An exothermic reaction occurred. After drying with anhydrous sodium sulfate the ethereal solution was distilled under nitrogen. Thirty-five grams of pale yellow liquid was collected, b. p. 60–67° at 30 mm. Similar treatment of the lower layer yielded 40 g. of light yellow oil with the same boiling range and refractive index. They were combined and fractionated through a Vigreux column. Sixty-five grams (94.2%) of nearly colorless oil was obtained, b. p. 82–85° at 45 mm., $n^{27}\text{D}$ 1.4506, $d^{27}_4$ 0.8965. A small amount of water was observed to form during each distillation, and the product gave positive Beilstein and Baeyer tests. A small dark residue remained after the first distillations. On heating a portion of this residue, fumes of hydrogen bromide were evolved. Another portion on being stored for three months had developed the characteristic odor of ethylmethylfulvenol. Calculated *MR* for ethylmethylfulvenol, 43.53; found 44.7.

Difficulty was experienced in effecting complete reduction. For each 10 g. of fulvenol in 10 ml. of absolute ethanol a total of 2 g. of Adams catalyst was used, 0.5 g. being added to the charge at the end of each twelve-hour period. One-half gram of ferric chloride was added with the last increment of catalyst. Approximately 0.16 mole of hydrogen was absorbed; theory requires 0.145. The product, about 8 g. of oil, gave negative Beilstein and Baeyer tests. The *p*H of the aqueous washings was 1.0, and titration of an aliquot of this with standard sodium hydroxide showed the presence of 0.008 equivalent of halide ion per 10 g. of original oil. The oil, after drying over anhydrous sodium sulfate, was distilled. A small fraction, b. p. 153–155° was obtained, which corresponds[18] to the reported b. p. of *s*-butylcyclopentane. The main fraction was collected at 163–167° (80%). Refractionation of this gave pure ethylmethylfulvanol, b. p. 167°; $n^{20}\text{D}$ 1.4266.

*Anal.* Calcd. for $C_9H_{18}O$: C, 76.0; H, 12.75. Found: C, 75.86; H, 12.81.

**Action of Ethyl Sodioacetoacetate on *cis*-3,5-Dibromocyclopentene.**—In the previously described apparatus was placed 1.0 mole of sodium shot and 200 ml. of absolute ether. One mole of ethyl acetoacetate in 200 ml. of absolute ether was introduced, under nitrogen, during a four-hour period. Absolute ether (200 ml.), was again added, and the curd-like mass was allowed to stand overnight. One-half mole of freshly prepared *cis*-3,5-dibromocyclopentene, b. p. 56–58° at 2 mm., in 200 ml. of absolute ether was added dropwise. No observable reaction occurred, and the mixture was allowed to stand overnight. Most of the ether was then removed by distillation, and it was noticed during this operation that the curd-like particles were slowly replaced by crystalline material. After refluxing for two hours, it was again allowed to stand overnight. After addition of water the *p*H of the mixture was 9.0. This was adjusted to 7.0 with dilute hydrochloric acid, and the ether layer was washed once with water and dried over anhydrous sodium sulfate. Upon fractional distillation under nitrogen at 5 mm., 68 g. (70% yield) of pale yellow oil was collected, b. p. 108–109°. A negligible amount of high-boiling residue remained, and no definite fraction could be obtained from it. The oil reacted with bromine, liberating hydrogen bromide, and gave a strong enol (ferric chloride) test. A Beilstein test was feebly positive. It had $n^{27}\text{D}$ 1.4970. *MR* calculated for ethyl $\alpha$-(1-cyclopentadienyl)-acetoacetate, 53.0; found 51.2.

Reduction was effected at 40 p. s. i. g.: twenty-four grams (0.123 mole) in 25 ml. of absolute ethanol was treated with 0.5 g. of Adams catalyst. Hydrogen was absorbed rapidly at first, but the rate became progressively slower. In a twelve-hour period 0.214 mole was taken up, as compared with 0.226 mole required by theory. After removal of the catalyst, the product was fractionated through a short column under nitrogen. The main fraction, 21.5 g., had b. p. 118–120° at 12 mm. The yield of colorless material was 90%. It was free of halogen, and slowly gave the ferric chloride enol test. Upon refractionation it had b. p. 120° at 12 mm., and was pure ethyl $\alpha$-cyclopentylacetoacetate.[13]

*Anal.* Calcd. $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.90; H, 8.96.

