successfully employed in the preparation of two heterocyclic biurets. Reduced to its simplest terms, this reaction may be represented by the equation

$$RNH_2 + H_2NCONHCONHNO_2 \longrightarrow RNHCONHCONH_2 + N_2O + H_2O$$

In this way we have prepared 1-(2-pyridyl)- and 1-(2-thiazolyl)-biuret in yields of 34 and 13%, respectively.

Experimental[4]

1-(2-Pyridyl)-biuret.—2-Aminopyridine (47 g., 0.5 mole) and nitrobiuret[5] (74.1 g., 0.5 mole) were dissolved in 830 ml. of water which had been heated to 70°. The temperature of the stirred solution was raised from 65 to 75° over a period of 2.75 hours; during this time gaseous evolution and precipitation occurred. The temperature of the reaction mixture was then raised to 90° over a period of 1 hour. The colorless granular crystals were filtered from the cooled solution and dried under vacuum over phosphorus pentoxide, yield 30.5 g. (33.8%), m.p. 194–195.5° with gaseous decomposition. Recrystallization from 95% ethanol gave an 87% recovery of colorless platelets, m.p. 197–198° with slight gaseous decomposition. Recrystallization of these crystals from water gave fine crystals, m.p. 196.2–197.2°. *Anal.* Calcd. for $C_7H_8N_4O_2$: C, 46.66; H, 4.48; N, 31.10. Found: C, 46.46; H, 4.50; N, 31.56, 30.76.

1-(2-Thiazolyl)-biuret was prepared in an analogous manner, yield 12.5%, m.p. 205–214° with gaseous decomposition and resolidification. The melting point may be raised to 217–218° by recrystallization from 95% ethanol. *Anal.* Calcd. for $C_5H_6N_4O_2S$: C, 32.25; H, 3.25; N, 30.09; S, 17.22. Found: C, 32.37; H, 3.43; N, 29.74; S, 17.05.

Biuret Tests.—Phenylbiuret and 1-(2-pyridyl)-biuret gave a blue-violet color when treated with dilute copper sulfate and sodium hydroxide. 1-(2-Thiazolyl)-biuret gave an emerald green color.

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(4) All melting points have been corrected for thermometer stem-emergence.

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RECEIVED JUNE 20, 1951

The Exchange of Deuterium for Hydrogen in *n*-Heptane[1]

BY JOSEPH A. DIXON[2] AND ROBERT W. SCHIESSLER

The simultaneously-occurring hydrogenation and hydrogen exchange reactions of an olefin and deuterium over nickel or platinum have been the subject of numerous investigations,[3] and the exchange of deuterium for hydrogen between a saturated hydrocarbon and deuterium has been well demonstrated.[4] The hydrogen atoms of benzene and ethylene have been shown to participate in an exchange with deuterium atoms of heavy water.[5] Horrex, Greenhalgh and Polanyi published the only report of exchange between heavy water and a saturated hydrocarbon[6] over metal catalysts. They obtained exchange between both cyclohexane and isopentane and a water containing 14% D_2 at 100° and one-half atmosphere over a platinum catalyst. The product cyclohexane was reported to contain 0.67% deuterium.

Ingold, Raisin and Wilson examined hydrogen exchange between sulfuric acid and aliphatic hydrocarbons.[7] Little exchange was obtained with *n*-hexane or *n*-heptane.

While examining various routes for the preparation of a perdeuterated normal paraffin we have studied the liquid and vapor phase reactions of a saturated straight-chain hydrocarbon with heavy water.

In Table I are shown the results of experiments with deuterium oxide or hydrogen oxide and *n*-heptane. The *K* of the last column of the Table is a measure of the extent of exchange and is defined by

$$(\text{C–H}) + (\text{O–D}) \rightleftarrows (\text{C–D}) + (\text{O–H})$$

$$K = \frac{(\text{C–D})\,(\text{O–H})}{(\text{C–H})\,(\text{O–D})}$$

where (C–D) and (C–H) refer to the number of carbon–deuterium and carbon–hydrogen bonds, respectively, in the hydrocarbon and the (O–D) and (O–H) represent the oxygen–deuterium and oxygen–hydrogen linkages in the water. The density is a linear function of the ratio of hydrogen to deuterium in hydrocarbons and heavy water. The number of C–D, C–H, O–D and O–H bonds is obtained from the densities of the product water and product hydrocarbon by simple calculations.

