14} loss, %
2	23.3	6	20.5
3	26.3	7	21.0
4	23.5	10	23.7
Av.	24.4	11	9.6
		12	29.1
		Av.	20.8

These calculations, although admitting of much uncertainty, yet may be taken as evidence that the assumption is valid that the labeled 1-phenylcyclohexene formed directly from IIa upon dehydration possesses equal amounts of radioactivity in the 1- and 2-positions.

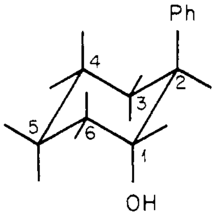
3. It is apparent that 4-phenylcyclohexene (V) must have 3-phenylcyclohexene IV as a precursor. A similar situation obtains for the formation of 1-benzylcyclopentene (VI); that is, it must have benzalcyclopentane (VII) as a precursor (Chart III). It is interesting and surprising that VII should isomerize to VI, with the migration of a double bond from a conjugated to a non-conjugated position. This isomerization is supported, however, by the fact (see Experimental section) that the olefin obtained upon acid-catalyzed dehydration of either phenylcyclopentylcarbinol or 1-benzylcyclopentanol could not be ozonized to produce significant yields of benzaldehyde.

4. The reaction mechanism outlined in Chart III is the simplest mechanism for the dehydration which is consistent with all of the experimental

observations. This mechanism, however, leaves unexplained the following facts: (a) that phenyl migration accompanies the dehydration of *trans*-2-phenylcyclohexanol (II) to 1-phenylcyclohexene (III), whereas phenyl migration does not accompany the isomerization of 3-phenylcyclohexene (IV) to the same olefin III; and (b) that ring contraction of II is preferred over phenyl participation by a factor of about five. By a consideration of the possible conformations which may be assumed by II and IV, these questions are capable of rationalization.



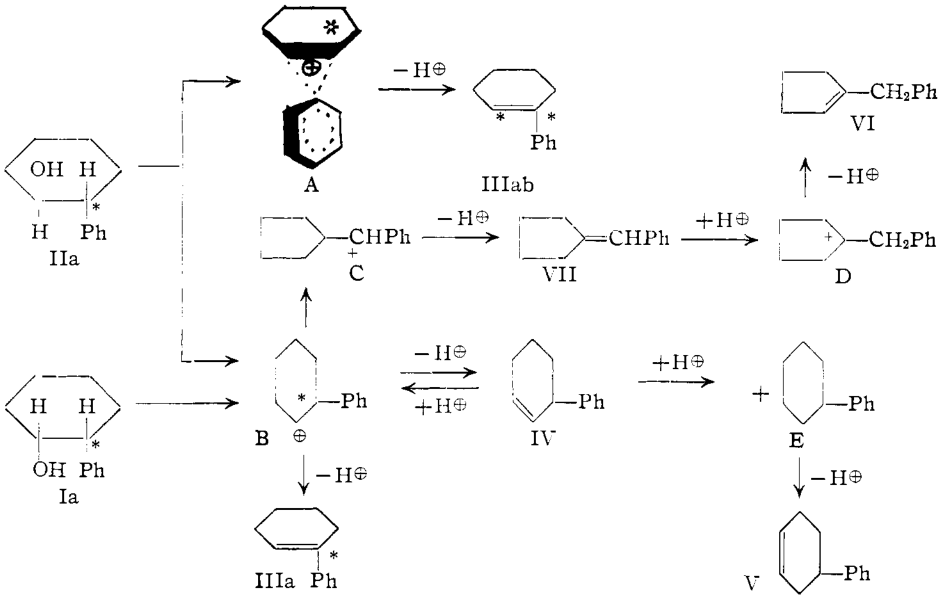
II-1



II-2

CHART III

PROPOSED MECHANISM FOR THE PHOSPHORIC ACID-CATALYZED DEHYDRATION OF *cis*- AND *trans*-2-PHENYLCYCLOHEXANOL



In conformation II-1, the hydroxyl group and the 1-, 2- and 3-carbon atoms all lie in the same plane, thus permitting easy access of the 3 carbon to back-side attack on carbon 1, with resultant expulsion of the hydroxyl group and ring contraction. Although these conformations are undoubtedly in equilibrium, II-1 must surely be preferred over II-2, in which both phenyl and hydroxyl are in axial rather than in equatorial positions. It is only II-2, moreover, which can permit phenyl participation during hydroxyl removal, for only in this conformation are phenyl, hydroxyl and the 1 and 2 carbons in the same plane, thus permitting back-side attack of phenyl on carbon 1 with resultant hydroxyl expulsion and formation of 1-phenylcyclohexene (III). That ring contraction is preferred over phenyl participation by a factor of approximately 5 may, therefore, be rationalized if one assumes a lowered activation energy for ring contraction in II-1 through the "equatorial effect" and an increased activation energy for phenyl migration through the "axial effect."[11a,b]

That ring contraction is preferred over simple elimination is not surprising, since it is only conformation II-2 which allows one of the hydrogens on the 6-carbon ready access to back-side attack on carbon 1. The question of the relative ability of hydrogen to migrate with respect to either alkyl or aryl groups, however, is anomalous, since it has been shown in a previous paper[1] that for the pinacol rearrangement of triphenylethylene glycol, the phenyl/hydrogen migration ratio may vary from 7.3 to 0.04, depending upon the acid catalyst used to effect the rearrangement.

