172. *Acylation and Allied Reactions catalysed by Strong Acids. Part X.* The Alleged Activity of Silver Perchlorate as a Friedel–Crafts Catalyst.*

By H. Burton and P. F. G. Praill.

Contrary to various statements in the literature, silver perchlorate has been found not to be a catalyst for the acetylation of *m*-xylene with acetic anhydride or for the polymerisation of styrene at room temperature.

THE designation of silver perchlorate as a " Lewis acid " (Lewis, *J. Franklin Inst.*, 1938, **226**, 293), because of the tendency of silver to complete a stable shell of two electron pairs, as in the formation of $Ag(NH_3)_2^+$, has given rise to the idea that silver perchlorate can act as a Friedel–Crafts catalyst. The catalysts normally used in the Friedel–Crafts reaction, *e.g.*, metal halides, sulphuric acid, etc., are true catalysts since they can be recovered unchanged, except for halogen transfer, provided that they do not combine with the end-product. When secondary reactions are excluded, it is well known that the catalysts are able to give stoicheiometrically greater yields than would be possible if each molecule gave rise to only one molecule of product; the reason for this is known to be the constant regeneration of the catalyst by the reactants. The process by which this could occur with silver perchlorate is not easy to envisage and one would not expect it to be a catalyst in the above sense. The ability of silver perchlorate to form complexes with many unsaturated organic substances, *e.g.*, aromatic hydrocarbons is, however, well known, and may be taken as an indication of its " Lewis acid " character; this property probably has no relation to its ability to act as a catalyst in the above sense.

Silver perchlorate has been used as a component in a system for effecting acylation (Mackenzie and Winter, *Trans. Faraday Soc.*, 1948, **44**, 159, 171, 243; Barrera and Costa, *Ann. Chim.*, 1949, **4**, 82; Cauquil and Barrera, *Bull. Soc. chim.*, 1949, **16**, 689; Burton and Praill, *J.*, 1950, 2034; 1951, 522, 529) but in these cases there is no evidence that it acts as a catalyst. Its sole function is the formation, by metathesis, of an organic perchlorate, which then reacts with the substance under investigation to give an acyl derivative;

$$R{\cdot}CO{\cdot}X + AgClO_4 \longrightarrow R{\cdot}CO^+ClO_4^- + AgX$$

$$R'H + R{\cdot}CO^+ClO_4^- \longrightarrow R'{\cdot}CO{\cdot}R + H^+ + ClO_4^-$$

The presence of the true catalyst, $HClO_4$, can be shown by carrying out the reaction in an excess of an acid anhydride, when the yield may exceed that stoicheiometrically possible on the amount of acyl perchlorate used. This is due to regeneration of the acylium ion by the reaction :

$$H^+ + (R{\cdot}CO{\cdot})_2O \rightleftharpoons (R{\cdot}CO{\cdot})_2OH^+ \rightleftharpoons R{\cdot}CO^+ + R{\cdot}CO_2H$$

We have shown (*locc. cit.*, and Part VIII, J., 1953, 827) that silver perchlorate has no observable catalytic effect on the acylation of aromatic compounds and, although it is not so easy to prove, we believe that this is true for alkylation also.

We cannot support the recent assertion that silver perchlorate can act as a catalyst in

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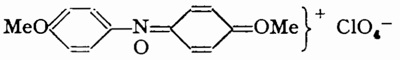
* Part IX, preceding paper.

the acetylation of *m*-xylene by acetic anhydride (Cauquil, Barrera, and Barrera, *Bull. Soc. chim.*, 1951, **18**, 791; *Compt. rend.*, 1951, **233**, 1117). All the results quoted could be equally well explained if the silver perchlorate used had contained a little perchloric acid. It is exceedingly difficult to remove all traces of perchloric acid from silver perchlorate. Nevertheless, the amount of acid which it normally contains, after careful drying over phosphoric oxide and potassium hydroxide, is so small, that under our conditions its contribution as a catalyst would be insignificant. Contrary to these authors, we now show that mixtures containing 1 mol. of silver perchlorate, 3 mols. of acetic anhydride (*i.e.*, those likely to be most efficient according to the above workers), and 4 mols. of *m*-xylene give no detectable amounts of ketone after 24 hours at room temperature. A small amount was, however, produced at 95° during 5 hours. In view of these results we carried out similar reactions using the more reactive anisole, and then found that the yields of ketone, based on the amount of silver perchlorate used, varied from 1 to 6% for periods of 24 to 64 hours at room temperature. We thought that this result might be explained if the chloride content (given as 0·001%) of the acetic anhydride used was due to the presence of acetyl chloride. However, the anhydride used, which had been refluxed for several hours with silver acetate and redistilled over fresh silver acetate, still gave similar amounts of *p*-methoxyacetophenone. It thus seemed possible that traces of perchloric acid might be responsible for the reaction. Accordingly, a suspension of powdered silver perchlorate in acetic anhydride was shaken for several hours with a little silver acetate, and the anisole then added to the mixture. The amount of ketone formed was barely detectable. This was also the case when a drop of water (*ca.* 0·06 mole) was added to mixtures of similar composition although in these circumstances a marked pink colour developed in the mixture. The effect of water was not altogether unexpected since we had shown previously (*loc. cit.*) that small quantities of acetic acid have little effect on the production of ketone but that beyond a certain concentration the yield is markedly decreased. Little importance attaches to the pink colour because we have shown that a similar, but more intense, colour can be produced in mixtures containing anisole, acetic anhydride, perchloric acid, and traces of silver nitrate. The colour is undoubtedly due to the formation of a compound of type (I) described by Kehrmann and Decker (*Ber.*, 1921, **54**, 2439). It is not improbable that traces of silver nitrate are occluded by the silver oxide used in the preparation of silver perchlorate. Our specimen of silver perchlorate in fact gave a slight positive reaction for nitrate with the diphenylamine reagent.