The experiments indicate: (1) Nickel and platinum catalysts are ineffective for the catalysis of hydrogen exchange between water and a straight-chain paraffin in the liquid phase. (2) Vapor phase interchange of the hydrogen isotopes between heavy water and a normal paraffin takes place readily over a kieselguhr-supported nickel catalyst. Exchange proceeded at 135° in the vapor and did not take place at 150° in the liquid.

Undoubtedly the inability of the hydrocarbon to compete with the water for catalyst surface is the dominant factor in the failure of the present liquid phase experiments.[8]

The exchange is accompanied by scission of carbon–carbon bonds. This is very unfortunate if the goal is a completely deuterium-substituted straight-chain hydrocarbon. Experiments 11 to 13 were performed with ordinary water. The change in density is excellent evidence that the hydrocarbon skeleton is being altered. Infrared spectra[9] of the hydrocarbon product from Experi-

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(1) American Petroleum Institute Project 42. Advisory Committee: H. Sutherland (Chairman), E. M. Barber, J. R. Bates, L. C. Beard, G. H. Denison, L. M. Henderson, R. G. Larsen, R. F. Marschner, L. A. Mikeska and J. H. Ramser.

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(7) C. K. Ingold, C. G. Raisin and C. L. Wilson, *J. Chem. Soc.*, 1643 (1936).

(8) The serious retardation of nickel-catalyzed hydrogenations by small amounts of water has been observed frequently in this and other laboratories.

(9) These spectra were determined by The Petroleum Refining Laboratory of The Pennsylvania State College. The infrared spectrometer was a Perkin and Elmer Model 12-A.

TABLE I

No.	*n*-Heptane, g.	D_2O, g.	Time, hr.	Catalyst	Temp., °C.	Phase[b]	*K*[a]
				Liquid phase experiments			
1	7.5	9.2	21	2 g. Raney nickel[l]	Reflux	L	0
2	10.5	16.4	24	Trace of sulfuric acid	Reflux	L	0
3	30.3	13.0	18	5 g. U. O. P. nickel[c] finely powdered	Reflux	L	0
4	30.0	12.0	24	2 g. platinized asbestos[c]	Reflux	L	0
5	24.0	9.0	24	0.8 g. platinum(IV)[c] oxide	25	L	0
6	30.0	9.0	55	3 g. platinum oxide[c]	80–100	L	0
7	55.0	12.5	36	1.5 g. platinum oxide[c]	150	L	0
				Vapor phase experiments			
			No. of passes,[d]				
8	39.6	14.3	6	Pelleted U. O. P. nickel[e]	165–180	V	1.1×10^{-1}
9	36.8	13.6	4	Pelleted U. O. P. nickel[e]	160–180	V	1.3×10^{-1}
10	24.0	16.2	5	Pelleted U. O. P. nickel[e]	120–135	V	8.0×10^{-3}
		H_2O, g.					d^{20}_4[f]
11	24.5	9.1	4	Pelleted U. O. P. nickel[e]	160–180	V	-8×10^{-4}
12	24.6[g]	10.1	4	Pelleted U. O. P. nickel[e]	170–180	V	-5×10^{-4}
13	100.5	36.5	72[h]	Pelleted U. O. P. nickel[e]	150–155	V[k]	1.4×10^{-3}[j]

