Anal. Calcd. for $C_{13}H_{10}O_4N_2S$: C, 53.77; H, 3.47; N, 9.65. Found: C, 53.52; H, 3.86; N, 9.75.

MERCK & CO., INC.
RAHWAY, N. J.

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Hydrogen Fluoride as a Condensing Agent. XIV. Alkylation Studies[1]

BY J. H. SIMONS AND G. C. BASSLER

As a condensing agent hydrogen fluoride is related to both the metallic halide and the acidic agents. It promotes reactions with alkyl halides, with olefins, and also with hydroxy compounds. For the metallic halide promoted reactions an alkyl halide–metallic halide complex may be postulated as the reactive intermediate. With the acidic agents a complex between the olefin and the acid can be postulated. With hydrogen fluoride the mechanism is obscure, but because of its relationships to the other types of agents, information obtained which aids in the interpretation of its reactions may be of general value. The following experiments were performed to obtain such information.

It seemed desirable to answer three questions concerning alkylations promoted by hydrogen fluoride. First, does hydrogen fluoride act by forming the alkyl fluoride, which then reacts and regenerates the hydrogen fluoride? It is known that hydrogen fluoride is readily removed from aliphatic compounds, *i. e.*, alkyl fluorides lose hydrogen fluoride readily to form olefins. It is also known that olefins, alkyl chlorides, and alcohols react with hydrogen fluoride under certain conditions to form fluorides. Second, what is the relative ease of reaction of olefins and alkyl fluorides with aromatic compounds in the presence of hydrogen fluoride? Third, what is the relative ease of reaction of alcohols and other alkyl halides? Three different sets of experiments were performed to answer these questions.

A sample of pure tertiary amyl fluoride was desired but it was found that this compound would not undergo distillation even at reduced pressure and at −12° without partial decomposition into the olefins and hydrogen fluoride. This was independent of whether the initial substance was prepared from tertiary amyl alcohol and aqueous hydrogen fluoride or the olefin and anhydrous hydrogen fluoride. A mixture of olefin and fluoride was made by adding to 200 cc. of amylenes (prepared by the dehydration of *t*-amyl alcohol) dry-ice and 17 g. of anhydrous hydrogen fluoride. Dry sodium carbonate was added in excess, and the mixture was filtered through a Büchner funnel packed with dry-ice. This procedure should produce a mixture of olefins and tertiary amyl fluoride.[2] Three reaction mixtures were prepared: (1) 60 cc. of amylenes, 21 g. of HF and 50 cc. of benzene; (2) 60 cc. of *t*-amyl fluoride and olefin mixture, 15 g. of HF, and 50 cc. of benzene; (3) 60 cc. of *t*-amyl fluoride and olefin mixture and 50 cc. of benzene. These were allowed to stand in ice for one hour and then an iced solution of sodium carbonate was added. The organic layers were removed, washed, and dried over potassium carbonate. From number 1 about 27 g. of high boiling material was obtained which consisted chiefly of polyalkylated benzene. From number two about 4 g. of high boiling material was obtained and of this it is estimated that perhaps half was aliphatic polymers. From number 3 less than 2 g. of high boiling residue was obtained which probably was chiefly aliphatic polymer.

The following substances were then used for reaction with toluene under similar conditions and for a time short of complete reaction for the most rapid reaction: (1) cyclohexene, (2) cyclohexyl fluoride, (3) cyclohexanol, (4) cyclohexyl chloride, (5) cyclohexyl bromide, and (6) cyclohexyl iodide; 1.5 moles of toluene was added to 3.2 to 3.3 moles of hydrogen fluoride and 0.33 mole of the cyclohexyl compound then added. The mixture was allowed to stand for two hours at room temperature and then the flask was again placed in ice and water carefully added. The organic materials were separated, neutralized, dried, and distilled. The yields of *p*-cyclohexyltoluene obtained were as follows: (1) 74%; (2) 75.6%; (3) 45%; (4) 8%; (5) 0%, and (6) 0%.

The above experiments were then repeated using the following aliphatic compounds in the same molar proportions: (1) octene-1, (2) a mixture made by adding hydrogen fluoride to octene-1 at low temperature (2-fluoroöctane apparently cannot be distilled without decomposition), (3) octanol-2, (4) 2-chloroöctane, and (5) 2-bromoöctane. Yields of 2-*p*-octyltoluene were as follows: (1) 73%; (2) 13.5%, (3) 42%, (4) 0%, and (5) 0%. In number two a considerable residue was found which is probably aliphatic polymer.

These experiments strongly indicate that the aliphatic fluoride alone is not reactive but that the presence of hydrogen fluoride is also necessary. It also appears that an olefin reacts as readily or more readily than the fluoride. In the second series of experiments the yields are about the same but in the first and third the yield is less when the fluoride is used. This however, is complicated by the difficulties of obtaining the pure fluoride and the polymerization of the aliphatic compounds. The high yield obtained when the alcohol is used is interesting in view of the fact that water is a product of the reaction and remains to dilute the hydrogen fluoride. The decreasing yields as the atomic weight of the halide increases may be correlated in two ways. The reaction produces the hydrogen halide and the order of decreasing

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[1] For the previous paper of this series see Simons, Passino and Archer, THIS JOURNAL, **63**, 608 (1941).

