4. The most probable structure of the two theoretically possible *dl*-1,2-dihydroxybutyric acids is suggested.

5. A modified procedure for the oxidation of the lactone of 3-hydroxy-*iso*crotonic acid with silver and barium chlorates is given.

6. The results of a comparative study of the oxidation of maleic anhydride with silver and barium chlorates are given.

CHICAGO, ILLINOIS

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ELECTRON DISPLACEMENT IN CARBON COMPOUNDS. V. THE ADDITION OF HYDROGEN CHLORIDE TO 3-ETHYL-2-PENTENE[1]

BY HOWARD J. LUCAS

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In order to account for the products formed when strong acids add to derivatives of ethylene, investigators have proposed different hypotheses. Markownikoff[2] many years ago laid down the rule that when hydrogen bromide or other similar compound adds, the negative atom goes to that unsaturated carbon atom which is joined to the larger number of other carbon atoms. But there are many exceptions to this rule, the best recognized being acrylic acid, which with hydrogen bromide forms β-bromo-acrylic acid instead of α-bromo-acrylic acid.

An extension of the Lewis theory of molecular structure[3,4] offers another explanation for these phenomena based upon the electron attraction of radicals.

Making use of the formula diagrams, it is evident that a comparison of these values for H, CH_3 and C_2H_5 is all that need be considered. If the usually accepted order of electron attraction, *viz.*, H > CH_3 > C_2H_5, is correct,[4] then carbon atom C—2 must have a stronger attraction for the four electrons of the double bond than C—3, since its other four electrons are attracted more strongly by H and CH_3 than are the other four electrons about C—3.[5] Thus C—2 is negative with respect to C—3 (b) and when

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[1] Presented at the Claremont meeting of the Pacific Section, American Association for the Advancement of Science, June 15, 1928.

[2] Markownikoff, *J. prakt. Chem.*, **48**, 345, 452 (1892).

[3] Lewis, THIS JOURNAL, **38**, 762 (1916).

[4] Lucas and Moyse, *ibid.*, **47**, 1459 (1925); Lucas, *ibid.*, **48**, 1827 (1926). See also Kharasch and Grafflin, *ibid.*, **47**, 1948 (1925); Kharasch and Marker, *ibid.*, **48**, 3130 (1926).

[5] From their work on the polarization of the isomeric heptanes, Smyth and Stoops, THIS JOURNAL, **50**, 1889 (1928), conclude that any electron shifts existing in these hydrocarbons are so small that they have no appreciable effect upon properties. They also maintain that these and other results provide strong evidence against the assumption

hydrogen chloride adds the halogen should go largely to C—3, producing 3-chloro-3-ethylpentane.

(a) Electron displacement structure (b) Polarity due to electron displacement

Polarity and electron structures of 3-ethyl-2-pentene

The hypothesis of alternate polarity would predict that the isomeric 2-chloro-3-ethylpentane would be the principal product.

Hydrogen chloride was selected as the addendum because (a) the aliphatic chlorides are more stable than the bromides and iodides, a very important factor when dealing with easily dissociated secondary and tertiary halides,[6] and (b) the bromides of the higher alcohols boil at temperatures close to those of the alcohols themselves, whereas the chlorides boil considerably lower.

In order to obtain the desired chlorides it was first necessary to prepare the corresponding alcohols, 3-ethyl-2-pentanol and 3-ethyl-3-pentanol (triethylmethanol). The former was obtained from 3-ethyl-2-pentanone by reduction with sodium according to the procedure used for other alcohols,[7] and the latter from ethyl bromide and diethylketone by the Grignard method. In carrying out the synthesis of these two alcohols the author was assisted by W. P. Baxter, whose valuable aid is hereby gratefully acknowledged.

The preparation of the two chlorides, 2-chloro-3-ethylpentane and 3-chloro-3-ethylpentane, was accomplished at room temperature by stirring the corresponding alcohol with concentrated hydrochloric acid and zinc chloride and removing the acid layer every few hours. This process resembles the method of Norris and Taylor,[8] who heat the reacting substances, but is a modification which seemed desirable in order to avoid elevated temperatures at which isomeric change would be more rapid. Such a change has been observed in the case of certain alkyl halides.[9] Zinc chloride is a necessary catalyst for the reaction between hydrochloric acid and 3-ethyl-2-pentanol, which undergoes only a 75% conversion

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of any considerable variation in the position of the electron pairs even in other series of compounds. See also Smyth, *ibid.*, **46**, 2151 (1924); Krchma and Williams, *ibid.*, **49**, 2408 (1927).

[6] Whereas the chloride obtained from 3-ethyl-2-pentanol could be distilled at atmospheric pressure with only slight decomposition, the bromide evolved hydrogen bromide strongly when heated.