## Summary

1. *cis*- and *trans*-3,5-dibromocyclopentene do not react with Grignard reagents in the normal fashion, but yield polymeric products.
2. *cis*-3,5-Dibromocyclopentene does not form a dimagnesium derivative, but is dehydrobrominated to cyclopentadiene.
3. *cis*-3,5-Dibromocyclopentene forms a monomagnesium derivative, since the Barbier reaction with butanone forms ethylmethylfulvenol.
4. A mechanism is proposed for the formation of cyclopentadiene from *cis*-3,5-dibromocyclopentene and magnesium.
5. *cis*-3,5-Dibromocyclopentene monoalkylates ethyl sodioacetoacetate, introducing the cyclopentadienyl group on the methylene carbon atom.

BALTIMORE 18, MD.

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[18] Willstätter, *Ber.*, **46**, 525 (1913).

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

# Studies on the Mechanism of Chugaev and Acetate Thermal Decompositions. I. *cis*- and *trans*-2-Phenylcyclohexanol

BY ELLIOT R. ALEXANDER AND ANTON MUDRAK

The conversion of an alcohol to an olefin by the thermal decomposition of a xanthate prepared from it is called the Chugaev reaction. The formation of olefins from the pyrolysis of carboxylic esters appears to be a related transformation. The unusual feature of these reactions is that they usually avoid the rearrangements which are frequently encountered in the dehydration of certain alcohols by other methods. Thus, pinacolyl alcohol (I) leads to *t*-butylethylene (II) by a Chugaev dehydration[1] (Equation 1) and pure 2-alkyl-1,3-butadienes (IV) have been obtained from the pyrolysis of the corresponding 2-alkyl-3-acetoxy-1-butenes (III)[2] (Equation 2). Dehydration of the alcohols by other methods led to products in which rearrangement had occurred.

Little is known of the actual mechanism of these reactions, and since they are thermal decompositions, the possibility of free radical processes must be considered. It has been suggested, however, that the transformations are initiated by the intramolecular hydrogen bonding of a sulfur

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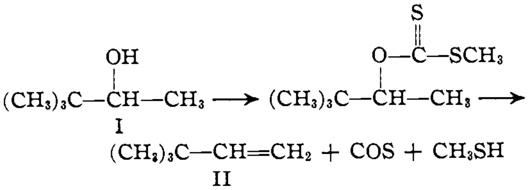
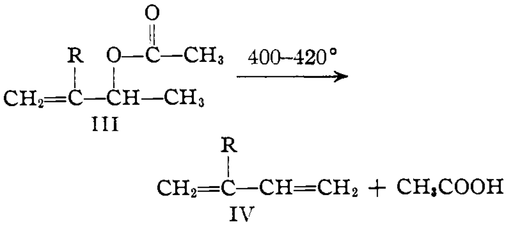
[1] Fomin and Sochanski, *Ber.*, **46**, 244 (1913).

[2] Marvel and Williams, THIS JOURNAL, **70**, 3842 (1948).

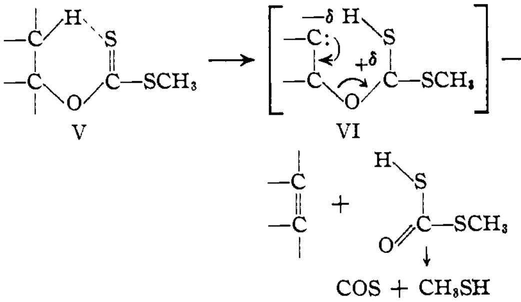


$$\underset{\mathrm{I}}{(\mathrm{CH_3})_3\mathrm{C{-}}\overset{\mathrm{OH}}{\mathrm{CH}}\mathrm{{-}CH_3}} \longrightarrow (\mathrm{CH_3})_3\mathrm{C{-}}\overset{\mathrm{O{-}C(=S){-}SCH_3}}{\mathrm{CH}}\mathrm{{-}CH_3} \longrightarrow \underset{\mathrm{II}}{(\mathrm{CH_3})_3\mathrm{C{-}CH{=}CH_2}} + \mathrm{COS} + \mathrm{CH_3SH} \quad (1)$$