Considering next the conversion of IV[7b] to 1-phenylcyclohexene III *without phenyl migration*, to V and to ring-contracted products, we are again faced with the peculiar position of hydrogen as a migrating group[1] relative to phenyl. It seems, however, that a concerted protonation of the double bond and concurrent ejection of hydrogen from the adjacent 3- or 6-positions of IV is a likely explanation for this result. That hydrogen ejection and ring contraction should be favored to the exclusion of phenyl migration seems reasonable in view of the possible conformations[11a] of a protonated 3-phenylcyclohexene structure. These facts are certainly not predictable, however, on the basis of conformational knowledge. Undoubtedly one of the factors favoring formation of 5-membered rings in this instance is the high relative stability of the potential benzyl-type carbonium ion produced upon contraction of the protonated form of IV.

5. Curtin and Schmukler[11b] have shown ring-contraction to be favored over phenyl migration by a factor of at least 100 in the deamination of *cis*-2-amino-1-phenylcyclohexanol, and by a factor of about 3 in the rearrangement of *cis*-2-chloro-1-phenylcyclohexanol. The latter is in the expected qualitative agreement with the ring contraction/

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(11) (a) See, for example, H. D. Orloff, *Chem. Revs.*, **54**, 347 (1954), and D. H. R. Barton, R. C. Cookson, W. Klyne and C. W. Shoppee, *Chemistry & Industry*, 21 (1954); (b) D. Y. Curtin and S. Schmukler, THIS JOURNAL, **77**, 1107 (1955), have pointed out the importance of the "axial effect" in increasing the activation energy for phenyl participation in conformation II-2. Equally important is the "equatorial effect" for conformation II-1 by which the activation energy for ring contraction is decreased (see also references 11a).

phenyl migration ratio of about 5 for the dehydration of IIa.

6. Dehydration of the *cis* isomer Ia to produce labeled 1-phenylcyclohexene (IIIa) in preponderant yield, and without phenyl migration, is very simply rationalized. In the chair form, the *cis*-alcohol I may assume two conformations: (a) axial phenyl, equatorial hydroxyl and (b) equatorial phenyl, axial hydroxyl. In neither of these does the phenyl group have access to the back-side of carbon 1. Thus phenyl migration can never occur. In the latter conformation, however, *trans*-elimination of water is possible. To explain the high preference for elimination over ring contraction (a factor of greater than 10) it need only be assumed that the "axial-effect" of the phenyl group[11b] causes a preference for that reaction produced through the conformation in which phenyl is equatorial.

Acknowledgment.—The authors wish to acknowledge support and the helpful interest given this research by Professor W. M. Lauter. The authors also acknowledge helpful discussions with Dr. J. F. Eastham.

Experimental

1-Phenylcyclohexene-1-C^{14} (IIIa).—Cyclohexanone-1-C^{14}, prepared by the method of Speer and co-workers,[12] was converted with phenylmagnesium bromide to 1-phenylcyclohexanol-1-C^{14}, and the latter alcohol was dehydrated to the olefin as previously described by Sabatier and Mailhe.[13] Thus, from 42.5 g. (0.43 mole) of the ketone there was obtained 58.7 g. (85%) of twice-distilled 1-phenylcyclohexene-1-C^{14}, b.p. 132–134° (20 mm.). This preparation was repeated several times yielding products whose molar radioactivities were 1–3 mc.

2-Phenylcyclohexanone-2-C^{14}.—By the method of Levy and Sfiras,[14] 45.5 g. (0.46 mole) of IIIa was converted to 51.0 g. (63%) of once-distilled 2-phenylcyclohexanone-2-C^{14}, b.p. 155–161° (15 mm.). After four crystallizations from petroleum ether (30–60°) a pure product was obtained, m.p. 63–64.5°.

