Mechanisms of Elimination Reactions. XXIV. *trans*-2-Phenylcyclohexyltrimethylammonium Hydroxide[1]

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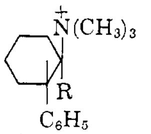
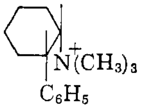
Base-promoted elimination from the *cis* and *trans* isomers of 2-phenylcyclohexyltrimethylammonium ion (I) to give 1-phenylcyclohexene (II) has received some attention in recent years.[2-4]

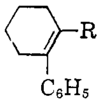
In particular, elimination from the *trans* isomer (Ia) is of interest as it represents a case in which *cis* elimination is preferred over an alternate *trans* elimination possibility. Although the rate and product data[4] suggest that elimination from Ia did not involve a base-catalyzed isomerization of Ia to Ic, followed by the relatively rapid elimination[4] from Ic to II, a simple experimental test was obvious to determine whether isomerization *via* the ylid III was involved.



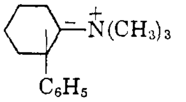
Ia. R = H
b. R = D



Ic



IIa. R = H
IIb. R = D



III

If isomerization *via* III occurred, then transformation of Ib to Ic would occur with deuterium exchange, and the product 1-phenylcyclohexene (II) would be unlabeled. This unlabeling result would, in fact, occur if either alpha- exchange or alpha-elimination was involved, but would not be observed if the only processes involved were beta-elimination (concerted or carbanion[4]) processes. Accordingly Ib was prepared and subjected to base-promoted elimination under conditions previously studied for Ia. The 1-phenylcyclohexene which resulted appeared (infrared analysis) to be entirely the deuterated species IIb and to contain none of the deuterium-free substance IIa, although the amount of hydrogen available in the solvent would have given over 98% unlabeling, had complete exchange occurred. This experiment thus rules out the possibility of epimerization of the quaternary ammonium ion at the nitrogen-bearing carbon atom as being involved in the elimination reactions and indicates that the *cis* elimination process is real and is not an artifact.

EXPERIMENTAL

The deuterium-labeled compounds were prepared substantially as described earlier[4] for the unlabeled compounds, except for the introduction of deuterium by the reduction of 2-phenylcyclohexanonoxime with lithium aluminum deuteride rather than hydride. The *cis* and *trans* amines were benzoylated, separated, and hydrolyzed, then converted to quaternary compounds. The melting points of the labeled compounds did not differ substantially from those of the unlabeled compounds.

Reaction of trans-2-phenylcyclohexyl-1-d-trimethylammonium iodide with ethanolic potassium hydroxide. trans-2-Phenylcyclohexyl-1-*d*-trimethylammonium iodide (Ib) (1.05 g., 3.04 mmoles) was dissolved in 13 ml. of 0.3*N* ethanolic potassium hydroxide, and the solution was sealed in a Pyrex tube and heated at 106° for 24 hr. After being cooled, the tube was opened and the contents were washed into a separatory funnel containing 10 ml. of dilute hydrochloric acid. The contents of the funnel were extracted with three 5-ml. portions of cyclohexane to remove the phenylcyclohexenes, and the cyclohexane solution was dried over anhydrous calcium sulfate. The extraction was continued with three 5-ml. portions of chloroform to remove unchanged starting material, and the chloroform solution was dried over calcium sulfate. The chloroform was then removed by distillation to leave a residue which solidified on standing. This was recrystallized from water to give 120 mg. (11%) of brownish crystals, m.p. 230–235°. An infrared spectrum of this material was identical with that of starting material, proving that the recovered starting material Ib contained little, if any, undeuterated substance Ia.

The solvent was removed from the cyclohexane solution and the product IIb (1-phenylcyclohexene-2-*d*) was distilled to give 154 mg. (32%) of a colorless liquid, b.p. 85° (0.7 mm.). An infrared spectrum of this material when compared with that of 1-phenylcyclohexene (IIa) indicated that very little, if any, 1-phenylcyclohexene was present.

The infrared spectra of the deuterated compounds were different from those of the hydrogen-containing compounds. Differences were mainly in intensity of bands accompanied by small shifts, but there were certain bands which were not common to the hydrogen- and deuterium-containing compounds. 1-Phenylcyclohexene has an absorption band at 847 cm.$^{-1}$ This was completely absent in the recovered 1-phenylcyclohexene-2-*d* which, in addition, had a band at 2240 cm.$^{-1}$ not present in the undeuterated compound. The original and recovered *trans*-2-phenylcyclohexyl-1-*d*-trimethylammonium iodide had a band at 2170 cm.$^{-1}$ not found in the nondeuterated compound. There was also no absorption at 885 cm.$^{-1}$, a wave length where strong absorption is found in the hydrogen-containing compound Ia. The above were the only distinct band differences. In other cases shoulders appeared or disappeared.

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