[7] Wislicenus, *Ann.*, **219**, 309 (1883).

[8] Norris and Taylor, THIS JOURNAL, **46**, 753 (1924).

[9] Wischnegradsky, *Ann.*, **190**, 342 (1878), observed that in the reaction of secondary *iso*-amyl alcohol with hydrochloric and hydriodic acids, the products are tertiary halides, not secondary. Michael and Zeidler, *ibid.*, **393**, 81 (1912), and Michael, Scharf and Voigt, THIS JOURNAL, **38**, 653 (1916), observed that pure *iso*butyl bromide slowly changed to the tertiary compound.

after forty hours without zinc chloride, but is completely converted after sixteen hours in the presence of zinc chloride. Although no attempt was made to determine the minimum time necessary for complete conversion, it is probable that a shorter time would suffice. In view of the fact that tertiary butyl alcohol reacts readily with concentrated hydrochloric acid alone,[10] it is probable that the tertiary heptyl alcohol would have behaved in a similar fashion. However, in order to obtain complete conversion the tertiary chloride was prepared in the same way as the secondary, that is by the use of zinc chloride at room temperature. The attempt to extend the method to primary *iso*butyl alcohol was unsuccessful, no chloride resulting even after several days.

The unsaturated hydrocarbon, 3-ethyl-2-pentene, is readily obtained from the tertiary alcohol, 3-ethyl-3-pentanol, by heating at 100° under a reflux cooler with anhydrous oxalic acid. It combines with hydrogen chloride dissolved in glacial acetic to give a quantitative yield of a heptyl chloride, the properties of which are given in Table I.

In Table I are listed the two heptyl alcohols, the heptene, the two heptyl chlorides, the reaction product and some of the physical properties of these compounds. The boiling points, taken with short Anschütz thermometers, needed no correction and are given as read; the densities were determined on small samples by the plummet method and are corrected for buoyancy; the refractive indices were determined with an Abbé re-

TABLE I

PHYSICAL CONSTANTS

	Boiling points (corr.)			Densities, $^{25}_{25}$ Dried over		Refractive Indices	
	50 mm.	90 mm.	743 mm.	K_2CO_3	P_2O_5	n^{20}_D	n^{25}_D
1 3-Ethyl-2-pentanol	82.0–82.5	....	151.0–151.5	0.8359	....	1.4284	1.4264
2 3-Ethyl-3-pentanol	72.5–73.5	83.5–84.0	140.5–141.5	.8438	....	1.4305	1.4281
3 3-Ethyl-2-pentene	....	....	95.0–95.5 (745)	.7190	....	....	1.4128
4 2-Chloro-3-ethylpentane	60.0–63.5	77.0–77.5	142.5–143.0	.8911	0.8874	1.4319	1.4295
5 3-Chloro-3-ethylpentane	83.0–83.5 (100)	78.5–79.0 (93)	143.0–144.0 (decompn.)	.8945	.8917	1.4334	1.4311
6 Reaction product	....	78.0–79.0	....	.8948	.8916	....	1.4311

Constants previously given are for 1, b. p. 148–152°; d°, 0.8531 (ref. 14); for 2, b. p. 141–143° (ref. 17a), 142° (764 mm.) (ref. 17b), 141–148° (746 mm.)(ref. 17f), 130–140° (ref. 17g); d^{20}_{20}, 0.84016 (ref. 17a); for 3, b. p., 97–98°; d^{20}_{0}, 0.72225; d^{15}_{0}, 0.72544 (ref. 17d); for 5, b. p., 143–144°; d^{25}_{4}, 0.8644; n^{25}_{D}, 1.43276 (ref. 17e).

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[10] Davis and Murray, *Ind. Eng. Chem.*, **18**, 844 (1926).

fractometer which was checked at frequent intervals against the standard prism.

The close agreement in the properties of the reaction product and of 3-chloro-3-ethylpentane indicates that this substance constitutes 95–100% of the material formed when hydrogen chloride in glacial acetic acid adds to 3-ethyl-2-pentene. The reaction therefore follows the course predicted on the assumption that the electron attractions of the atoms and radicals attached to the unsaturated carbon atoms are in the order H > CH_3 > C_2H_5. The course is similar to that between this heptene and sulfuric acid, the product of which was assumed to be the tertiary alcohol, since it was completely decomposed on repeated distillation at atmospheric pressure.[11]

Experimental Part

3-Ethyl-2-pentanone (Unsymmetrical Diethylacetone).—This was obtained in 30% yield by passing a mixture of acetic and diethylacetic acids over thorium oxide at 410–430° and in 31% yield through the acetoacetic ester synthesis in which the diethylacetoacetic ester first produced was decomposed by barium hydroxide according to the general method of Wislicenus.[12] A modification was introduced by using, in place of the 0.25 *N* solution of barium hydroxide, one approximately twice as concentrated. The material obtained by the pyrolysis method boiled at 136–140° and had a refractive index, n_D^{20}, of 1.4076; that by the decomposition of the ester boiled at 136–137° under a pressure of 745 mm.[13] and had a refractive index, n_D^{20}, of 1.4073.