***cis*-2-Phenylcyclohexanol-2-C^{14}** (Ia).—2-Phenylcyclohexanone-2-C^{14} (8.0 g.) was dissolved in 100 ml. of absolute ethanol. Raney nickel catalyst (1.2 g.) was added and the mixture was hydrogenated at atmospheric pressure until the theoretical amount of hydrogen had been absorbed (37 hours). The catalyst was removed by filtration, the solvent was removed from the filtrate with the aid of an air stream, and the last traces of the solvent were removed in vacuum. The residue partially crystallized on cooling, the oil was removed by filtration, and the solid was recrystallized from petroleum ether (30–60°) to yield a first crop of the *cis*-alcohol (4.16 g.), m.p. 42–44°.[3] Concentration of the mother liquor yielded two further crops, m.p. 40–42° (total yield, 72%); phenylurethan; m.p. 127–128°.[3]

***trans*-2-Phenylcyclohexanol-2-C^{14}** (IIa).—2-Phenylcyclohexanone-2-C^{14} (16 g., 0.14 mole) was dissolved in 75 ml. of absolute ethanol and 500 mg. of platinum oxide was added. The mixture was reduced overnight in a Parr hydrogenator with an initial pressure of 37.1 p.s.i. of hydrogen. The catalyst was removed by filtration and the solvent was evaporated so that 16.1 g. of a white solid was obtained. The alcohol was recrystallized from petroleum ether (30–60°) several times to yield 11.4 g, (70.5%) of *trans*-2-phenylcyclohexanol-2-C^{14}, m.p. 56–57°. The phenylurethan prepared from IIa had a m.p. of 137–138°.[13,15,16]

3-Phenylcyclohexene-C^{14} (IV).—Cyclohexanone-1-C^{14} (28.4 g., 0.29 mole) was dissolved in 75 ml. of absolute methanol and 400 mg. of platinum oxide was added. The mixture was reduced overnight in a Parr hydrogenator with an initial pressure of 53.5 p.s.i. of hydrogen. In the morning the theoretical amount of hydrogen had been absorbed, so the catalyst was filtered, and the methanol was removed by distillation through an 18-inch Vigreux column. To the residue (28.4 g.), which was almost pure cyclohexanol-1-C^{14}, was added 12 g. of powdered fused potassium hydrogen sulfate and the mixture was distilled through an 18-inch Vigreux column at such a rate that the temperature at the top of the column remained between 75 and 80°.[17] In this way 23.6 ml. (83%) of cyclohexene-C^{14} distilled. Non-radioactive cyclohexene (2 ml.) was added to the residue and it was distilled to scavenge the carbon-14 cyclohexene. The water in the distillate was separated from the cyclohexene-C^{14}, washed once with ether, the ether wash was combined with the cyclohexene-C^{14}, dried with magnesium sulfate and distilled. Pure cyclohexene-C^{14} (23 ml.) distilled at 81–82°. Non-radioactive cyclohexene (2 ml.) was again added to the residue and distilled until the total volume of cyclohexene-C^{14} was 25 ml. (0.246 mole). N-Bromosuccinimide (43.8 g., 0.246 mole), 25 ml. (0.246 mole) of cyclohexene-C^{14} and 100 ml. of carbon tetrachloride were heated under reflux on a steam-bath for 1 hour, cooled, and the succinimide was removed by filtration. The carbon tetrachloride was removed from the filtrate by distillation and 21.4 g. (0.133 mole) of 3-bromocyclohexene-C^{14} was obtained, b.p. 60–63° (12 mm.).[18] To the phenyl Grignard reagent (0.146 mole, 10% excess) prepared from 3.55 g. of magnesium and 22.9 g. of bromobenzene in 100 ml. of ether was added with cooling 21.4 g. (0.133 mole) of 3-bromocyclohexene-C^{14}. After addition was completed the mixture was refluxed for 0.5 hour and decomposed with dilute hydrochloric acid. The ether solution was dried with anhydrous sodium carbonate, filtered, the ether was removed from the filtrate by distillation and the residue was distilled. 3-Phenylcyclohexene distilled at 76–79° (2 mm.) and weighed 14.8 g. (0.094 mole or 32% based on cyclohexanone-1-C^{14}), $n^{20}\mathrm{D}$ 1.5448.

4-Phenylcyclohexene (V).—This olefin was prepared by a modification of the method of Konigsberger and Salmon.[8] 1,3-Butadiene (109 g., 2.2 moles), styrene (68 g., 0.64 mole) and 40 mg. of N-phenyl-2-naphthylamine were heated in a sealed tube at 100° for 120 hours, after which time the tube was cooled and opened. The plastic product was dissolved in hot benzene and most of the polystyrene was precipitated by the addition of methanol. The clear supernatant liquid was decanted, and the precipitate was subjected to the benzene-methanol treatment two more times. The solvent was removed from the decanted liquid by flash distillation and the residue was distilled. There was obtained 23.7 g. (0.15 mole) of 4-phenylcyclohexene, b.p. 115–116.6° (15 mm.), $n^{20}\mathrm{D}$ 1.5412.

