A. A solution of 10 g. (0.057 mole) of gramine and 4.7 g. (0.019 mole) of 1,6-dibromohexane in 75 ml. of methanol deposited colorless prisms on standing overnight at room temperature. These were collected, washed with ethanol and then ether. After drying *in vacuo* over phosphorus pentoxide, the product melted 177–178.5° (cor.) and weighed 5.8 g. (52% yield on the basis of gramine). Additional material, which could be purified by methanol recrystallization, was recovered from the filtrates by precipitation with ether.

Anal. Calcd. for $C_{20}H_{22}N_3Br$: C, 62.50; H, 5.77; N, 10.93. Found: C, 62.78; H, 5.77.

B. Reaction of 1,10-dibromodecane with gramine in similar fashion afforded a crystalline solid which was recrystallized from methanol; m.p. alone and mixed with the product described in A was 177–178.5° (cor.).

Anal. Found: C, 62.11; H, 5.72; N, 10.80.

C. A similar reaction of 5.2 g. (0.03 mole) of gramine with 7.4 g. (0.045 mole) of 1-bromohexane in acetonitrile solution yielded 5.2 g. (92%) of crystalline precipitate after 4 days at room temperature; m.p. 178–180°, undepressed when mixed with the product from A or B. Negligible amounts of additional precipitate were obtained on addition of ether to the filtrate.

Indole-N-methylgramine (V).—N-Methylindole, b.p. 125–130° (20 mm.), $n^{23}\text{D}$ 1.6071, was prepared from indole[5] with the exception that sodium hydride was used in place of sodium. V, b.p. 113–116° (0.5 mm.), $n^{23}\text{D}$ 1.5734, was obtained from N-methylindole as described by Snyder and Eliel[3] who reported b.p. 94–96° (0.2 mm.), $n^{20}\text{D}$ 1.5743.

Reaction of V with Dibromohexane (VI).—A solution of 4.8 g. (0.026 mole) of V in 50 ml. of methanol treated with 2.1 g. (0.0086 mole) of dibromohexane yielded no precipitate after 5 days at room temperature. Addition of anhydrous ether precipitated an oil which was washed with fresh ether, dissolved in ethanol and reprecipitated. The thick viscous oil was dried over phosphorus pentoxide *in vacuo* to yield 2.4 g. of white crystalline deliquescent solid (A). The material evolved gas at 144–145°, solidified at 151° and remelted 192–202°.

A was fractionally crystallized from propanol and ether. During crystallization undue heating was avoided as decomposition appeared to take place if the solution was heated much above 50°. The head fraction, after two further recrystallizations from propanol, afforded 100 mg. of white crystals (B), m.p. 220° (decomp.). B was not further investigated.

After several recrystallizations of the mother liquor material from propanol and ether 900 mg. of white hygroscopic solid (C), which softened and evolved gas at 100°, turned red at 125° and fused at 140°, was obtained.

Anal. Calcd. for bis-(indole-N-methylgramine)quaternary salt, VI, $C_{30}H_{44}Br_2N_4$: C, 58.06; H, 7.15. Found: A: C, 57.18; H, 7.20. C: C, 57.72; H, 7.58. *Anal.* of B: C, 38.08; H, 7.83.

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(5) R. Weissgerber, *Ber.*, **43**, 3520 (1910).

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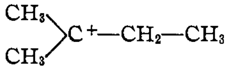
The Mechanism of the Acid-catalyzed Hydration of Olefins[1]

BY JOSEPH B. LEVY, ROBERT W. TAFT, JR., AND LOUIS P. HAMMETT

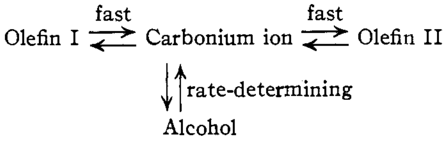
RECEIVED OCTOBER 18, 1952

In a study of the rates of the acid-catalyzed hydration of the two isomeric olefins trimethylethylene (I) and *asym*-methylethylethylene (II) by methods whose application to other olefins has been described[2] we have had occasion to observe that at 50% reaction neither olefin has been measurably converted to the isomer. The result is of importance in connection with the mechanism of the hydration because an identical carbonium ion (III) is obtained by the addition of a proton to



$$(CH_3)_2C^+—CH_2—CH_3$$

either of these olefins. Consequently, the reaction scheme consisting in the rapid and reversible addi-



tion of a proton to the olefin followed by a rate-determining reaction of the ion with a water molecule is definitely excluded as the mechanism of the hydration reaction.

The two olefins would be expected to hydrate to a single product *t*-amyl alcohol and this has been reported[3] to be the case. A further careful test on our part shows that the most probable alternative, methylisopropylcarbinol, does not constitute as much as 2% of the product of the hydration of I.

