

Further details of this work will be published elsewhere.

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¹ Claesson, I., and Claesson, S., *Arkiv Kemi, Min. Geol.*, **19**, A, No. 5 (1944). Claesson, S., *Dis. Farad. Soc.*, **7**, 321 (1949).

² Landler, C.R. *Acad. Sci., Paris*, **225**, 234 (1947).

A New Method for working up Processing Mixtures containing Anhydrous Aluminium Chloride

ON working up the mixture in order to isolate the products of reactions catalysed by anhydrous aluminium chloride, the first step is usually decomposition with an ice-acid mixture¹. However, difficulties are often encountered in the separation of the aqueous phase containing the aluminium salts, due to the formation of stable emulsions. This makes the repeated washing of the organic phase necessary to ensure complete extraction of the aluminium salts, a rather tedious operation.

In our experiments we found that a solution of sodium fluoride could be used with advantage at this stage, and also to eliminate interference during later stages. The favourable effect is due to the formation of the complex Na_3AlF_6 which is soluble in water. The advantages of the method may be summarized as follows.

1. The aqueous solution, when it contains sodium aluminium fluoride, is readily and quickly separable from the organic phase, in our experiments, nitrobenzene.

2. When the second step of working up the reaction mixture is steam distillation of an alkaline solution, no separation of the aqueous phase is necessary. Further, as the aqueous phase is already alkaline, no addition of alkali is required to secure the alkaline reaction of the medium.

3. When a neutral solution is wanted during processing, a slightly acidified solution of sodium fluoride can be used. The exact amount of hydrochloric acid necessary can be determined by blank tests on a solution of anhydrous aluminium chloride at the same concentration as the reaction mixture. These blanks are of great importance as the quantity of acid required depends on the quality of the sodium fluoride.

4. Since the method facilitates the working up and analysis of very small quantities, it is particularly suitable for micropreparation and kinetic studies. Although stoichiometrically 6 moles of sodium fluoride are required for each mole of aluminium chloride, we find it best to use at least 7 moles of the reagent.

As an example, part of an unpublished kinetic study will be given here, where a quantitative determination of the ketone was carried out on the mixture obtained by the Fries rearrangement of thymyl acetate in nitrobenzene, in the presence of aluminium chloride.

Preparation of thymyl-methyl ketone. 2.4031 gm. (12.4 m.moles) of 99.14 per cent thymyl acetate was treated with a solution of 4.17 gm. (31.3 m.moles) of anhydrous aluminium chloride (B.D.H.) in nitro-

benzene, and the mixture was made up to 20 ml. with nitrobenzene. The mixture was allowed to stand for 5 hr. in a thermostat of 40° C., and then an aliquot of 2 ml. was transferred by pipette into an equal volume of ethanol. This mixture was refluxed for 30 min. with 30 ml. of a solution of sodium fluoride (containing 35 gm. sodium fluoride), 3 ml. of 1 N sodium hydroxide and 24 ml. of ethanol. After cooling, the solution was made up at room temperature to 100 ml. with water and allowed to stand overnight in a glass cylinder, 2.5 cm. in diameter, when nitrobenzene separated. A portion of 50 ml. was withdrawn from the clear supernatant with a pipette, treated with 3 ml. of 1 N hydrochloric acid and distilled until the temperature of vapour reached 98° C. (approximately 5 min.). The residue was allowed to stand for 2 hr. in an ice box, then the precipitated crystals were filtered through a glass filter, dried at 110° C. for an hour and weighed together with the filter. Thymyl-methyl ketone was then separated from inorganic contaminants by treating the filter with 3 × 5 ml. of hot ethanol. After drying the filter for 20 min. at 110° C., it was again weighed. The difference was 0.0881 gm. The almost white, crystalline product obtained by evaporating the ethanolic solution had a melting point of 122.5–125° C. For $\text{C}_{12}\text{H}_{16}\text{O}_2$, molecular weight 192.25: calculated (per cent): C, 74.97; H, 8.39: found (per cent): C, 74.95; H, 8.07.

The ketone obtained by the classical Rosenmund method² was nearly black, m.p. 115–122° C.

The correction for the solubility of the ketone gives a gross yield of 0.092 gm.; thus by the Fries rearrangement a yield of 94.6 per cent was obtained. With suitable modifications the quantity of unconverted ester can also be determined by titration³.

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PHYSICAL SCIENCES

Calculation of a 'Cosmic Ray Age' for the Iron Meteorite 'Carbo'

THE potassium of the iron meteorite 'Carbo', compared with ordinary potassium, is substantially enriched in the isotopes potassium-40 and -41, as shown in the recent isotopic analysis by Voshage and Hintenberger¹. At least 15 per cent of these isotopes in their sample of 'Carbo' appear to have been produced through the action of cosmic rays. Stoenner and Zähringer² found that the concentration of potassium may vary considerably within an iron meteorite. Their analyses were based on the detection of potassium-41 and the assumption that the potassium had the same isotopic composition as terrestrial potassium. If, however, their value of 0.031 p.p.m.