1-Benzylcyclopentene (VI).—To 0.57 mole (20% excess) of benzylmagnesium chloride was added 40 g. (0.48 mole) of cyclopentanone. The excess Grignard reagent was decomposed by the addition of just sufficient water to completely hydrate the magnesium salts. The ether solution was decanted and the ether was removed in an air stream. After removal of the last traces of ether in a vacuum, the residue crystallized, and after repeated crystallizations from hexane, 82 g. (98%) of the pure 1-benzylcyclopentanol was obtained, m.p. 58–60°.

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 82.04, 82.00; H, 9.13, 9.20.

Denisenko[9] reported that this compound was a liquid, b.p. 129–130° (11 mm.). 1-Benzylcyclopentanol (44.4 g., 0.25 mole) was refluxed for 4 hours with 200 ml. of 20% aqueous oxalic acid. The two layers were separated and the aqueous layer was extracted with ether, the ether extract was combined with the olefin, washed with water, 5% aqueous sodium bicarbonate, again with water and dried with anhydrous magnesium sulfate. The ether was removed by distillation at atmospheric pressure and the residue was distilled through an 18-inch Vigreux column. 1-Benzylcyclopentene (23.9 g., 66%) distilled at 103–107° (11 mm.), $n^{20}\mathrm{D}$ 1.5367.[9,10]

Benzalcyclopentane (VII).—To 23.9 g. (0.15 mole) of 1-benzylcyclopentene at 0° was added 14.0 g. of dry hydrogen

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(12) R. J. Speer, N. L. Humphries and A. Roberts, THIS JOURNAL, **74**, 2443 (1952).

(13) P. Sabatier and A. Mailhe, *Compt. rend.*, **138**, 1323 (1904).

(14) J. Levy and J. Sfiras, *ibid.*, **187**, 45 (1928).

(15) J. von Braun, H. Gruber and G. Kirschbaum, *Ber.*, **55**, 3668 (1922).

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

(17) L. Brunel, *Bull. soc. chim.*, [III], **33**, 270 (1905).

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

bromide over a 30-minute period. The cloudy solution was refluxed with 25% methanolic potassium hydroxide for 1.5 hours and allowed to stand overnight. Water (300 ml.) was added and the lighter olefin layer was separated. The aqueous layer was extracted with ether, the ether extract was combined with the olefin layer, washed with water and dried with anhydrous sodium carbonate. The ether was removed by distillation at atmospheric pressure and the residue was distilled through an 18-inch Vigreux column. There was obtained 7.8 g. of benzalcyclopentane, b.p. 108–118° (8.5 mm.), $n^{20}\text{D}$ 1.5518.[19]

Preparation of Solid Derivatives of Olefins III, IV, V, VI and VII. (a) **Potassium Permanganate Oxidation of 1-Phenylcyclohexene (III) to δ-Benzoylvaleric Acid (VIII).**—In a typical experiment, 500 mg. (3.16 mmoles) of 1-phenylcyclohexene was dissolved in 40 ml. of acetone and a solution of 2.5 g. of potassium permanganate in 80 ml. of water was added. The mixture was stirred for 15 minutes after which time the oxidation was complete. The manganese dioxide was removed by filtration, and the filtrate was heated on a steam-bath to remove most of the acetone. The basic filtrate was extracted with chloroform, made acid with dilute sulfuric acid and extracted with ether. The ether extract was washed with water and the ether was evaporated leaving 205 mg. (31%) of δ-benzoylvaleric acid which was recrystallized alternately from hexane and water until its melting point was 77–78°.[20]

(b) **1-Phenylcyclohexene Nitrosochloride (X).**—In one of several experiments 910 mg. (5.77 mmoles) of 1-phenylcyclohexene was dissolved in 2 ml. of glacial acetic acid and 0.6 ml. of hydrochloric acid was added. The flask was cooled in an ice-bath while 2.5 g. of isoamyl nitrite dissolved in 2 ml. of glacial acetic acid was added, with stirring, over a 15-minute period. The reaction mixture was stirred for an additional 15 minutes at 0°, 5 ml. of methanol was added, and the nitrosochloride (629 mg.) which precipitated was filtered, washed with methanol, with water and dried, m.p. 128–131° dec. Recrystallization from a mixture of methanol and chloroform produced the pure nitrosochloride, m.p. 134–135° dec. in agreement with the literature.[21]

(c) **2-Phenyl-2-cyclohexenone Oxime (XI).**—To 1-phenylcyclohexene nitrosochloride (629 mg., 2.8 mmoles) prepared as previously described was added 10 ml. of ethanol and 450 mg. of potassium hydroxide dissolved in 2 ml. of water. The mixture was refluxed for 2 hours, poured into 100 ml. of water, cooled and filtered. The 2-phenyl-2-cyclohexenone oxime (313 mg. or 60%) obtained had a melting point of 151–153°. After two recrystallizations from methanol, the pure product was obtained, m.p. 156.5–157.5°.[21]