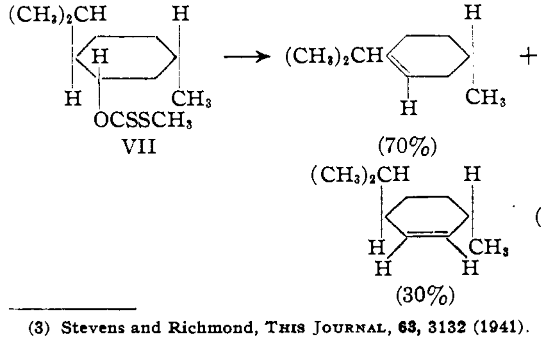
$$\underset{\mathrm{III}}{\mathrm{CH_2{=}}\overset{\mathrm{R}}{\mathrm{C}}\mathrm{{-}}\overset{\mathrm{O{-}C(=O){-}CH_3}}{\mathrm{CH}}\mathrm{{-}CH_3}} \xrightarrow{400\text{–}420°} \underset{\mathrm{IV}}{\mathrm{CH_2{=}}\overset{\mathrm{R}}{\mathrm{C}}\mathrm{{-}CH{=}CH_2}} + \mathrm{CH_3COOH} \quad (2)$$

atom[3,4] or an oxygen atom.[5] Thus, for the Chugaev dehydration, the course of the reaction can be outlined as follows (Equation 3)[4]

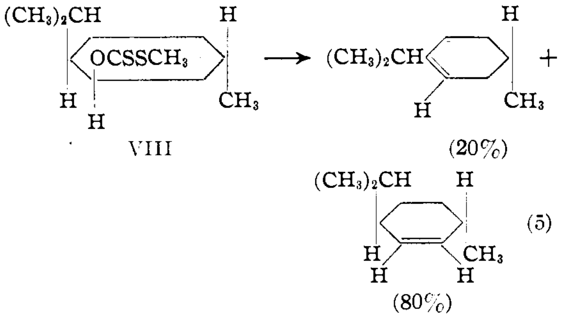


(3)

An analogous sequence may be written for the pyrolysis of carboxylic esters. Support for this mechanism is found in a study of cyclic systems in which *xanthate decompositions lead predominantly to elimination of the cis-β-hydrogen atom.* Methyl *l*-menthylxanthate (VII), for example, gave 70% of 3-menthene (Equation 4) whereas methyl *d*-neomenthylxanthate (VIII) gave 80% of 2-menthene (Equation 5).[6] The decalols also have been investigated,[6] and again *cis*-elimination seems to be indicated. For acetate decompositions, however, there appears to be no stereochemical evidence that the *cis* hydrogen atom is actually the one which is eliminated preferentially in cyclic systems.



(4)



(5)

From the point of view of mechanisms, these reactions are of particular interest, for if the sequence shown in equation 3 is correct, the electronic behavior indicated in VI constitutes an instance in which *a departing group is not displaced by the rearward attack of an unshared electron pair.* In a number of other elimination reactions which have been studied,[7,8,9] *trans* elements appear to be involved.

Accordingly, a study of these reactions, discussed in this and subsequent communications, was undertaken in order to obtain more stereochemical evidence concerning this seemingly unique elimination reaction. In this paper is described the thermal decomposition of the methyl xanthates and acetates of *cis*- and *trans*-2-phenylcyclohexanol. These alcohols were particularly convenient since their dehydration by phosphoric acid has already been studied.[7]

## Experimental[10]

***cis*-2-Phenylcyclohexanol.**—The *cis* isomer was prepared by the catalytic hydrogenation of *o*-phenylphenol.[7] From 255 g. (1.5 moles) of technical *o*-phenylphenol was obtained one fraction of *cis*-2-phenylcyclohexanol amounting to 72.4 g. (41%), m. p. 42–43°, and a second fraction which was not further purified, amounting to 29.1 g. (16%), m. p. 38–40°.