[2] Grosse and Linn, *J. Org. Chem.*, **3**, 26 (1938).

yields is the order of increasing boiling point or decreasing ease of removal from the reaction zone. The order is also the order of decreasing ease of ionization, should an ionic mechanism be postulated.

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The Preparation of 2,2- and 3,3-Dimethylpentane

BY HAROLD SOROOS AND H. B. WILLIS

Wibaut and co-workers[1] have stated that they were unable to prepare 2,2- and 3,3-dimethylpentane by the condensation of tertiary alkyl halides with Grignard reagents, as reported by Edgar and co-workers.[2] Because of the attractiveness of this one-step reaction for the preparation of branched-chain paraffins, it seemed of interest to us to retest the method.

In order to remove any uncertainty that may still exist regarding the workability of the process, an exact description is given below of the method as applied by us.

Grignard Reagents.—All the Grignard reagents were prepared in the conventional manner, using 6.0 gram atoms of magnesium turnings (the magnesium used should be of a good grade, free of slag, and, preferably, from extruded bar rather than castings), 6.6 moles of alkyl halide, and 1500 cc. of anhydrous ether. Because of its high volatility, a larger excess (about 25%) of ethyl chloride was used in preparing the ethylmagnesium chloride, and when the magnesium had practically all dissolved, the excess was removed by refluxing the ether for a short time. After allowing the Grignard reagents to stand overnight, and after samples of the clear reagents had been analyzed by titration, they were transferred under nitrogen to graduated separatory funnels, where their volumes were noted. Care was taken to see that only the clear reagent and none of the sludge was transferred. Each was then transferred, under nitrogen, to a 5-liter 3-neck round-bottom flask, equipped with a separatory funnel, reflux condenser and vapor-proof mechanical stirrer for addition of the *t*-alkyl chlorides.

The Coupling of RMgX with RX.—To each of the Grignard reagents was added an equivalent amount (based on the volume and titration of an aliquot of each Grignard reagent) of the appropriate *t*-alkyl chloride. Mercuric chloride was not used in these tests since recent work in this Laboratory has shown that it has little or no effect on the yield. In the case of the Grignard reagents prepared from alkyl chlorides, the *t*-alkyl chloride was added rapidly and the reaction mixture was allowed to stand in a cooling bath at 25–30° without further attention. Reaction started in four to ten hours.

In the case of the Grignard reagents prepared from alkyl bromides, it was first necessary to start the reaction by the addition of only a small portion of the tertiary chloride. When the reaction had definitely started, as evidenced by the liberation of heat and the precipitation of magnesium bromide etherate, the remainder of the halide was added at such a rate that the temperature of the reaction could be maintained at 33–39° by slight cooling with an ice–water-bath. Failure to follow this procedure results in a very vigorous reaction which is difficult to control.

All the reaction mixtures were allowed to stand in cooling baths at 23–30° for six days. The condensers were then set for distillation, water was added slowly to the mixtures, and the ether and hydrocarbons were steam distilled. The ether solutions of the products were washed with water and dried over anhydrous sodium carbonate. The hydrocarbons were recovered from their ether solutions by fractionation. The yields of crude products were as follows: 2,2-dimethylpentane, 27% from *t*-BuCl with *n*-PrMgCl and 29% with *n*-PrMgBr; 3,3-dimethylpentane, 43% from *t*-AmCl with EtMgCl and 41% with EtMgBr.

Purification of Hydrocarbons.—The respective crude hydrocarbons from two runs were combined, were washed successively with concentrated sulfuric acid and 5% sodium bicarbonate solution, were refluxed and distilled from sodium–potassium alloy, and, finally, were fractionated carefully through an efficient column packed with crushed carborundum. The properties and yields of the finished products were as follows: 2,2-dimethylpentane, b. p. (760 mm.) 78.7–79°, d^{20}_4 0.6736, n^{20}_D 1.3822, yield 20%; 3,3-dimethylpentane, b. p. (760 mm.) 85.7–86.0°, d^{20}_4 0.6931, n^{20}_D 1.3910, yield 31%.

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[1] Wibaut, Hoog, Langedijk, Overhoff and Smittenberg, *Rec. trav. chim.*, **58**, 329 (1939).

[2] Edgar, Calingaert and Marker, THIS JOURNAL, **51**, 1483 (1929).

NEW COMPOUNDS

Glycyl-*l*-methionine

Chloroacetyl-*l*-methionine was prepared from *l*-methionine by the method described by Fischer and Suzuki[1] for the preparation of diglycyl-*l*-cystine. Five grams of *l*-methionine was dissolved in 20 ml. of *N* sodium hydroxide. While the methionine solution was being vigorously stirred there was added simultaneously, from two dropping funnels, 4.52 g. of chloroacetyl chloride and 40 ml. of *N* sodium hydroxide. The addition required thirty minutes. The solution was then acidified with 90 ml. of *N* hydrochloric acid and the acidified solution was extracted five times with 150-ml. portions of ethyl ether. After removal of the ether by distillation the sirupy residue was crystallized by rubbing with petroleum ether and ethyl ether. The yield varied in several preparations from 5.0 g. to 5.4 g. (65–71% of theoretical). The melting point of the several preparations of chloroacetyl-*l*-methionine was 105–107°.

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[1] Fischer and Suzuki, *Ber.*, **37**, 4575 (1904).