(d) **Methoxychloromercury Derivative of 3-Phenylcyclohexene (XII).**—3-Phenylcyclohexene (300 mg., 1.9 mmoles) was dissolved in 5 ml. of absolute methanol, 606 mg. (1.9 mmoles) of mercuric acetate was added, and the mixture was shaken until solution was complete. It was allowed to stand at room temperature for 46 hours, filtered, and to the filtrate was added 70 ml. of 10% aqueous sodium chloride solution. The resulting cloudy solution was allowed to stand for 4 hours before it was filtered. The crude derivative weighed 749 mg. (93%) after being washed with water and dried. Two recrystallizations from ethanol gave the pure compound, m.p. 154–155°. The above procedure is a modification of the method of Wright.[22]

Anal. Calcd. for $C_{13}H_{17}OHgCl$: C, 36.71; H, 4.03; Hg, 47.16. Found: C, 36.72, 36.49; H, 4.08, 4.00; Hg, 47.02, 47.20.

(e) **β-Phenyladipic Acid from 4-Phenylcyclohexene.**—In a typical experiment 500 mg. (3.16 mmoles) of 4-phenylcyclohexene was dissolved in 10 ml. of glacial acetic acid and cooled in an ice-bath. A solution of chromium trioxide (850 mg.) in 0.5 ml. of concentrated sulfuric acid, 3 ml. of water and 5 ml. of glacial acetic acid was added dropwise over a 10-minute period while the reaction mixture was being stirred. The reaction mixture was allowed to warm to room temperature and was stirred for an additional 15 minutes, after which time it was poured into 200 ml. of water and extracted with ether. The ether extract was washed with water and extracted with 10% sodium hydroxide solution. The basic extract was made acid with dilute sulfuric acid and extracted with ether. The ether extract was washed with water and evaporated to dryness. There was obtained by this method 232 mg. (33%) of a solid, m.p. 137–140°. After two recrystallizations from a mixture of ether and benzene, a pure sample of β-phenyladipic acid was obtained, m.p. 147–148°.[23]

(f) **1-Benzylcyclopentene Nitrosochloride.**—To a stirred solution of 500 mg. (3.16 mmoles) of 1-benzylcyclopentene (VI) in 1 ml. of glacial acetic acid and 1 g. of isoamyl nitrite cooled in an ice-bath was slowly added 1 ml. of concentrated hydrochloric acid. The mixture was stirred for an additional 15 minutes, 20 ml. of methanol was added, and the mixture was filtered. The white nitrosochloride (96 mg. or 14%) was washed with methanol, water and again with methanol; m.p. 108–109° dec. Two recrystallizations from a mixture of chloroform and methanol gave the pure product, m.p. 109.5–110.5° dec.

Anal. Calcd. for $C_{12}H_{14}ONCl$: C, 64.43; H, 6.31; Cl, 15.85. Found: C, 64.15, 63.86; H, 6.40, 6.35; Cl, 16.03, 16.19.

(g) **Ozonolysis of Benzalcyclopentane to Benzaldehyde 2,4-Dinitrophenylhydrazone.**—Benzalcyclopentane (0.9157 g.) was dissolved in 30 ml. of ethanol and a solution of 2.65 g. of 2,4-dinitrophenylhydrazine in 9 ml. of concentrated sulfuric acid, 5 ml. of water and 40 ml. of ethanol was added. The clear solution was ozonized for 45 minutes at room temperature after which the solid was filtered, washed with ethanol, hot water, hot ethanol and dried. The yield was 1.092 g. (66%), m.p. 211–218°. Two crystallizations from dioxane gave pure benzaldehyde 2,4-dinitrophenylhydrazone, m.p. 237–238°.[24] The melting point was not depressed when mixed with an authentic sample of benzaldehyde 2,4-dinitrophenylhydrazone.

Oxidation of Various Derivatives of 1-Phenylcyclohexene and 3-Phenylcyclohexene to Benzoic Acid. (a) **Oxidation of δ-Benzoylvaleric Acid to Benzoic Acid.**—In a typical experiment, 400 mg. (1.94 mmoles) of δ-benzoylvaleric acid, 2 g. of potassium permanganate, 2 ml. of 10% aqueous sodium hydroxide solution and 30 ml. of water were refluxed for 3 hours, cooled, and the excess potassium permanganate was destroyed with sodium bisulfite. The manganese dioxide was removed by filtration and washed with water. The basic filtrate was extracted with chloroform, made acid with dilute sulfuric acid and extracted with ether. The ether extract was washed with water and the solvent was evaporated so that 210 mg. (88%) of crude benzoic acid was obtained. Two recrystallizations from water produced the pure compound, m.p. 121–122°.