(I)

The observation by Cauquil and her collaborators (*locc. cit.*) that when the above mixtures are heated some of the ketone is oxidised to a carboxylic acid is also readily explained if perchloric acid existed in the mixtures. It must be pointed out that when mixtures such as these are heated there is always a possibility that some slight oxidation by the metal perchlorate may initiate the formation of perchloric acid; also that once oxidation by perchloric acid has commenced any hydrogen chloride formed would serve to regenerate perchloric acid from the silver salt.

It has also been claimed that silver perchlorate is a Friedel–Crafts type of polymerisation catalyst. Thus, Eley and Richards (*Trans. Faraday Soc.*, 1949, **45**, 425) state that silver perchlorate will polymerise 2-ethylhexyl vinyl ether, although it would appear from their results that the catalytic power is poor when compared with, *e.g.*, that of stannic chloride; it was also shown that water had an appreciable accelerative effect on the reaction. However, the catalytic activity could be accounted for if traces of a much more efficient catalyst were present. This could be an alkyl perchlorate formed from traces of halide remaining in the vinyl ether. Alternatively, the silver perchlorate used might have contained a trace of free perchloric acid. Salomon's results (*Rec. Trav. chim.*, 1949, **68**, 903) on the polymerisation of styrene and related compounds could be similarly explained. We have found that styrene is unaffected by approx. 10% of its weight of silver perchlorate during 48 hours at room temperature.

EXPERIMENTAL

Materials.—Silver perchlorate was treated as described previously (Part II). Acetic anhydride was an " AnalaR " reagent, and *m*-xylene and anisole were dried and freshly redistilled.

A solution of silver perchlorate (0·05 mole) in acetic anhydride (0·15 mole) and *m*-xylene (0·2 mole) was kept in a tightly stoppered flask in the dark at room temperature for 24 hours. The mixture was then poured into cold water and extracted thrice with ether. After the combined extracts had been washed with water, thrice with 2N-sodium hydroxide, and again with water, the dried (Na_2SO_4) solution was evaporated. As much as possible of the unchanged *m*-xylene was distilled off (0·18 mole) and the residue treated with Brady's reagent; there was no indication of 2 : 4-dinitrophenylhydrazone formation. Acidification of the alkaline washings gave no 2 : 4-dimethylbenzoic acid.

The experiment was repeated with anisole in place of *m*-xylene; 0·0005 mole of *p*-methoxyacetophenone was isolated as the 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 220°. No *p*-methoxybenzoic acid was detected.

Other experiments were carried out under these conditions with the results referred to in the text. In every case the recovery of *m*-xylene or anisole was at least 90%, and in no case was any acidic product isolated.

In the experiment to remove any perchloric acid from the silver perchlorate, the latter was crushed with a glass rod beneath the acetic anhydride, pure silver acetate (0·1 g.) was added, and the mixture was shaken for 3 hours before adding the anisole.

An experiment in which *m*-xylene (0·1 mole), acetic anhydride (0·05 mole), and silver perchlorate (0·05 mole) were heated on a steam-bath for 5 hours (internal temp. 95—97°) gave a deep orange-coloured mixture; a small amount of flocculent solid separated. The small amount of ketone (0·002 mole) was isolated as the 2 : 4-dinitrophenylhydrazone. The alkaline washings contained a small amount of material (0·1 g.) which was partly soluble in aqueous sodium hydrogen carbonate.

Silver perchlorate (0·95 g.) was dissolved in styrene (10 g.) which had been washed with 2N-sodium hydroxide, dried, and distilled; the solution was kept in the dark for 48 hours at room temperature. Distillation of the mixture at 10—11 mm. gave 8·3 g. of unchanged styrene. In a control experiment without the silver perchlorate 8·6 g. of styrene were similarly recovered.

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