3-Ethyl-2-pentanol.—This has been obtained, along with other products, by the action of chloro-acetone upon ethylmagnesium bromide.[14] The reduction of 3-ethyl-2-pentanone by means of metallic sodium according to the method used for the reduction of other ketones[7] using, however, twice the amount of sodium necessary for the reaction and diluting the ketone with four times its volume of ether in order to decrease the amount of pinacol produced, gave the desired alcohol in 70% yield and the corresponding pinacol in 8% yield. Complete reduction of the ketone can be brought about by using the excess of sodium recommended. The alcohol, 48 g., distilled at 82.0–82.5° (corr.) under a pressure of 50 mm. and at 151–151.5° (corr.) under 743 mm. without decomposition. It has a pronounced camphor-like odor.

4,5-Dimethyl-3,6-diethyl-4,5-octanediol.—The pinacol obtained in the reduction of 3-ethyl-2-pentanone after two crystallizations from alcohol melted at 100.7–101.2° (corr.). Three determinations of its molecular weight by the micro method of Smith and Young[15] gave 235,[16] which agrees well with 230, the value calculated from $C_{14}H_{30}O_2$.

3-Ethyl-3-pentanol.[11,17]—From 86 g. (1 mole) of diethyl ketone, b. p. 101.2–103.2°,

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[11] Brooks and Humphrey, This Journal, **40**, 835 (1918).

[12] Wislicenus, *Ann.*, **190**, 250 (1877); **206**, 308 (1880).

[13] Other values for the boiling point are 137.5–139°, Franklin and Duppa, *Ann.*, **138**, 212 (1866); 138° (760 mm.), Clarke, *Am. Chem. J.*, **39**, 574 (1908); 138°, Tiffeneau and Dorlencourt, *Compt. rend.*, **143**, 127 (1906).

[14] Fourneau and Tiffeneau, *Compt. rend.*, **145**, 437 (1907).

[15] Smith and Young, *J. Biol. Chem.*, **75**, 289 (1927).

[16] Molecular weight determinations were made by Mr. W. G. Young.

[17] (a) Barataeff and Saytzeff, *J. prakt. Chem.*, [2] **34**, 463 (1886); (b) Weigert, *Ber.*, **36**, 1004 (1903); (c) Ipatieff, *J. Russ. Phys.-Chem. Soc.*, **27**, 363 (1895), *Jahresb.*, **1895**, 971; (d) Saytzeff, *J. prakt. Chem.*, [2] **57**, 38 (1898); (e) Schreiner, *ibid.*, [2] **82**,

110 g. (1 mole) of ethyl bromide and 24.5 g. (1 mole) of magnesium in 200 cc. of absolute ether, there was obtained 70 g. (63% yield) of crude 3-ethyl-3-pentanol distilling at 68–72° under 49 mm. The material from two batches was fractionally distilled under a pressure of 50 mm. to prevent decomposition. The fractionation was performed six times, the refractive index being used as a check on the purity. During the last three distillations this value was practically constant. The boiling point of the final product, which has a pronounced camphor-like odor much resembling that of the isomeric alcohol, was 72.5–73.5° (corr.) at 50 mm., 83.5–84.0° (corr.) at 90 mm. and 140.5–141.5° (corr.) at 743 mm. It had refractive indices as follows: n_D^{20}, 1.4305 and n_D^{25}, 1.4281.

2-Chloro-3-ethylpentane.—The chlorides were prepared at room temperature of approximately 22° in order to decrease the possibility of isomeric change.[9] This chloride was prepared by stirring 10 g. (0.09 mole) of 3-ethyl-2-pentanol with 3 successive portions of 21 g. (0.2 mole) of concentrated hydrochloric acid and 22 g. (0.2 mole) of anhydrous zinc chloride over a period of fourteen hours, renewing the acid at approximately five-hour intervals. The product was shaken with small quantities of water in order to remove most of the acid and dried with anhydrous potassium carbonate. Two fractional distillations, the first at 90 mm. over a range of 70–77° and the second at 50 mm. over a range of 62.0–62.5° (corr.), gave 3.7 g. (35% yield) of product. The two fractions of each distillation differed but slightly in refractive index, the best values being n_D^{20}, 1.4318 and n_D^{25}, 1.4299. At the end of both distillations there was no tendency for the thermometer thread to rise, indicating absence of any higher boiling material such as the alcohol. The density, d_{25}^{25}, was 0.8911. After standing over phosphorus pentoxide for twenty-four hours, n_D^{25} was 1.4295.