Experimental

Test for Interconversion of the Olefins.—Gaseous olefin I was shaken at 35° with 0.973 *M* nitric acid under the conditions of a rate measurement[2] until the pressure had dropped to about half of the initial value and olefin II was treated similarly at 20°. The residual olefin was then removed in each case and its infrared absorption observed in the gaseous state with a path length of 10 cm. and at a pressure equal to the vapor pressure of the olefin at 20° (*ca.* 380 mm. for I and 450 mm. for II). Under these conditions I has an absorption band with a peak at 1120 cm.$^{-1}$ for which log I_0/I was 1.2 both for the pure substance and for the partially reacted sample. At this frequency log I_0/I for II was about 0.1, both for the pure substance and for the partially reacted sample. II has a band at 1660 cm.$^{-1}$, for which log I_0/I was found to be 0.9 both for the pure substance and for the partially hydrated sample. At this frequency log I_0/I was about 0.2 both for pure I and for the partially hydrated sample.

Reaction Product.—A sample of several ml. of trimethylethylene was allowed to react at 35° for several days with 0.973 *M* nitric acid under conditions essentially identical with those prevailing during a rate measurement. The resulting solution was filtered, saturated with ammonium sulfate, and extracted with ether. The ether solution was dried and the ether evaporated through a small column. All of the residue (1.4 g.) was then distilled through the column at 99 to 102° (uncor.), $n^{25}\text{D}$ 1.4017. Under the same conditions a purified known sample of *t*-amyl alcohol boiled at 100.8 to 101.3° and had $n^{25}\text{D}$ 1.4028, and a purified known sample of methylisopropylcarbinol boiled at 110.0 to 111.0° and had $n^{25}\text{D}$ 1.4069. These values are consistent with data in the literature.

A 15% solution of the hydration product in carbon tetrachloride absorbed strongly in the infrared at 1190 cm.$^{-1}$ but not detectably at 1110 cm.$^{-1}$. *t*-Amyl alcohol has a strong broad absorption band at 1190 ± 10 cm.$^{-1}$ and methylisopropylcarbinol has a similar one at 1100 ± 10 cm.$^{-1}$. On the basis of the absorption shown at 1110 cm.$^{-1}$ by a solution containing the tertiary and secondary alcohols in the ratio of 9:1 we estimate that the hydration product cannot contain as much as 2% of the methylisopropylcar-

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[1] The work reported herewith was carried out as project NR 056-062 under contract N6onr-271 between the Office of Naval Research and Columbia University. Reproduction in whole or in part permitted for any purpose of the United States Government.

(2) (a) J. B. Levy, R. W. Taft, Jr., D. Aaron and L. P. Hammett, THIS JOURNAL, **73**, 3792 (1951); (b) R. W. Taft, Jr., B. Levy, D. Aaron and L. P. Hammett, *ibid.*, **74**, 4735 (1952).

(3) (a) H. J. Lucas and Yun-Pu Liu, *ibid.*, **56**, 2138 (1934); (b) Yun-Pu Liu and Tien-Chi Wei, *J. Chinese Chem. Soc.*, **4**, 297 (1936).

binol. A sample of methylisopropylcarbinol treated with nitric acid under the same conditions as in the hydration of the trimethylethylene was not converted to the *t*-amyl alcohol to an extent measurable by the infrared spectrum.

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Preparation and Some Reactions of *n*-Heptafluoropropylmagnesium Iodide

BY O. R. PIERCE AND M. LEVINE

RECEIVED SEPTEMBER 5, 1952

An investigation of the reaction of heptafluoro-1-iodopropane with magnesium metal has been reported by Henne[1,2] and Haszeldine.[3] A study of the perfluoropropyl Grignard reagent was initiated in this Laboratory to develop techniques applicable to the preparation of a fluorine-containing silane. The investigation reported here outlines the experimental conditions which were studied in an attempt to obtain maximum yields of the Grignard reagent as indicated by addition products, using acetone, ethyl trifluoroacetate, heptafluorobutyraldehyde and 1,1,1-trifluoro-2-propanone. It should be pointed out that the Grignard reagent acts as a catalyst in aldol-type condensation reactions thereby reducing the yield of addition products in those instances in which the carbonyl compound contained α-hydrogen atoms.

Experimental

Preparation of Heptafluoro-1-iodopropane.—This material was prepared as described previously.[4]

Preparation of 3,3,4,4,5,5,5-Heptafluoro-2-methyl-2-pentanol.—Magnesium turnings, 6 g. (0.25 mole), were placed in a three-necked, round-bottom flask fitted with an efficient stirrer, separatory funnel, and reflux condenser to which was attached a Dry Ice cooled trap. The entire apparatus was dried and 100 ml. of dry tetrahydrofuran was added. A small amount of heptafluoro-1-iodopropane was introduced into the reaction flask at room temperature and the mixture was stirred vigorously until reaction had started as indicated by evolution of heat and the formation of a brown precipitate. The reaction flask was cooled immediately to −30 to −40°, and maintained at this temperature during the addition of 74 g. (0.25 mole) of heptafluoro-1-iodopropane. The extent of reaction was followed by the formation of a precipitate as the magnesium metal disappeared. The reaction became exothermic in those experiments when cooling of the reaction flask was not accomplished immediately following initiation of Grignard formation. When all the halide had been added, stirring of the mixture was continued for two hours.