[a] This constant is a measure of extent of reaction, see Discussion. [b] L, liquid; V, vapor. [c] Catalyst reduced in hydrogen atmosphere at room temperature before introduction of heavy water. [d] Number of times the entire charge of water and hydrocarbon passed through the catalyst bed. [e] Catalyst reduced by heating at 200–250° for eight hours in a stream of hydrogen. [f] Difference in density between the hydrocarbon product and the *n*-heptane. [g] *n*-Octane. [h] See experimental for description of apparatus used. [j] Viscosity increased (7 ± 1) × 10^{-3} cs. [k] Pressure rose gradually to 1.5 atmospheres several times during the reaction period. The gas which was being produced was intermittently vented. [l] Raney nickel prepared by the procedure described in Adkins, "Reactions of Hydrogen," Wisconsin University Press, Madison, Wisc., 1937, p. 20. It was washed three times with acetone and twice with heptane before use.

ment 11 and the original *n*-heptane were identical. If the hydrocarbon were cracking to give principally lower molecular weight straight chain fragments, the density would be a much more sensitive criterion than the infrared spectra. Experiment 13, which was of much greater duration, produced not only very material changes in physical properties of the product hydrocarbon but also considerable quantities of gaseous material. It appears that in addition to the cracking some considerable carbon skeletal rearrangements may have taken place to produce a product with an increased viscosity and density.

Evidently the preparation of a completely deuterated straight-chain hydrocarbon by successive equilibrations of hydrocarbon and heavy water is a poor procedure if a product of unchanged carbon skeleton is desired.

Experimental

Materials.—*n*-Heptane was obtained from the Westvaco Chlorine Products Co., d^{20}_4 0.68397, n^{20}_D 1.3870, f.p. −90.66°; NBS values[10] 0.68368, 1.38764, −90.595°, respectively. The hydrocarbon was passed through a short column of silica gel before use.

n-Octane was prepared by the modified[11] Wolff–Kishner reduction of 2-octanone, d^{20}_4 0.7026; NBS[10] 0.7026. The octane was passed through silica gel before use.

Deuterium oxide was supplied by the Stuart Oxygen Co. and had a minimum deuterium content of 99.5%.

Nickel on kieselguhr was purchased from the Universal Oil Products Co. No exchange was observed over this catalyst unless it was first reduced in a stream of hydrogen at elevated temperatures. In the present work, the reduction was performed at 200 to 250° for eight hours.

Platinized asbestos obtained from Fisher Scientific Co. had 10% platinum by weight.

Liquid Phase Experiments.—Experiments 1 to 5, Table I were performed in a 100-ml. three-neck flask equipped with a mercury-seal stirrer, gas inlet tube and condenser. The hydrocarbon and catalyst were charged to the flask and the catalyst reduced in a hydrogen atmosphere. The hydrogen was replaced by nitrogen and the deuterium oxide charged to the flask. At the completion of the run the water was frozen, the hydrocarbon layer separated and distilled from powdered calcium hydride in an all-glass distilling system. No hydrogen exchange takes place between the hydride and hydrocarbon under these conditions. Densities were determined with an accuracy of ±0.0001.

Experiment 6 was accomplished in a Burgess–Parr low pressure hydrogenation apparatus. The catalyst was reduced *in situ* before the introduction of the heavy water. At the end of the reaction period the products were isolated as above.

Experiment 7 was performed in an Aminco high pressure hydrogenation apparatus.

Vapor Phase Experiments.—Runs 8 to 12 Table I were made by simply distilling the water and hydrocarbon together through a horizontal catalyst chamber, which was 22-mm. o.d. Pyrex, packed with catalyst pellets for a length of six inches and surrounded by a 750-watt heater. The temperatures recorded in the table are those of the outside wall.

Experiment 13 was accomplished in an apparatus which provided continuous and repeated passage of the hydrocarbon and water vapors through a heated catalyst chamber.

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RECEIVED MARCH 21, 1951

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On the Oxidation of Glycerol-1-C^{14} by 1,2-Glycol-cleaving Reagents[1]

BY ALBERT P. DOERSCHUK

The reaction that occurs between periodic acid in buffered aqueous solution and glycerol to yield quantitatively formaldehyde and formic acid is well known. A comparison of the glycerol reaction with reactions of other 1,2-glycols and peri-

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(1) This work was supported in part by a grant from the Nutrition Foundation, Inc.