When the alcohol was stirred for forty hours with concentrated hydrochloric acid in the proportions given above with replacement every six or seven hours but without the zinc chloride, the product after shaking out with water and drying over potassium carbonate was by weight only 75% converted and had a refractive index, n_D^{20}, 1.4293. When distilled at 50 mm. the temperature was slightly higher than before, *viz.*, 63–65°, and the indices of the different fractions differed by 0.0011. It was evident that the reaction had not gone to completion even after forty hours.

3-Chloro-3-ethylpentane.—This was prepared by stirring at room temperature 11.6 g. (0.1 mole) of 3-ethyl-3-pentanol with four successive portions of 21 g. (0.2 mole) of concentrated hydrochloric acid and 22 g. (0.2 mole) of anhydrous zinc chloride over a period of eighteen hours, renewing the acid at approximately five-hour intervals. After separating the heptyl chloride, washing five times with water and drying over potassium carbonate, the weight of the crude product was 12.6 g., a yield of 94%. In the operations which followed, drying over phosphorus pentoxide, distilling under a pressure of 100 mm. at 83.0–83.5° (corr.) and drying again over both drying agents, the refractive index was not changed, n_D^{25} being 1.4311. Standing for twenty-four hours over phosphorus pentoxide did not change the value.

After the chloride had been distilled at reduced pressure, distillation at atmospheric pressure could be carried on with but slight decomposition. Without a previous distillation the undistilled material evolved hydrogen chloride copiously when heated, probably due to the catalytic influence of suspended matter.[18]

3-Ethyl-2-pentene.—This was obtained by heating equal weights of 3-ethyl-3-pentanol and anhydrous oxalic acid on a boiling water-bath under a reflux cooler for five hours.[11,17d] The hydrocarbon was distilled over, separated from the water, refluxed with metallic sodium and finally distilled from the sodium, coming over at 95–96°.

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292 (1910); (f) Mazurewitsch, *J. Russ. Phys.-Chem. Soc.*, **42,** 1582 (1910); *Chem. Cent.*, **1911,** I, 1500; (g) Davies and Kipping, *J. Chem. Soc.*, **99,** 298 (1911).

[18] Rice, This Journal, **48,** 2099 (1926).

After refluxing again with sodium, the material distilled at 95.0–95.5° (corr.) at 745 mm. The yield was 84%.

Hydrogen Chloride and 3-Ethyl-2-pentene.—Dry hydrogen chloride was passed into 30 g. of glacial acetic acid, the solution was then cooled by ice and water and the gas was passed in until saturation was reached, 3 g. (0.08 mole) dissolving. To this was added 10.0 g. (0.10 mole) of 3-ethyl-2-pentene and additional hydrogen chloride was passed in until a total of 5 g. (0.14 mole) had dissolved. The mixture stood overnight at 8–10°, ice and water were then added and the chloride layer was washed five times with cold water. The weight of the undried chloride layer was 13.3 g., theoretical yield, 13.2 g. This indicated that addition was practically quantitative. After drying over anhydrous potassium carbonate the refractive index, n_D^{25}, was 1.4311 and the density, d_{25}^{25}, was 0.8951. The material distilled completely at 78–79° under 90–91 mm. pressure. The refractive index was unchanged and the density was 0.8948. After standing for twenty-four hours over phosphorus pentoxide the refractive index was still 1.4311.

The refractive index of the reaction product was identical with that of 3-chloro-3-ethylpentane, but the density was too high, being slightly above the value for this chloride. The three materials were allowed to stand for about a month over phosphorus pentoxide, the densities then being, 2-chloro-3-ethylpentane, 0.8874, 3-chloro-3-ethylpentane, 0.8917, and the reaction product, 0.8916. This brought all of the densities down and left the value for the reaction product slightly less than that of 3-chloro-3-ethylpentane. The refractive indices were not again determined although it is possible that they may have changed. The properties of the reaction product are thus practically identical with those of 3-chloro-3-ethylpentane.

Summary

The heptyl chlorides, 2-chloro- and 3-chloro-3-ethyl pentane have been prepared in a pure state from the corresponding alcohols at room temperature by stirring with concentrated hydrochloric acid and zinc chloride. Some physical properties have been determined.

Hydrogen chloride in glacial acetic acid reacting with 3-ethyl-2-pentene gives a heptyl chloride which is practically pure 3-chloro-3-ethylpentane.

The product formed agrees with the prediction made on the assumption that the electron attractions of hydrogen, methyl and ethylene are in the order $H > CH_3 > C_2H_5$, and not with the hypothesis of an alternately polarized carbon chain.

PASADENA, CALIFORNIA