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Elimination Reactions in Cyclic Systems. III. Mechanism of the Formation of 1-Phenylcyclohexene from Trimethyl-*trans*-2-phenylcyclohexylammonium Hydroxide

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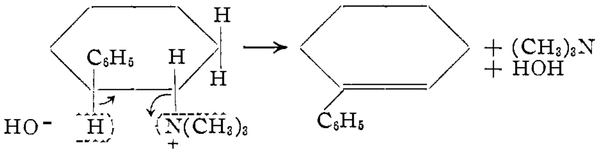
In a recent publication[1] it was shown that the product from a Hofmann degradation of trimethyl-*trans*-2-phenylcyclohexylammonium hydroxide was practically pure 1-phenylcyclohexene. Rather than assume that this product resulted from a direct *cis* elimination and that the reaction constituted an exception to the general rule that *trans* eliminations are favored,[2] the authors postulated that 3-phenylcyclohexene was first formed in the reaction, by a *trans* elimination, and that this initial product was rearranged under the reaction conditions to 1-phenylcyclohexene.



Our investigations of elimination reactions in cyclic systems[3-5] suggested that the increased acidity of the hydrogen attached to the carbon holding the phenyl group might be sufficiently great to allow a *cis* elimination involving this hydrogen to occur more rapidly (giving 1-phenylcyclohexene) than the *trans* elimination involving a relatively non-acidic hydrogen (giving 3-phenylcyclohexene), which was suggested.[1] To test this hypothesis we have prepared 3-phenylcyclohexene and investigated its tendency to rearrange in the presence of base.

An attempt was made at first to obtain 3-phenylcyclohexene from *trans*-2-phenylcyclohexanol by the method of Price and Karabinos.[6] Since this method was found to give a mixture of products,[7] it was abandoned in favor of pyrolysis of the xanthate of *cis*-2-phenylcyclohexanol.[8] This sample of 3-phenylcyclohexene gave an infrared spectrum almost identical with that from the reaction of 3-bromocyclohexene with phenylmagnesium bromide.[9] Reduction of 3-phenylcyclohexene gave phenylcyclohexane identical with a sample obtained by reduction of 1-phenylcyclohexene. It is evident from the ultraviolet absorption spectrum of the sample of 3-phenylcyclohexene obtained by the xanthate method that no more than a small percentage of 1-phenylcyclohexene can be present. These results support the structure assignments and analyses of Alexander and Mudrak.[8]

The extent of rearrangement of 3-phenyl- to 1-phenylcyclohexene on treatment with bases was followed by means of changes in refractive index. Under the conditions used by Arnold and Richardson[1] for the Hofmann reaction no rearrangement was observed.

In order to be sure that the non-homogeneous nature of our reaction mixture was not responsible for the failure of rearrangement, 3-phenylcyclohexene was heated with potassium hydroxide in alcohol solution at 100°. After one-fourth hour the extent of rearrangement was 0%; after 24 hr., 4.5%; after 96 hr., 9.8%; after 192 hr., 14.2%.

A slow rate of isomerization for a similar system was observed by Quelet[10] for the base-catalyzed transformation of allyl-*p*-bromobenzene to propenyl-*p*-bromobenzene. Refluxing for 24 hours with a solution of potassium ethoxide in ethanol caused 40% isomerization; seven hours reflux with potassium amyloxide in amyl alcohol gave 75% isomerization. The slower rate of isomerization observed by us for 3-phenylcyclohexene is consistent with the fact the ionization of a hydrogen in an open-chain system, exemplified by ethyl acetoacetate, is about one hundred times as fast as in a comparable cyclic system, exemplified by 2-carbethoxycyclohexanone.[11] 1,4-Pentadiene also appears to be stable to alkali since it is formed from 1,5-diiodo- or 1,5-dichloropentane by treatment with alcoholic potassium hydroxide.[12]

The possibility that traces of silver oxide might in some way cause rearrangement of 3-phenylcyclohexene to 1-phenylcyclohexene also was eliminated, since 3-phenylcyclohexene was found to be unaffected by heating with a suspension of silver oxide under the reaction conditions.

It is highly probable that 1-phenylcyclohexene is formed in the Hofmann degradation[1] by a *cis* elimination, as indicated in the equation. This is then another example wherein increased acidity of the hydrogen being eliminated promotes a *cis* elimination in preference to a possible *trans* elimination.[3-5]

Experimental

Materials.—*cis*-2-Phenylcyclohexanol was prepared by the method of Price and Karabinos[6] as modified by Berti.[13]

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(1) R. T. Arnold and P. N. Richardson, THIS JOURNAL, **76**, 3649 (1954).

(2) See the discussion in "Structure and Mechanism of Organic Chemistry," by C. K. Ingold, Cornell University Press, Ithaca, N. Y., 1953, Chapter VIII.

(3) J. Weinstock, R. G. Pearson and F. G. Bordwell, THIS JOURNAL, **76**, 4748 (1954).

