[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

The Autoxidation of Ethylcyclohexane[1]

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RECEIVED MAY 3, 1956

In the oxidation of pure ethylcyclohexane by molecular oxygen at 120°, oxidative attack was found to be general for all ring hydrogens as well as the side chain secondaries. As might be expected, the tertiary hydrogen was most reactive of all. The secondary ring hydrogens appeared somewhat less reactive than the secondary side-chain hydrogens; those ring hydrogens farthest from the ethyl group were the least reactive.

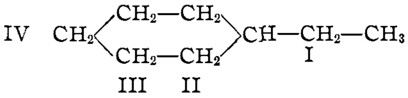
This study of the liquid phase oxidation of ethylcyclohexane by molecular oxygen was undertaken in order to determine whether all ring hydrogens are reactive and to what extent. The presence of secondary hydrogens in the side chain afforded a further means of comparison.

The oxidation was carried out at 120° by bubbling dry oxygen into the pure hydrocarbon for a period of 48 hours. At the end of about 30 hours, vigorous bubbling of the liquid with the evolution of gas was noted. The gas was shown to be mainly acetaldehyde. At the end of 48 hours, the oxidate contained small amounts of acetic, valeric and adipic acids.

At the end of the oxidation period, the oxidate was washed free of acid, dried, and then heated at 120° in an atmosphere of nitrogen to decompose the hydroperoxides which had formed. After decomposition was complete, mixed 2,4-dinitrophenylhydrazones were formed from a sample of the oxidate. The mixture was separated by silicic acid chromatography into three zones by the general procedure of Malmberg.[2] Zone I (top) consisted of cyclohexanone; zone II, 3- and 4-ethylcyclohexanone; zone III, 2-ethylcyclohexanone and methyl cyclohexyl ketone.

A sample of ethylcyclohexane was oxidized to 1% hydroperoxide concentration. The oxidate was assumed to consist mainly of unreacted hydrocarbon with small amounts of mixed alcohols, ketones and hydroperoxides; the amount of acids present at this stage of the oxidation were found to be insignificant. In order to convert the oxidized material to compounds containing a common functional group, the mixture was reduced with $LiAlH_4$ (reduction of both ketones[3] and hydroperoxides[4] to alcohols). The relative amounts of the isomeric alcohols were estimated by a method of differential infrared absorption spectroscopy with a reference series of synthetically prepared alcohols. It will be noted that the secondary side chain hydrogens appear to be somewhat more reactive than the secondary ring hydrogens. Of special interest is the relative inertness of the ring hydrogens farthest from the ethyl group.

On the basis of the alcohols, the reactivity ratio of an average secondary hydrogen to the tertiary hydrogen is about 6:1; the reactivity of secondary hydrogens to each other is: I, 3.4; II, 1.8; III, 2.1; IV, 1.



When the ratio is calculated from the amount of ketone obtained, the reactivity of secondary hydrogens to each other is: I, 4.0; II, 3.1; III, 3.2; IV, 1. Because of the tendency of the hydroperoxide in position I to undergo structural fragmentation to acetaldehyde and cyclohexyl radical during the degradative heating, the activity of the hydrogens in this position is probably greater than calculated. The amount of tertiary reactivity is also probably higher than indicated because of the tendency of the tertiary hydroperoxide to undergo structural fragmentation to cyclohexanone and ethyl radical. Except for acetic acid which originated from acetaldehyde and/or ethyl radicals, the acids presumably originated from cyclohexanone and/or cyclohexyl radicals.

Experimental

Material.—Ethylcyclohexane (Dow Chemical Co.) was distilled at high efficiency and a fraction (b.p. 131.8, n^{20}_D 1.4330) taken.

Apparatus and Method.—Into a 100-ml. 2-neck elongated glass reaction vessel, fitted with a water-cooled condenser and sintered glass inlet tube, was passed dry oxygen at a slow rate. The vessel was filled with ethylcyclohexane and surrounded by an oil-bath maintained at 120°. A tube from the top of the condenser led to a Dry Ice–acetone trap.