**2-Phenylcyclohexanone.**—This ketone was prepared by the method of Newman and Farbman,[11a] which consists in treating 2-chlorocyclohexanone with phenylmagnesium bromide. Thus, from 368 g. (2.77 moles) of 2-chlorocyclohexanone, 490 g. (3.13 moles) of bromobenzene, 75.4 g. (3.1 moles) of magnesium and 700 ml. of ether was obtained 199 g. (41%) of 2-phenylcyclohexanone, m. p., 56–59°.[7,11a] In our hands this method was more satisfactory than the chromic acid oxidation of *cis*-2-phenylcyclohexanol.[7]

***trans*-2-Phenylcyclohexanol.**—To a stirred solution of 2-phenylcyclohexanone (52.2 g., 0.3 mole) in 150 ml. of commercial absolute ethanol was added portionwise 13.8 g. (0.6 mole) of metallic sodium freshly cut into small pieces. When all of the metal had dissolved, the reaction mixture was diluted with 250 ml. of water and the solution was extracted with one 100-ml. portion and two 50-ml. portions of ether. The combined ether extracts were washed with water, dried over anhydrous magnesium sulfate, and distilled. The fraction boiling at 78–88° (0.3–0.4 mm.) weighed 35.8 g. Recrystallization of the partially solidified distillate from petroleum ether (90–120°) gave 19.0 g. (36%) of *trans*-2-phenylcyclohexanol, m. p. 56–57.5°.[7] The phenylurethan melted at 136–137°.[7] In our hands

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[3] Stevens and Richmond, This Journal, **63**, 3132 (1941).

[4] Hückel, Tappe and Legutke (ref. 6), propose a similar mechanism.

[5] Hurd and Blunck, This Journal, **60**, 2421 (1938).

[6] Hückel, Tappe and Legutke, *Ann.*, **543**, 191 (1940).

[7] Price and Karabinos, This Journal, **62**, 1159 (1940).

[8] Winstein, Pressman and Young, *ibid.*, **61**, 1640 (1939).

[9] Michael, *J. prakt. Chem.*, **52**, 308 (1895).

[10] All melting points and boiling points are uncorrected.

[11a] Newman and Farbman, This Journal, **66**, 1550 (1944).

this method was more satisfactory than the sodium amalgam reduction of 2-phenylcyclohexanone.[7]

**Methyl *cis*-2-Phenylcyclohexylxanthate.**—To a solution of 17.6 g. (0.1 mole) of *cis*-2-phenylcyclohexanol in 65 ml. of dry ether was added 2.5 g. (0.108 mole) of metallic sodium freshly cut into small pieces. The mixture was stirred for thirty hours at room temperature and 10 ml. (12.6 g., 0.16 mole) of carbon disulfide was added in portions. Excess sodium was removed mechanically and stirring was continued for one hour. Methyl iodide (15 ml., 34 g., 0.24 mole) was added and the mixture was stirred overnight. More methyl iodide (5 ml.) was then added and stirring was continued for one hour longer. The inorganic salts were removed by filtration and the volatile material was evaporated under reduced pressure at room temperature. In the final stages of evaporation an oil pump was used to remove the last traces of low-boiling material. The reddish-orange residue was then cooled in an ice-bath and crystallization was induced by scratching. The crude product was recrystallized from 95% ethanol to yield 24.1 g. (90%) of the xanthate, m. p. 44–46°. An analytical sample, which separated in the form of white plates, was obtained after two more recrystallizations from the same solvent, m. p. 49–50°.

*Anal.* Calcd. for $C_{14}H_{18}OS_2$: C, 63.11; H, 6.81. Found: C, 63.25; H, 6.87.

**Methyl *trans*-2-Phenylcyclohexylxanthate.**—The *trans* isomer was prepared by the procedure which has been described for methyl *cis*-2-phenylcyclohexylxanthate. The *trans*-xanthate, however, could not be obtained in crystalline form. All efforts to crystallize the resulting oil were unsuccessful and decomposition occurred on attempted distillation even when a mercury diffusion pump was employed.