(4) F. G. Bordwell and R. J. Kern, *ibid.*, **77**, 1141 (1955).

(5) F. G. Bordwell and M. L. Peterson, *ibid.*, **77**, 1145 (1955).

(6) C. C. Price and J. V. Karabinos, *ibid.*, **62**, 1159 (1940).

(7) See C. J. Collins and H. J. Schaeffer, Abstracts of Minneapolis Meeting of the American Chemical Society, September, 1955, p. 56-O; C. C. Price, J. A. McCoy and E. Eliel, *ibid.*, p. 55-O.

(8) E. R. Alexander and A. Mudrak, THIS JOURNAL, **72**, 1810 (1950).

(9) A. Berlande, *Bull. soc. chim.*, [5] **9**, 644 (1942). We wish to thank Dr. C. J. Collins for providing us with samples of 3-phenylcyclohexene made by this method.

(10) R. Quelet, *Bull. soc. chim.*, [4] **45**, 80 (1929).

(11) R. G. Pearson and R. L. Dillon, THIS JOURNAL, **75**, 2439 (1953).

(12) N. Demjanow and M. Dojarenko, *Ber.*, **40**, 2589 (1907); H. B. Dykstra, J. F. Lewis and C. E. Boord, THIS JOURNAL, **52**, 3396 (1930).

(13) G. Berti, THIS JOURNAL, **76**, 1213 (1954).

It was found that alkaline Raney nickel gave material which could not be crystallized. Well-washed Raney nickel gave material which after recrystallization from Skellysolve F at −10° melted at 42–44° (reported[6] m.p. 41–42°).

cis-Phenylcyclohexyl methyl xanthate was prepared by the method of Alexander and Mudrak[8] except that the lithium salt of the alcohol, prepared by means of phenyllithium in ether, was used rather than the sodium salt prepared by the action of sodium in ether. The xanthate was obtained as crystals, m.p. 47–50° (reported[8] m.p. 49–50°).

Pyrolysis of Methyl *cis*-2-Phenylcyclohexylxanthate.—The method of Alexander and Mudrak[8] was used. A 300-ml. flask was equipped with an efficient spiral condenser which was vented *via* a mercury bubbler to a flask containing 45% potassium hydroxide solution which in turn was vented to a hood. In the flask was placed 20.0 g. (0.075 mole) of the xanthate and the flask heated by a metal-bath to 215° for 40 minutes and then to 235–240° for five minutes. The condenser was washed with a small amount of pentane and the product distilled through a 12-cm. Vigreux column to give the following fractions: (1) 1.63 g., b.p. 84–86° at 2.3 mm., $n^{25}\mathrm{D}$ 1.5417, $\lambda_{\max}$ 260 mμ (ϵ 356), at 248 mμ, ϵ 232; (2) 4.80 g., b.p. 86° at 2.3 mm., 85° at 2.2 mm., $n^{25}\mathrm{D}$ 1.5418; (3) 4.95 g., b.p. 85° at 2.2 mm. (also contained material chased from the column by use of an infrared heat lamp), $n^{25}\mathrm{D}$ 1.5421, $\lambda_{\max}$ 260 mμ (ϵ 647), at 248 mμ, ϵ 605; total yield, 11.38 g., 95.5% of theory. The sample of 3-phenylcyclohexene prepared by the method of Berlande[9] had $n^{25}\mathrm{D}$ 1.5432, $\lambda_{\max}$ 253 mμ (ϵ 816), at 248 mμ, ϵ 787. The infrared spectra of fractions 1 and 3 were identical. The spectrum of Collins' sample[9] determined at the same time was identical with the above spectra except that a few of the shoulders were of slightly higher intensity.

A sample of 1-phenylcyclohexene had $n^{25}\mathrm{D}$ 1.5664; $\lambda_{\max}$ 248 mμ (ϵ 12,170).

Phenylcyclohexane. A. From 1-Phenylcyclohexene.—A mixture of 15.8 g. (0.10 mole) of 1-phenylcyclohexene, 25 ml. of methanol, and 100 mg. of 10% palladium-on-charcoal was shaken in a hydrogen atmosphere in a Parr apparatus. The hydrogen uptake became slow after 44 minutes (6.0 lb. used, 86% of theory) so the reaction was stopped, the catalyst removed by filtration, and the product distilled to give (1), 8.3 g., b.p. 111–113° at 13 mm., $n^{25}\mathrm{D}$ 1.5250; (2), 3.1 g., b.p. 113–115°, $n^{25}\mathrm{D}$ 1.5278.

B. From 3-Phenylcyclohexene.—A mixture of 1.0 g. (6.33 mmoles) of 3-phenylcyclohexene, 150 mg. of 10% palladium-on-charcoal and 15 ml. of methanol was stirred in an atmospheric pressure hydrogenation apparatus. In 35 minutes 158 ml. (100% of theory) of hydrogen was absorbed. The catalyst was removed by filtration, the methanol solution diluted with water and extracted with pentane, and the pentane extract washed with water, filtered and distilled. There was obtained 0.90 g. (90%) of product, b.p. 59° at 0.5 mm., $n^{25}\mathrm{D}$ 1.5237; reported for phenylcyclohexane,[14] b.p. 238, $n^{20}\mathrm{D}$ 1.5249. The infrared spectra of the two samples showed them to be the same compound.

