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

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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).