The Octanes

BY FRANK C. WHITMORE AND K. C. LAUGHLIN

It is of interest to note that all eighteen of the structurally isomeric octanes have now been synthesized. This was accomplished when the three remaining trimethylpentanes were prepared by us [THIS JOURNAL, **55**, 2608 (1933)], although we were not aware at the time that we had completed the octane series. The preparation of the other isomers may be found as follows: Tafel and Jürgens, *Ber.*, **42**, 2548 (1909); Richard, *Ann. chim. phys.*, (8) **21**, 323 (1910); Noller, THIS JOURNAL, **51**, 594 (1929); Edgar and Calingaert, *ibid.*, **51**, 1546 (1929); Whitmore, Stehman and Herndon, *ibid.*, **55**, 3807 (1933); Parks and Huffman, *Ind. Eng. Chem.*, **23**, 1138 (1931); de Graef, *Bull. soc. chim. Belg.*, **40**, 315 (1931). Optical isomers of 3-methylheptane and 2,4-dimethylhexane have also been prepared [Levene and Marker, *J. Biol. Chem.*, **91**, 405, 761 (1931)].

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COMMUNICATIONS TO THE EDITOR

THE MUTAROTATION OF α-d-GLUCOSE IN HEAVY WATER

Sir:

It is generally accepted today that mutarotation in reducing sugars and sugar derivatives of various types depends on the presence of a displaceable hydrogen atom. A rearrangement of bonds consequent upon the displacement of this particular hydrogen atom, as in the keto-enolic isomeric changes, causes the reversible conversion of an oxide sugar into the intermediate aldehyde. Hudson [*Z. physik. Chem.*, **44**, 487 (1903)] has shown that the equal velocities of mutarotation of the α- and β-forms of sugars are due to opposite parts of one balanced reaction, and [Hudson and Dale, THIS JOURNAL, **39**, 320 (1917)] that the velocity coefficients for α- and β-glucose, determined at eight temperatures from 0.7 to 40°, are identical. Since the mutarotation of the sugars is evidently due to the wandering of a mobile hydrogen atom, it was thought interesting to investigate the effect produced by the wandering of a heavy hydrogen atom in a sugar molecule. The following experiment was carried out at 18°. A sample of 1.0024 g. of α-d-glucose was dissolved in 5 cc. of distilled water, and the change of the rotation was measured in a 2-dm. semi-micro tube with sodium light. The first reading was taken six minutes after the addition of water. The velocity-coefficient was found to be $k_1 + k_2 =$

0.00546. The experiment was duplicated with heavy water of d_4^{20} 1.06. The velocity coefficient was found to be $k_1^1 + k_2^1 = 0.00290$. From these results it can be concluded (1) that on solution in heavy water of a reducing sugar the displaceable hydrogen atom of that sugar is *immediately* replaced by a heavy hydrogen atom of the heavy water, and (2) that the mutarotation is indeed due to oxo-cyclo desmotropy, *i. e.*, to a change in which the double bond of a $>C=O$ group is replaced by a ring formed by the migration of a hydrogen atom. The corresponding experiments with 100% heavy water will be carried out shortly.

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THE DEUTEROAMMONIAS

Sir:

Three different samples of heavy water have been brought to reaction in the vapor phase with magnesium nitride to form ammonias in which the hydrogen atoms are predominantly of mass 2. The densities of the three products, relative to that of ordinary ammonia measured under the same conditions, were, respectively, 1.12, 1.158 and 1.174. Assuming equal equations of state for all the ammonias, these densities correspond to ammonias containing, respectively, 68, 90 and 99% of heavy hydrogen. The gases have the odor of ammonia. The physical properties show a progressive change with isotope concentration as is seen from the following data:

Percentage of heavy hydrogen	0	68	90	99
Freezing point, °Abs.	195.2	197.9	198.6	199
Boiling point, °Abs.	239.75	241.7	242.1	242.3

By means of a differential tensimeter using ammonia as reference the following vapor pressures were obtained for the 99% product:

T, °Abs.	202.3	213	226.1	232.1	238.6
P_{NH_3}	77	184	364	511	714
P_{ND_3}	63	154	313	445	628

Assuming the latent heat of vaporization of ammonia to be 5797 cal. per mole at 1 atmosphere, the vapor pressure curve of the product gives a value for the latent heat of vaporization of ND_3 of 5990 calories per mole.

With the assistance of Dr. G. I. Lavin we have examined the absorption spectra of the products in the far ultraviolet and found them to be similar to, but quite distinct from, that of ammonia, well defined spectrograms having been obtained. Densitometer curves made from our plates by Dr. Garman of New York University show that the principal bands are