(b) **Oxidation of 1-Phenylcyclohexene Nitrosochloride to Benzoic Acid.**—To 147 mg. (0.62 mmole) of 1-phenylcyclohexene nitrosochloride was added a solution of 1 g. of chromium trioxide in 3 ml. of concentrated sulfuric acid, 3 ml. of water and 20 ml. of glacial acetic acid. The mixture was refluxed for 1 hour, cooled, poured into 200 ml. of water and extracted with ether. The ether extract was washed with water and extracted with 10% sodium hydroxide solution. The basic extract was made acid with dilute sulfuric acid and extracted with ether. On solvent evaporation there was 70.6 mg. (93%) of crude benzoic acid. One crystallization from water, followed by vacuum sublimation at 100° (12 mm.) produced the pure acid, m.p. 121–122°.

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[19] (a) We were unable to obtain a sample of benzalcyclopentane (VII) which contained more than 70% of the olefin (see Additional Methods and Results section). That the most satisfactory preparation did in fact contain VII, however, was evidenced by the yield (66%) of benzaldehyde 2,4-dinitrophenylhydrazone obtained upon ozonolysis of this material. The data of Tables V and VI for compound VII, therefore, were multiplied by two-thirds to obtain the percentage yields of this compound given in Tables II and III. We are indebted to C. C. Price, E. L. Eliel and J. A. McCoy for the information that they have experienced similar difficulty in preparing VII in a pure form. They report $n^{20}\text{D}$ of 1.5752 for the purified samples of VII. (b) L. H. Groves and G. A. Swan, *J. Chem. Soc.*, 871 (1951), report the preparation of this compound by the oxalic acid-catalyzed dehydration of cyclopentylphenylcarbinol. We were unable, however, to obtain a significant yield of benzaldehyde upon ozonolysis of the product obtained by their method. Similar difficulties were encountered in the attempted dehydrations of 1-benzylcyclopentanol.

[20] K. von Auwers and W. Treppman, *Ber.*, **48**, 1217 (1915).

[21] C. F. Koelsch, THIS JOURNAL, **73**, 2951 (1951).

[22] G. F. Wright, *ibid.*, **57**, 1993 (1935).

[23] R. H. Manske, *ibid.*, **53**, 1104 (1931).

[24] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 3d Edition, 1948, p. 229.

TABLE V

RADIOCHEMICAL AND DILUTION DATA FOR THE PHOSPHORIC ACID DEHYDRATION OF *cis*-2-PHENYLCYCLOHEXANOL-2-C^{14} (Ia) AND OF *trans*-2-PHENYLCYCLOHEXANOL-2-C^{14} (IIa)

Expt.	Reactant and wt.	Carrier olefin and wt., g.[a]	Aliquot of reacn. mixt., %	Radioactivity assay of deriv. mc./mole	Yield of added olefin from dehydration, %	Radioactivity assay of benzoic acid mc./mole
1	Ia, 2.8855 g.	III 0.6606	10	0.3401 ± 0.0004[b]	87.7	0.3312
	1.330 mc./mole	IV 0.6118	40	.0519 ± .0002	2.4	
2	IIa, 2.0684 g.	III 1.4669	40	.1161 ± .0007[c]	18.8	.0890 ± 0.00005
	1.334 mc./mole					
3	IIa, 2.1107 g.	III 0.9204	50	.2338 ± .0002[c]	20.8	.1723 ± .0012
	1.326 mc./mole	IV .8285	20	.0554 ± .0004	9.6	
4	IIa, 4.9099 g.	III .7128	40	.9228 ± .0008[c]	23.4	.7057 ± .0022
	2.518 mc./mole	IV .7831	20	.2315 ± .0001	9.0	
		V 1.0533	11.2	.0686 ± .0004	6.0	
		VI 2.0280	5.6	.0933 ± .0006	31.6	
5	IIa, 2.5957 g.	V 0.8810	30	.1082 ± .00005	5.7	
	2.518 mc./mole	VI 1.0466	10	.1700 ± .00005	32.5	
		VII 0.8458	10	.1908 ± .0006	29.8	

[a] The olefin in this column was added to the aliquot of the reaction mixture specified in column four. [b] Assayed as 2-phenyl-2-cyclohexenone oxime. [c] Assayed as 1-phenylcyclohexene nitrosochloride.