***cis*-2-Phenylcyclohexyl Acetate.**—The acetates were prepared by reaction of the alcohol with acetyl chloride in pyridine solution.[11b] From 22.0 g. (0.12 mole) of *cis*-2-phenylcyclohexanol, 110 ml. of dry pyridine, and 16.5 g. (0.21 mole) of acetyl chloride was obtained 23.1 g. (85%) of the corresponding acetate, b. p. 91–106° (0.2–0.3 mm.) $n^{20}D$ 1.5148.

*Anal.* Calcd. for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.08; H, 8.56.

***trans*-2-Phenylcyclohexyl Acetate.**—The *trans* acetate was prepared by the same method that was used for the *cis* isomer. From 17.8 g. (0.1 mole) of *trans*-2-phenylcyclohexanol, 90 ml. of pyridine and 12 ml. (13.3 g., 0.17 mole) of acetyl chloride was obtained 17.0 g. (78%) of *trans*-2-phenylcyclohexyl acetate, b. p. 75–76° (0.2 mm.), $n^{21}D$ 1.5130.

*Anal.* Calcd. for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.08; H, 8.56.

**Saponification of the Acetates of *cis*- and *trans*-2-Phenylcyclohexanol.**—A solution of 1.0 g. of acetate and 25 ml. of 5% alcoholic potassium hydroxide was boiled under a reflux condenser for one and one-half hours. After standing for one hour the solution was diluted with 100 ml. of water and the product was extracted with three small portions of ether. After drying the combined extracts with anhydrous magnesium sulfate, the ether was evaporated. From the *cis*-acetate a product melting at 40–42° was obtained by recrystallization from low-boiling petroleum ether (42–50°). The residue from the saponification of the *trans* acetate melted at 58–59° after one recrystallization from the same solvent. Thus in neither case did isomerization occur during acetylation.

**Decomposition of Methyl *cis*-2-Phenylcyclohexylxanthate.**—The xanthate (5.0 g.) was placed in a 50-ml. round-bottomed flask fitted with a Friedrich condenser. A gas-bubbler was attached to the condenser so that the course of the decomposition could be followed. The flask was immersed in a Wood's metal bath and the temperature was gradually increased. A slight decomposition began when the bath temperature reached 165°. It was then raised to 210–215°, maintained at that level for forty minutes, and then it was increased to 235–240° for five minutes. After cooling, the material in the flask was transferred to a 10-ml. modified Claisen flask and distilled. Two fractions, with a combined weight of 2.1 g. (71%), came over at 70–71° (2 mm.); $n^{20}D$ 1.5448 and 1.5451; $d^{20}_{25}$ 0.9753. In other runs the refractive indices varied from 1.5449 to 1.5457. These values are in fair agreement with that reported by Berlande for 3-phenylcyclohexene ($n^{26}D$ 1.5440).[12] Assuming a change of +0.0004 in the refractive index for each degree decrease in temperature, the reported value can be calculated as 1.5464 at 20°. On the basis of $n^{20}D$ 1.5448, the molecular refractivity (51.37) is in excellent agreement with the calculated value (51.36). Furthermore, preparation of a dibromide as described by Berlande gave a product melting at 109–110°. The reported melting point of 3-phenylcyclohexene dibromide is 111–112°.[13]

**Decomposition of Methyl *trans*-2-Phenylcyclohexylxanthate.**—Decomposition of the crude methyl *trans*-2-phenylcyclohexylxanthate was carried out as described above. The xanthate decomposed appreciably at a bath temperature of 110–115° and rapidly at 175°. In order to free the product of the odor of a mercaptan two distillations were required. Two fractions were collected: b. p. 80–85° (0.7 mm.); $n^{20}D$ 1.5655 and 1.5624. The refractive index of the combined fractions was 1.5644. Assuming that our lowest refractive index, $n^{20}D$ 1.5448, obtained from the decomposition of methyl *cis*-2-phenylcyclohexylxanthate represents nearly pure 3-phenylcyclohexene,[14] and using the value $n^{20}D$ 1.5670 for 1-phenylcyclohexene,[7] the value 1.5644 corresponds to 11.7% of 3-phenylcyclohexene and 88.3% of 1-phenylcyclohexene.

