NOTES.

The Reaction between Aluminium, Iodine, Ethyl Alcohol, and Water. Preparation of Ethyl Iodide.

By A. O. Jones and G. Melling Green.

In the preparation of alkyl iodides by means of aluminium in place of the usual phosphorus, the quantities of reagents used were calculated on the basis:

$$2Al \xrightarrow{3I_2} 2AlI_3 \xrightarrow{6H_2O} 2Al(OH)_3 + 6HI \xrightarrow{6EtOH} 6EtI + 3H_2O.$$

This scheme, however, does not represent the course of the reaction, since, although this was very vigorous, it came to an end when 50% of the iodine had been transformed into ethyl iodide, and there was also a considerable evolution of a gas which forms an explosive mixture with air and may be hydrogen or a hydrocarbon. Moreover, the percentage conversion was constant even when the quantities were slightly varied. If the ethyl iodide formed was now distilled, and sulphuric acid–alcohol mixture then added, a further quantity of iodide could be distilled, becoming progressively darker in colour owing to the reaction between the hydrogen iodide formed and sulphuric acid. Substitution of phosphoric acid for the sulphuric acid gave a much smaller yield of ethyl iodide.

The research is being continued in order to prove the course of the reaction and the nature of the aluminium complex formed.

Ethyl iodide may be quickly and conveniently prepared as follows. A mixture of 25 g. of iodine, 40 c.c. of 84% (by weight) alcohol, and 3 g. of aluminium foil in small pieces is warmed gently. Once started, the reaction increases progressively in vigour, but can be controlled by cooling; it subsides in about 10 minutes, and is complete in about an hour. The product is distilled until deep red fumes appear. A cold mixture of 35 c.c. of 84% alcohol and 20 c.c. of 85% sulphuric acid is added to the cooled residue. After 15 minutes, distillation is begun, and continued until no more oily drops form in the water in the receiver. The yield of crude iodide is 13 c.c. (approx. 80%).—Technical College, Huddersfield. [*Received, June 29th*, 1926.]

The Isomeric Fluorobenzaldehydes and their Derivatives.

By John Baldwin Shoesmith, Charles Edwin Sosson, and Robert Henry Slater.

Ortho- and para-fluorobenzaldehydes have now been separated from the bisulphite compounds obtained as by-products in the preparation of the corresponding fluorobenzyl bromides (Shoesmith and Slater, this vol., p. 220). The b. p.s are: o-, 175°/760 mm.; p-, 181·5°/763 mm. (compare Rinkes, *Chem. Weekblad*, 1919, **16**, 206). *m*-Fluorobenzaldehyde could not be obtained pure in this way, but was prepared by passing a current of pure dry hydrogen for 24 hours into a commercial xylene solution of *m*-fluorobenzoyl chloride (Meyer and Hub, *Monatsh.*, 1910, **31**, 9344) of b. p. 73·4°/11 mm. in contact with palladinised barium sulphate (compare Rosenmund, *Ber.*, 1918, **51**, 591). An apparently theoretical yield of the aldehyde bisulphite compound, when dried over phosphoric oxide, became a 60% yield, the same phenomenon being noted with benzoyl chloride. m-*Fluorobenzaldehyde* is a colourless oil of b. p. 173°/760 mm. (Found: F, 14·8. C_7H_5OF requires F, 15·3%). The fluorine content was estimated by mixing 0·20 g. of the aldehyde with 0·40 g. of starch and placing small quantities of this powder and of sodium peroxide (10 g. in all were used) alternately in a Parrs bomb. The bomb was closed, well shaken, and fired in the usual way. This modification of Hahn and Reid's method (*J. Amer. Chem. Soc.*, 1924, **46**, 1652) was necessary because the aldehyde, starch, and sodium peroxide explode spontaneously when mixed in an open vessel. The fluorine was then estimated as calcium fluoride in the usual manner.

The fluorobenzaldoximes crystallise from ligroin in fine, white plates: *o*-, m. p. 63° (Rinkes gives 62·6°) (Found: N, 10·2%); *m*-, m. p. 63° (Found: N, 10·1%); *p*-, m. p. 86·5° (Rinkes gives 81·2°) (Found: N, 10·2%).

The *fluorobenzaldehydephenylhydrazones* crystallise from aqueous alcohol in white plates: *o*-, m. p. 89·5° (Found: N, 13·2. $C_{13}H_{11}N_2F$ requires N, 13·1%); *m*-, m. p. 114° (Found: N, 13·15%); *p*-, m. p. 147° (Found: N, 13·2%).

The *fluorobenzaldehyde*-p-*nitrophenylhydrazones* crystallise from dilute acetic acid in fine, orange, rectangular needles: *o*-, m. p. 205° (Found: N, 16·3. $C_{13}H_{10}O_2N_3F$ requires N, 16·3%); *m*-, m. p. 202° (Found: N, 16·2%); *p*-, m. p. 212° (Found: N, 16·4%).

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The Oxidation of Sabinol with Hydrogen Peroxide. By GEORGE GERALD HENDERSON and ALEXANDER ROBERTSON.

THIS work was undertaken with the object of comparing the products of the action of hydrogen peroxide on the terpene alcohol sabinol with those formerly obtained by oxidising sabinene itself with the same reagent. According to Semmler (*Ber.*, 1900, **33**, 1459), sabinol yields sabinylglycerol, $C_{10}H_{15}(OH)_3$, and α-tanacetonedicarboxylic acid when oxidised with potassium permanganate, but we have found that these compounds are not formed when hydrogen peroxide is used as the oxidising agent. Sabinol (b. p. 208—209°/760 mm., $d_{4°}^{20°}$ 0·9420, n_D 1·4874; prepared from oil of savin), in solution in glacial acetic acid, was slowly attacked by 30% aqueous hydrogen peroxide. The crude oxidation product contained a mixture of two isomeric compounds, $C_{10}H_{16}O(OH)_2$, partly free and partly in the form of acetates, which were respectively identical with the two glycol anhydrides, m. p. 172° and 174°, obtained by oxidising sabinene in a similar manner (J., 1923, **123**, 1849). The identity was proved by analysis, by determination of the mixed melting points, and by preparation of the well-defined di-*p*-nitrobenzoates. No other definite product was found except a trace of cymene.

In the paper just referred to, we stated that, although the glycol anhydrides evidently reacted with hydrogen bromide, attempts to isolate definite bromo-derivatives were not successful. The experiment has now been repeated with a larger quantity of material and under modified conditions. A solution of 3 g. of the glycol anhydride of m. p. 172° in 60 c.c. of glacial acetic acid was saturated with hydrogen bromide, kept for 3 days and then heated at 50° for ½ hour. The acetic acid and the excess of hydrogen bromide were removed in a vacuum desiccator, and the dark residue was mixed with a small quantity of alcohol; a crystalline bromo-compound was then gradually deposited. After several crystallisations from alcohol, this compound was obtained in colourless needles, m. p. 159—160° (decomp.). The quantity obtained was too small to give a satisfactory analysis, but the result indicated that the compound is probably 1 : 2 : 3 : 4-tetrabromomenthane.

The formation of the compounds $C_{10}H_{16}O(OH)_2$ from sabinol as well as from sabinene lends support to the view expressed (*loc. cit.*) that these compounds are glycol anhydrides derived from 1 : 2 : 3 : 4-tetrahydroxymenthane, which perhaps is formed as an intermediate product in the oxidation process.—UNIVERSITY OF GLASGOW. [*Received, July* 1*st*, 1926.]