TABLE VI

RADIOCHEMICAL AND DILUTION DATA FOR THE PHOSPHORIC ACID ISOMERIZATION OF 1-PHENYLCYCLOHEXENE (III), 3-PHENYLCYCLOHEXENE (IV) AND BENZALCYCLOPENTANE (VII)

Expt.	Reactant and wt.	Carrier olefin and wt., g.[d]	Aliquot of reacn. mixt., %	Radioactivity assay of deriv., mc./mole	Radioactivity assay of benzoic acid, mc./mole	Radioactivity in benzoic acid, %
6	IIIa, 2.2922 g.	III 0.5539	20	0.4140 ± 0.0025[a]	....	....
	1.004 mc./mole					
	IV, 1.8858 g.		40	.8973 ± .0046[b]	....	....
7	IIIa, 1.8946 g.	III .5316	20	.3756 ± .0007[a]	....	....
	1.004 mc./mole					
	IV, 2.0852 g.		40	.8825 ± .0025[b]	....	....
		IV .5636	40	.0004	....	....
8	III, 3.8703 g.	IIIa .3737	100	.1409 ± .0004[a]	....	....
		1.334 mc./mole				
9	IIIa, 3.1477 g.	III 2.0729	100	.5707 ± .0007[a]	....	....
	1.004 mc./mole					
10	IV, 1.1580 g.	IIIa 0.5875	100	1.088 ± 0.0010[a]	....	....
		1.334 mc./mole				
11	IVa, 4.7652 g.	III 0.6340	15	0.3716 ± 0.0016[c]	....	....
	2.293 mc./mole	IV .8094	15	.7816 ± .0024	....	....
		V .7874	15	.2168 ± .0002	....	....
		VI .9761	25	.1543 ± .0006	....	....
		VII .3080	30	.0990 ± .0006	....	....
12	IVa, 4.5558 g.	III 2.1201	60	.1860 ± .0008[c]	0.0495 ± 0.0001	(26.6)[f]
	2.293 mc./mole	IV 2.0946	40	.9143 ± .0005	.2346 ± .0005	(25.7)[e]
13	VII, 2.4431 g.	IV 0.8132	100	2.235	....	....
		2.293 mc./mole				

[a] Diluted with carrier olefin—assayed as δ-benzoylvaleric acid. [b] Undiluted olefin IIIa—assayed as δ-benzoylvaleric acid. [c] Diluted with carrier olefin—assayed as 1-phenylcyclohexene nitrosochloride. [d] The olefin in this column was added to the aliquot of the reaction mixture specified in column IV. [e] Percentage radioactivity adjacent to the phenyl group in IV. [f] Percentage radioactivity adjacent to the phenyl group in III obtained from the isomerization of IV.

(c) **Oxidation of 2-Phenyl-2-cyclohexenone Oxime to Benzoic Acid.**—The oxime (171 mg.) and a solution of 2.5 g. of potassium permanganate in 40 ml. of water were refluxed for 5 hours. The mixture was then cooled, the excess permanganate was destroyed with sodium bisulfite, and the manganese dioxide was filtered. The basic filtrate was extracted with chloroform, made acid with dilute sulfuric acid and extracted with ether. The ether extract was washed with water and the solvent was evaporated. In this way 53 mg. (47%) of crude benzoic acid was obtained. Crystallization from water followed by vacuum sublimation at 100° (12 mm.) produced the pure compound, m.p. 121–122°.

(d) **Oxidation of the Methoxychloromercury Derivative of 3-Phenylcyclohexene.**—The oxidation of the compound was performed in exactly the same way as was the oxidation of 1-phenylcyclohexene nitrosochloride described above. In general, the yields of benzoic acid were 90–95%.

Dehydration of *cis*- and *trans*-2-Phenylcyclohexanol-2-C^{14} (Ia and IIa).—Equal weights of Ia or IIa and 85% phosphoric acid were mixed in a 25-ml. flask and refluxed for 4 hours. After the dehydration was complete the contents of the flask were cooled, water and ether were added, the layers were separated, and the aqueous layer was extracted with ether which was combined with the original ether extracts. The ether extract was washed with water until it was free of acid and made up to volume with ether in a 100-ml. volumetric flask.

The isolation of the olefins was accomplished by the following method: an accurately measured sample was removed from the volumetric flask and diluted with a known weight of non-radioactive olefin. The mixture then was usually subjected to some preliminary purification and the derivative was prepared as previously described. In the case of olefin III, the crude mixture was partially purified by the use of a column of alumina; for olefins IV, V and VI, the crude mixture of olefins was distilled, and for olefin VII, the derivative was prepared without preliminary purification. In Table V are summarized the details of the above-described experiments.

The calculation of the yields of the olefins may best be illustrated by a sample calculation for 1-phenylcyclohexene in experiment 1 (Table V). In the equation[6] $A_1(D_1 + X) = A_0X$

A_0 = specific act. of undiluted IIIa = spec. act. of starting material [Ia] = 1.330 mc./mole

A_1 = measd. spec. act. of deriv. = 0.3401 mc./mole (column V)

D_1 = wt. of non-radioactive 1-phenylcyclohexene (III) added = 0.6606 g. (column III)

X = wt. of 1-phenylcyclohexene-1-C^{14} (IIIa) of specific act. 1.330 mc./mole

then

$$(0.3401)(0.6606 + X) = 1.330(X)$$

$$\frac{X = (0.3401)(0.6606)}{0.990} = 0.227 \text{ g. of III in } 10\% \text{ of the reacn. mixt. (col. IV) or 2.27 g. of III in total reacn. mixt.}$$

Theoretical yield of olefins = 2.59 g.