**Pyrolysis of *cis*-2-Phenylcyclohexyl Acetate.**—The apparatus used for the pyrolysis of the acetates consisted of an electrically-heated, vertical Pyrex tube, 40 cm. long and 2 cm. in diameter, packed for a distance of about 30 cm. with Pyrex glass beads of about 6 mm. diameter. Ten ml. of the acetate was allowed to drop into the tube, heated to 575–600°, at a rate of about one drop per second. The pyrolysate was washed with 10% sodium hydroxide and water, dried over anhydrous magnesium sulfate, and distilled. Two fractions, b. p. 55–60° (0.6 mm.), $n^{20}D$ 1.5459 and 1.5470, were obtained. The combined fractions had a refractive index of 1.5464. On the basis of the calculations already described, this corresponds to a mixture of 7.2% of 1-phenylcyclohexene and 92.8% of 3-phenylcyclohexene.

**Pyrolysis of *trans*-2-Phenylcyclohexyl Acetate.**—The *trans* acetate was pyrolyzed by the procedure which has already been described for the *cis* isomer. Three fractions, b. p. 65–67° (0.6 mm.), were collected: $n^{20}D$ 1.5580, 1.5563 and 1.5689. The refractive index of the combined fractions (4.9 g., 68%) was 1.5640. This corresponds to a mixture of 13.5% of 3-phenylcyclohexene and 86.5% of 1-phenylcyclohexene.

**4-Phenylcyclohexanol.**—A solution of 9.7 g. (0.055 mole) of 4-phenylcyclohexanone[15] in 40 ml. of methanol was hydrogenated at low pressure using 4 g. of Raney nickel catalyst. In three hours and forty minutes, the theoretical amount of hydrogen was absorbed. The catalyst was removed by filtration and the solvent evaporated *in vacuo*. The residue solidified on cooling in an ice-bath to give 9.8 g. (98%) of a mixture of *cis*- and *trans*-4-phenylcyclohexanol[16] melting at 61–65°. This material was used in the next step without further purification.

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(11b) For the general method see Hickinbottom, "Reactions of Organic Compounds," Longman's Green and Company, New York, N. Y., 1948, p. 98.

(12) Berlande, *Compt. rend.*, **213**, 437 (1941).

(13) Berlande, *Bull. soc. chim.*, **9**, 644 (1942).

(14) Our value is in agreement with, but slightly lower than, that reported by Berlande. Since any trace of 1-phenylcyclohexene would raise the refractive index of the mixture, it seems probable that the lowest value for the refractive index is the most nearly correct. This conclusion is supported by the excellent agreement of the molecular refractivity with the calculated value.

(15) We are indebted to H. E. Ungnade of the University of Missouri for this material.

(16) H. E. Ungnade, *J. Org. Chem.*, **13**, 361 (1948).

**4-Phenylcyclohexene.**—This material was prepared by a Chugaev dehydration in the manner already described. From the mixture of 4-phenylcyclohexanols was obtained a mixture of xanthates as a heavy orange oil. A small amount of crystalline material separated from the mixture but was not characterized. Thermal decomposition of the xanthates was carried out by heating to 230–240°, until the evolution of gas ceased. The resulting olefin was then purified by refluxing for one hour while a current of air from a capillary tube was allowed to bubble through the liquid. The product was then distilled twice from a modified Claisen flask to yield 4.1 g. (47%) of 4-phenylcyclohexene, b. p. 50–51° (0.1 mm.); $n^{20}$D 1.5440; $d^{20}_{20}$ 0.9779.

*Anal.* Calcd. for $C_{12}H_{14}$: C, 91.08; H, 8.92; $M^{20}$D, 51.35. Found: C, 91.22; H, 9.17; $M^{20}$D, 51.17.

## Results and Discussion

In Table I are summarized the results of our experiments with the *cis-* and *trans*-2-phenylcyclohexyl acetates and xanthates. In column 3 is shown the experimentally determined refractive indices of the various mixtures of olefins obtained from which the values in columns 4 and 5 were calculated. Concerning these values an explanation is in order.