Behavior of 3-Phenylcyclohexene under Hofmann Conditions.—A mixture of 1.58 g. (0.01 mole) of 3-phenylcyclohexene, 0.6 g. (0.01 mole) of potassium hydroxide and 1.0 g. (0.01 mole) of triethylamine in 30 ml. of water was refluxed for 1.5 hours. The cooled mixture was then extracted with pentane and the pentane extract washed successively with water, 6 *N* hydrochloric acid, water, saturated sodium bicarbonate solution, and water again. The pentane solution was then filtered and distilled to give 1.45 g. (91.7% recovery) of material, b.p. 80° at 1.7 mm., $n^{25}\mathrm{D}$ 1.5418, infrared spectra identical with the starting material. High recovery was attained in this and the subsequent experiments by forcing the last traces of material out of the distillation column by means of an infrared lamp. This was necessary in order not to lose any 1-phenylcyclohexene which boils higher than the 3-phenylcyclohexene.

The above experiment was repeated using 25 ml. of isopropyl alcohol and 10 ml. of water instead of pure water as solvent. On distillation 1.30 g. (82%) of material was recovered, b.p. 81.5° at 1.7 mm., $n^{25}\mathrm{D}$ 1.4512, infrared spectrum identical with starting material.

Isomerization of 3-Phenylcyclohexene.—Fifty ml. of a solution containing 5.60 g. (0.0352 mole) of 3-phenylcyclohexene and 2.10 g. (0.0375 mole) of potassium hydroxide in commercial absolute alcohol was prepared. Ten-ml. aliquots were placed in Pyrex tubes, flushed with nitrogen, and sealed. The tubes were placed in a 100° steam-bath and removed after the stated intervals. A small amount of a white solid separated from solution when the tubes were first heated. The phenylcyclohexene was recovered by diluting the contents of a tube with water, extracting with pentane, washing the pentane layer, and distilling. In each case about 85% of the olefin was recovered. The refractive index was determined immediately after distillation and this used to calculate the percentage of isomerization.

Time, hours	$n^{25}\mathrm{D}$	Isomerized, %
0.25	1.5418	0
24	1.5428	4.5
96	1.5442	9.8
192	1.5453	14.2

The above samples on standing in stoppered clear glass vials on a desk top for between five and fifteen days had the following $n^{25}\mathrm{D}$: 1.5445 (15 days), 1.5430 (5 days), 1.5460 (10 days), 1.5456 (5 days). Ultraviolet absorption spectra measurements on the 2 five-day specimens gave percentage compositions which checked those determined by refractive index to within 1%. Apparently 3-phenylcyclohexene is not stable toward light and air; formation of a hydroperoxide seems likely since the sample gave a strong positive test with aqueous potassium iodide in the presence of acetic acid.

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Oxidation of Methyl 8-Nitrodehydroabietate

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At the time that the chromic acid degradation of methyl 6,8-dinitrodehydroabietate was being studied[2] a concurrent investigation of the oxidation of methyl 8-nitrodehydroabietate (I) and methyl dehydroabietate (VIII) was being made. We wish now to record the results of this work and in particular to report the successful degradation of the isopropyl side chain of the dehydroabietic structure with chromic acid.

In acetic acid with chromium trioxide at 70° I gives rise to an acidic mixture which loses carbon dioxide at 160°. The decarboxylated product is separable into neutral and acidic crystalline fractions which are interconvertible by treating the former with base and the latter with acetic anhydride. On the basis of physical properties, analyses, ultraviolet and infrared spectra and analogy with the degradation products of methyl 6,8-dinitrodehydroabietate,[2] the neutral substance is formulated as the nitro enol lactone III and the acidic fraction as the nitro keto acid II.

Reduction of II and III with tin and hydrochloric acid gave the corresponding amino keto acid IV and amino enol lactone V. Hypophosphorous acid deamination led to the same two products, neutral and acidic, whether the substance diazotized was IV or V. Furthermore, these two products were interconvertible with the same reagents as II and III. The neutral substance, therefore, is the enol lactone VII and the acidic product the keto acid VI. Assuming that the oxidation of methyl dehydroabietate (VIII) would follow the same path as that of I, the acidic fraction arising from the oxidation of VIII should give,

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[14] G. Egloff, "Physical Constants of Hydrocarbons," Vol. III, Reinhold Publishing Corp., New York, N. Y., 1946, p. 265.

[1] Monsanto Chemical Company, Dayton 7, Ohio.

[2] E. S. Hansen and H. H. Zeiss, THIS JOURNAL, **77**, 1643 (1955).