$(2.27/2.59) \times 100 = 87.7\%$ yield of III

Determination of Phenyl Migration Occurring during the Dehydration of *cis*- and *trans*-2-Phenylcyclohexanol-2-C^{14} (Ia and IIa).—The derivatives of 1-phenylcyclohexene (III) obtained from the dehydration of Ia and IIa (Table V) were oxidized to benzoic acid by one of the methods previously described. The radiochemical data are given in Table V. The latter calculations are straightforward, and are thus not included in the present write-up.

Isomerization of 3-Phenylcyclohexene (IV) and Mixtures of 1- and 3-Phenylcyclohexene (III and IV).—The isomerization experiments of the olefins III and IV were performed under the same conditions that were used for the dehydration. Equal weights of the olefin and phosphoric acid were refluxed for 4 hours. The isolation and the derivative preparation of the olefins was accomplished as previously described in this section for the dehydration reactions. The radiochemical and dilution data are summarized in Table VI.

Determination of Purity of 1- and 3-Phenylcyclohexene (III and IV).—In order to ensure that the derivatives prepared from the various olefins were not contaminated with "spurious" radioactivity, it was necessary to prepare a number of synthetic mixtures of radioactive and non-radioactive olefins, convert them into the corresponding derivatives, and prove that contamination was not a source of error. The results of these experiments are listed in Table VII and signify that these derivatives are almost certainly radiochemically pure.

TABLE VII

RADIOCHEMICAL DATA ON THE PURITY OF 1- AND 3-PHENYLCYCLOHEXENE AND THEIR DERIVATIVES

Expt.	Reactant and wt.	Deriv.	Radioactivity assay of deriv., mc./mole	Calcd. radio-activity of deriv., mc./mole
14	IIIa 4.0 g. 1.004 mc./mole	VIII	0.9955 ± 0.0016	1.004
15	IIIa 0.9931 g. 1.004 mc./mole III 1.0139 g.	VIII	0.4953 ± .0011	0.4968
16	IIIa 0.8624 g. 1.004 mc./mole IV 0.3252 g.	X	1.004 ± .000	1.004
17	IIIa 0.8665 g. 1.334 mc./mole IV 0.3201 g.	VIII	1.320 ± .0015	1.334
18	IVa 0.2198 g. 2.293 mc./mole IV 0.1707 g.	XII	1.286 ± .009	1.291
19	IIIa 1.8946 g. 1.004 mc./mole IV 2.0852 g.	XII	0.0004	0.000

The radioactivity assays reported in this paper were performed with a vibrating reed electrometer using a modification of the wet combustion procedure as described by Neville.[25]

The elemental analyses reported herein were performed by the Huffman Microanalytical Laboratories, Wheatridge, Colorado.

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[25] O. K. Neville, THIS JOURNAL, **70**, 3501 (1948).

OAK RIDGE, TENNESSEE

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MISSOURI]

The Acetylation of Some Dialkylbenzenes. II

BY DOROTHY V. NIGHTINGALE AND JAMES M. SHACKELFORD[1]

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When *m*- and *p*-cymene, *m*- and *p*-*sec*-butyltoluene are acetylated in the presence of aluminum chloride at 0 to +5°, the product in each case is a mixture of 2,4- and 2,5-dialkylacetophenones. If the acetylation of these hydrocarbons and of *p*-di-*sec*-butylbenzene is carried out with anhydrous ferric chloride as the catalyst, there is little or no migration of the *sec*-alkyl group.

In a previous publication,[2] it was established that the acetylation of *p*-di-*sec*-butylbenzene in the presence of aluminum chloride yielded 2,4-di-*sec*-butylacetophenone as the principal product. This was true even though the acetylation was carried out at −10 to −15°. Since this reaction was carried out according to a described procedure[3] for the preparation of aceto-*p*-cymene, it seemed desirable to examine the acetylation product of *p*-cymene.

The procedure described in "Organic Syntheses" is essentially the low temperature acetylation of *p*-cymene as described by Lacourt,[4] who also acetylated *m*-cymene.[5] She found that although the ketones obtained from both *m*- and *p*-cymene formed semicarbazones having different melting points, the melting points of their oximes were the same but no mixture melting points of the oximes were recorded.

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[1] Abstracted from a portion of the dissertation to be submitted by J. M. Shackelford for the degree of Doctor of Philosophy.

[2] D. V. Nightingale and H. B. Hucker, *J. Org. Chem.*, **18**, 1529 (1953).

[3] "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 3.

[4] A. Lacourt, *Bull. soc. chim. Belg.*, **38**, 1 (1929).

[5] A. Lacourt, *ibid.*, **39**, 374 (1930).