Acetone, 25 g. (0.5 mole) was added dropwise at −30° and the reaction temperature was allowed to rise gradually to 25°. The reaction mixture was then hydrolyzed with water resulting in the formation of magnesium salts. The contents of the flask were then poured onto a 10% sulfuric acid–ice mixture. Upon rectification, there was obtained 20 g. of unreacted heptafluoro-1-iodopropane and 12 g. of 3,3,4,4,5,5,5-heptafluoro-2-methyl-2-pentanol, b.p. 107–108°, $n^{20}{}_{D}$ 1.3250, which represents a conversion of 21% and a 48% yield. Assignment of the structure was based on agreement with the reported properties of the tertiary alcohol.[5]

Preparation of 1,1,1-Trifluoro-3,3,4,4,5,5,5-heptafluoro-2-pentanone.—The Grignard reagent was prepared as previously described. Ethyl trifluoroacetate, 18 g. (0.12 mole), was added dropwise at −30° to the reaction flask and the temperature of the mixture was allowed to warm to 25°. Heat was evolved and a gummy precipitate formed. The mixture was stirred at 50° for several hours. The reaction products were then heated to reflux and, upon cooling, were hydrolyzed with a 10% sulfuric acid–ice mixture. Upon rectification, there was obtained 18 g. (24%) of unreacted heptafluoro-1-iodopropane and 22.1 g. of material, b.p. 104–105°, $n^{20}{}_{D}$ 1.3449, $d^{20}{}_{4}$ 1.388. Since the infrared spectrum indicated the presence of a solvated ketone, this material was heated with phosphorus pentoxide, and there was obtained 15 g. (0.06 mole) of the ketone, CF_3–CO–C_3F_7, b.p. 30–31°, which represents a yield of 50% of the theoretical.

Anal. Calcd. for $C_5F_{10}O$: C, 22.57; H, 0.0; F, 71.4. Found: C, 22.28; H, 0.016; F, 70.0.

Preparation of 1,1,1,2,2,3,3,5,5,6,6,7,7,7-Tetradecafluoro - 4 - heptanol.—Heptafluorobutyraldehyde, 60 g. (0.3 mole), was added dropwise to the Grignard reagent (100 g. of heptafluoro-1-iodopropane and 8 g. of magnesium turnings), at −50°. The reaction mixture was allowed to come to room temperature at which point it became so viscous that additional solvent was added in order to continue stirring. Following hydrolysis and rectification, there was obtained 40 g. of material, b.p. 94–95°. Both the infrared spectrum and analytical data indicated that the alcohol was contaminated with a small amount of tetrahydrofuran, and it was found necessary to isolate the alcohol as the 3,5-dinitrobenzoate ester, m.p. 106–107°. The ester was found to react with ethanol and was recrystallized from petroleum ether and benzene. The conversion obtained in this manner represents 33% of the theoretical.

Anal. Calcd. for $C_{14}H_4O_6N_2F_{14}$: C, 29.9; H, 0.8. Found: C, 30.3; H, 0.98.

Reaction of the Grignard Reagent with 1,1,1-Trifluoro-2-propanone.—1,1,1-Trifluoro-2-propanone, 25 g. (0.25 mole), was added slowly to the Grignard reagent and the products were treated as previously described (the techniques of the reaction are such that it is inconvenient to add the Grignard reagent to 1,1,1-trifluoro-2-propanone). Distillation of the reaction mixture resulted in sublimation of a solid which, recrystallized from a mixture of benzene and petroleum ether, melted sharply at 93–94°. There are indications that this material is a polymer of 1,1,1-trifluoro-2-propanone.

Anal. Calcd. for $C_3H_3F_3O$: C, 32.1; H, 2.67. Found: C, 30.5; H, 2.63.

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[1] A. L. Henne and W. C. Francis, THIS JOURNAL, **73**, 3518 (1951).

[2] A. L. Henne and W. C. Frances, private communication.

[3] R. N. Haszeldine, *Nature*, **167**, 139 (1951).

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[5] E. T. McBee, O. R. Pierce and M. C. Chen, private communication.

The Chemistry of Scandium. IV. The Structure of Scandium Oxinate

BY L. POKRAS, M. KILPATRICK AND P. M. BERNAYS

RECEIVED AUGUST 13, 1952

In a recent paper[1] on the 8-hydroxyquinoline compound of scandium[2] it was noted that, as in the cases of the analogous thorium, uranium and plutonium derivatives, the compound includes an "extra" molecule of oxine. For such compounds it is difficult to understand the nature of the chemical binding between the expected normal oxinate and the "extra" oxine molecule. The

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[1] L. Pokras and P. M. Bernays, THIS JOURNAL, **73**, 7 (1951).

[2] The formula of the 8-hydroxyquinoline compound, $Sc(C_9H_6ON)_3 \cdot C_9H_7ON$, is abbreviated as $Sc(On)_3 \cdot HOn$; 8-hydroxyquinoline or oxine is written as HOn.