Identification of Products. Acetaldehyde.—During the period of bubbling and gassing the exit gases were passed through a solution of 2,4-dinitrophenylhydrazine in 2*N* hydrochloric acid. A precipitate collected over a 2-hour period was filtered and recrystallized from ethanol. It was identified[5] by comparison of its infrared spectrogram with that of an authentic sample of acetaldehyde 2,4-dinitrophenylhydrazone recrystallized from the same solvent.

Anal. Calcd. for $C_8H_8N_4O_4$: C, 42.87; H, 3.60. Found: C, 42.95; H, 3.65.

Ketones.—The ethylcyclohexane oxidate was washed with water, aqueous sodium carbonate and was finally dried over anhydrous sodium sulfate. It was then heated for approximately 100 hours at 120° under an atmosphere of nitrogen to decompose the hydroperoxides which had been formed. An aliquot portion (5 ml.) was shaken overnight with 200 ml. of 2,4-dinitrophenylhydrazine reagent in 2 *N* hydrochloric acid. The mixture was extracted with chloroform, the extract washed briefly with 1 *N* sodium hydroxide and the chloroform evaporated to dryness. The residue was then taken up in about 1 ml. of alcohol-free chloroform and placed on a chromatographic column containing silicic acid–Celite (2:1). The column was prepared with benzene and developed with 5% ether in ligroin. Authentic samples of the 2,4-dinitrophenylhydrazones of cyclohexanone, methyl cyclohexyl ketone, 2-, 3- and 4-ethylcyclohexanones were prepared. These samples were developed under the same conditions as the mixture from the oxidate and the position on the column noted. The mixed 2,4-dinitrophenylhydrazones from the oxidate were developed into three zones. Zone I was found to develop at the same rate as cyclohexan-

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[1] Presented in part before the Division of Organic Chemistry, 124th Meeting of the American Chemical Society, Chicago, Ill., September, 1953.

[2] E. W. Malmberg, THIS JOURNAL, **76**, 980 (1954).

[3] "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 474.

[4] G. A. Russell, THIS JOURNAL, **75**, 5011 (1953).

[5] J. H. Ross, *Anal. Chem.*, **25**, 1288 (1953).

one 2,4-dinitrophenylhydrazone and was identified by comparison of its infrared spectrogram with that of this compound; 3- and 4-ethylcyclohexanone 2,4-dinitrophenylhydrazones and zone II developed at the same rate. 2-Ethylcyclohexanone and methyl cyclohexyl ketone 2,4-dinitrophenylhydrazones developed at the same rate as zone III. The relative amounts of each compound in zones II and III were estimated by comparing the infrared spectrograms of the eluted zones with those of synthetically prepared mixtures. The zones were eluted with ether and weighed in order to obtain the relative amounts of all compounds on the column. The components eluted were found to be: cyclohexanone (12%), methyl cyclohexyl ketone (20%), 2-ethylcyclohexanone (31%), 3-ethylcyclohexanone (32%) and 4-ethylcyclohexanone (5%).

Alcohols.—A sample of oxidate (100 ml.) containing approximately 1% hydroperoxide (based on iodometric titration of active oxygen, assuming C_8-hydroperoxides only) was added to 2 g. of $LiAlH_4$ dissolved in 100 ml. of anhydrous ether. The mixture was refluxed for two hours and then allowed to stand overnight at room temperature. The excess $LiAlH_4$ was destroyed with dilute sulfuric acid, the ethereal solution washed with aqueous sodium carbonate, dried over anhydrous sodium sulfate and the ether removed. The dilute alcohol solution in ethylcyclohexane was then distilled on a small packed column until the alcohol content was about 8%. Infrared examination of this solution showed the complete absence of the carbonyl band. The sample was diluted with an equal volume of fresh ethylcyclohexane and analyzed.