TABLE I

THERMAL DECOMPOSITIONS OF *cis-* AND *trans*-2-PHENYLCYCLOHEXYL (R) ACETATES AND XANTHATES

| Starting material | Dec. temp., °C. | $n^{20}$D | Olefin calcd. from $n^{20}$D, % 3-Phenylcyclohexene | Olefin calcd. from $n^{20}$D, % 1-Phenylcyclohexene |
|---|---|---|---|---|
| *cis*-ROCOCH$_3$ | 575–600 | 1.5464 | 92.8 | 7.2 |
| *cis*-ROCS$_2$CH$_3$ | 210–240 | 1.5448–1.5457 | 96–100 | 0–4 |
| *trans*-ROCOCH$_3$ | 575–600 | 1.5640 | 13.5 | 86.5 |
| *trans*-ROCS$_2$CH$_3$ | 175 | 1.5644 | 11.7 | 88.3 |

In their work showing that the acid-catalyzed dehydration of *cis* and *trans*-2-phenylcyclohexanol involves the preferential removal of a *trans*-β-hydrogen atom, Price and Karabinos[7] calculated the percentages of olefins on the basis of the values $n^{20}$D 1.5530 for 3-phenylcyclohexene and $n^{20}$D 1.5670 for 1-phenylcyclohexene. Inspection of Table I will reveal that the products obtained from the *cis* isomers had lower indices of refraction than either of these values. An examination of the literature, however, revealed that Berlande[12] has since reported physical constants for 3-phenylcyclohexene in fair agreement with those obtained from the decompositions of our *cis* isomers (Berlande's values: $n^{26}$D 1.5440; $d^{26}$ 0.967; m. p. dibromide, 111–112°. Our values are $n^{20}$D 1.5448, $d^{20}_{20}$ 0.9753, m. p. dibromide 109–110°). Furthermore, since 1-phenylcyclohexene boils higher and has a higher refractive index than 3-phenylcyclohexene, it is probable that the first fraction of the mixture of olefins prepared from the thermal decomposition of methyl *cis*-2-phenylcyclohexylxanthate (which had the lowest refractive index of all the samples prepared) is the most nearly pure 3-phenylcyclohexene. This conclusion is further supported by the excellent agreement of the molecular refractivity (51.37) with the calculated value (51.36). It was on the basis of the value $n^{20}$D 1.5448 that the percentages shown in columns 4 and 5 were calculated. It is evident that in direct contrast to the acid catalyzed dehydration of *cis-* and *trans*-2-phenylcyclohexanols, *Chugaev and acetate thermal decompositions involve the preferential elimination of cis-β-hydrogen atoms.*

The identity of the material for which Price and Karabinos reported the value $n^{20}$D 1.5530 is uncertain. It is not 4-phenylcyclohexene. These investigators prepared 4-phenylcyclohexene from styrene and butadiene[17] (8% yield) and we have obtained similar constants by means of a Chugaev dehydration of 4-phenylcyclohexanol. It seems probable, however, that the material in question was a mixture of 1- and 3-phenylcyclohexene. If this interpretation is correct, the general conclusions which have been drawn concerning the acid catalyzed dehydration of these compounds[7] remain valid. Only the exact percentage of olefins formed is affected.

**Acknowledgment.**—We are indebted to Miss Emily Davis and Miss Rachel Kopel for the microanalyses which are reported in this paper.

## Summary

The thermal decomposition of the acetate or methyl xanthate of *cis*-2-phenylcyclohexanol leads predominantly to 3-phenylcyclohexene (92.8–100%) while similar decompositions of the acetates and xanthates from the *trans* alcohol lead to principally 1-phenylcyclohexene (86.5–88.5%). It has already been found[7] that the results are just reversed if dehydration of this same pair of isomeric alcohols is carried out with phosphoric acid. Consequently, this work supports both the conclusion reached by other investigators[6] that the Chugaev reaction proceeds with the preferential elimination of a *cis*-β-hydrogen atom and the suggestion that quasi six-membered rings are formed in the two reactions.[4,5,6]

URBANA, ILLINOIS RECEIVED AUGUST 26, 1949

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[17] Price and Karabinos, THIS JOURNAL, **62**, 2243 (1940).