The analysis was carried out in dilute solution to minimize departures from the Beer–Lambert law due to hydrogen bonding and other interference effects. The amount of absorbing material in the optical path was brought up to a sufficient value by use of relatively thick (1-mm.) cells. The solution was placed in a fixed-thickness cell in the sample beam of a Perkin–Elmer model 21 infrared spectrophotometer, and pure ethylcyclohexane in a variable-thickness cell in the reference beam. The variable cell had previously been adjusted to within 0.2% of the thickness of the sample cell by the method of interference maxima. Under these conditions the effective absorption coefficients are those of the solute less the absorption by an equivalent volume of solvent. The absorption coefficients were determined at two characteristic wave lengths for each alcohol by measurements on prepared solutions of a single alcohol in ethylcyclohexane. The wave lengths used were: 1-cyclohexylethanol, 9.38 and 10.68 μ; 1-ethylcyclohexanol, 8.57 and 10.56 μ; 2-ethylcyclohexanol, 10.36 and 12.25 μ; 3-ethylcyclohexanol, 9.65 and 12.32 μ; and 4-ethylcyclohexanol, 8.25 and 9.54 μ.

The solvent absorbs to some extent at each of these wave lengths, but this does not interfere with the application of the method provided a sufficient fraction (5 or 10%) of the total radiation in the beam reaches the detector. The measurements on the unknown dilute alcohol solutions at each of the wave lengths indicated yielded 10 simultaneous equations for the determination of the 5 concentrations. The solution to the equations was obtained by a trial and error method as the absorption coefficients showed some dependence on concentration, and the equations were therefore not accurately linear in the concentrations.

The percentage each of total alcohols was: 1-ethylcyclohexanol, 33.5; 1-cyclohexylethanol, 18.5; 2-ethylcyclohexanol, 19.5; 3-ethylcyclohexanol, 23.0, and 4-ethylcyclohexanol, 5.5.

Acids.—The oxidate was extracted several times with water, the extracts were combined and most of the water was distilled off under reduced pressure. The aqueous distillate was neutralized with sodium hydroxide to a phenolphthalein end-point and evaporated to a volume of 10 ml. To 5 ml. of this (*p*H adjusted to about 6) was added 10 ml. of ethanol and 0.5 g. of *p*-nitrobenzyl bromide and the solution refluxed for one hour. The derivative was recrystallized from aqueous ethanol to a constant melting point (77–78°), lit.[6] m.p. for acetic acid derivative, 78°. The infrared spectrogram of the derivative was identical with that of an authentic sample of *p*-nitrobenzyl acetate.

The residue remaining after distillation of the water extract was further concentrated under reduced pressure at 80°. The sirupy material remaining was refrigerated for several days. The crystalline material which separated was filtered with suction and recrystallized from aqueous ethanol to a constant melting point (151–152°), lit.[7] m.p. for adipic acid 151–152°. It did not depress the melting point of an authentic sample of adipic acid.

The oxidate, after being washed with several portions of water, was shaken with aqueous sodium carbonate. The carbonate extract was neutralized to a methyl red end-point and extracted with ether; an oily product remained on evaporation of the ethereal solution. A *p*-bromophenacyl derivative was formed and recrystallized to a constant melting point (74–75°), lit.[8] m.p. for valeric acid derivative, 75°. The infrared spectrogram of the derivative was identical with that of an authentic sample of *p*-bromophenacyl valerate.

Acknowledgment.—We are indebted to Professor William J. Taylor and Marita D. Wright for carrying out the infrared analysis of the mixed alcohols. We also wish to thank Dr. E. D. Loughran for the infrared work on the mixed 2,4-dinitrophenylhydrazones. This work was supported by the Air Research and Development Command under Contract No. (AF 18(600)787) with The Ohio State University Research Foundation.

COLUMBUS, OHIO

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(6) S. M. McElvain, "The Characterization of Organic Compounds," The Macmillan Co., New York, N. Y., 1945, p. 186.

(7) "Organic Syntheses," Coll. Vol. I, 2nd Edition, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 18.

(8) S. M. McElvain, ref. 6, p. 186.