[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

MIXED CATALYSTS IN THE FRIEDEL AND CRAFTS REACTION. THE YIELDS IN TYPICAL REACTIONS USING FERRIC CHLORIDE-ALUMINUM CHLORIDE MIXTURES AS CATALYSTS

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In a preliminary paper[1] it was shown that the yield of benzophenone from benzoyl chloride and benzene is practically a straight line function between pure ferric chloride and pure aluminum chloride. Boswell and McLaughlin[2] had found that the amount of hydrogen chloride evolved in the reaction of benzene with chloroform[3] was a maximum when an equimolecular mixture of ferric chloride and aluminum chloride was used, and Whitby and Gallay[4] that the yields of *o*-benzoylbenzoic acid from phthalic anhydride and benzene using one mole of ferric chloride and one mole of aluminum chloride were higher than the mean of those obtained using pure aluminum chloride and pure ferric chloride. We have now completed an investigation of a number of typical Friedel and Crafts reactions and have been able to make several generalizations in regard to the effect of varying the ratio of ferric chloride to aluminum chloride on the yields of the desired product.

Experimental

In most cases an excess of benzene was used as solvent and the general procedure was the same as given in the previous paper,[1] the chief difference being that a simple mixture of the powdered chlorides was used instead of a fused mixture. A number of experiments showed that fused and unfused mixtures gave the same results. Because of the larger amount of catalyst required in the case of anhydrides, 100 cc. of benzene was used instead of the usual 70 cc. in order to get satisfactory stirring. The time of refluxing of the reaction mixture was kept constant throughout a run but varied with the different reactions and was in all cases one hour after all visible evolution of hydrogen chloride had stopped. If the product could be readily distilled at atmospheric pressure the yield was based on distilled

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[1] Riddell and Noller, THIS JOURNAL, **52**, 4365 (1930).

[2] Boswell and McLaughlin, *Can. J. Res.*, **1**, 400 (1929).

[3] This reaction is not very satisfactory for a study of this kind, particularly when the amount of hydrogen chloride evolved is taken as a measure of the extent of the reaction taking place. In the first place the amount of hydrogen chloride evolved often bears little relation to the amount of the desired product that is formed [cf. Rubidge and Qua, THIS JOURNAL, **36**, 732 (1914)], and in the second place ferric chloride is known to have a chlorinating action on triphenylmethane, the main product of the reaction [Meissel, *Ber.*, **32**, 2422 (1899)].

[4] Whitby and Gallay, *Can. J. Res.*, **2**, 31 (1930).

product boiling over a suitable range. In other cases it was found that the results could be more easily reproduced by heating the product to 160° at 25 mm. and weighing the residue. The product was in all cases finally distilled to show its purity. As the proportion of ferric chloride increased, the isolation of the product became more difficult because of the presence of tarry by-products.

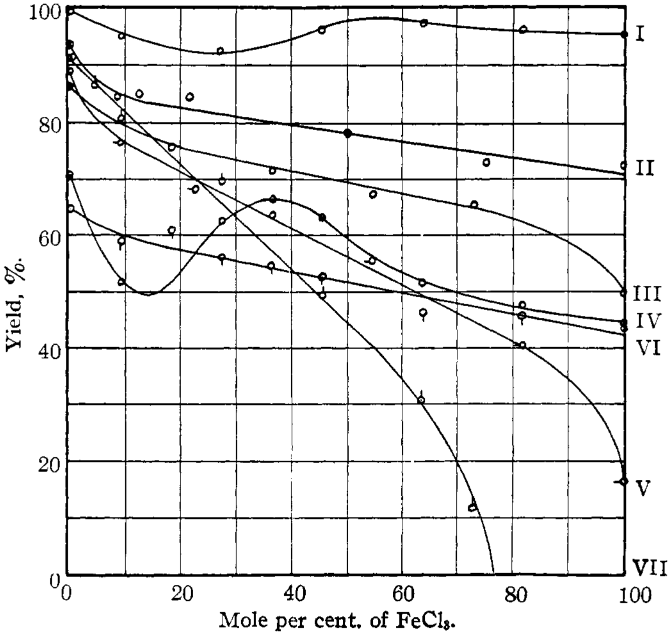

Fig. 1.—Reactions requiring 1 mole of catalyst: I, phenyl-*p*-tolylsulfone from *p*-toluenesulfonyl chloride and benzene; II, benzophenone from benzoyl chloride and benzene; III, *n*-butyrophenone from *n*-butyryl chloride and benzene; IV, triphenylcarbinol from carbon tetrachloride and benzene; V, *n*-propiophenone from *n*-propionyl chloride and benzene; VI, acetophenone from acetyl chloride and benzene; VII, benzophenone from benzene and excess carbon tetrachloride.

In the series on the preparation of benzophenone from carbon tetrachloride, excess carbon tetrachloride (70 cc.) was used as a solvent and the entire reaction run at 5–10.° Several series were also run using equivalent amounts of reactants and 100–150 cc. of carbon disulfide as a solvent. All the results are summarized in the curves of Figs. 1, 2 and 3.

Discussion

Before beginning work on the mixed catalysts, the amount of pure aluminum chloride necessary to give the highest yield was determined. It is quite generally known that one mole of aluminum chloride ($AlCl_3$) is required for each mole of acid chloride used, and two moles per mole of acid anhydride. We have found that in all cases studied the yield is directly proportional to the amount of catalyst up to these optimum amounts. A point that does not seem to have been previously recorded is that the yield rapidly falls off when more than these optimum amounts are used. We have also found that the reaction of benzene with excess carbon tetrachloride to give diphenyldichloromethane and of carbon tetrachloride with excess benzene to give triphenylchloromethane both require one mole of catalyst even though no oxygen compounds are involved. The reaction of benzoyl chloride and benzene using varying amounts of pure ferric chloride likewise gives the maximum yield when one mole of ferric chloride per mole of acid chloride is used. Accordingly in all of the work on mixed catalysts 1.1 mole of catalyst was used per mole of acid chloride and 2.2 moles per mole of acid anhydride.

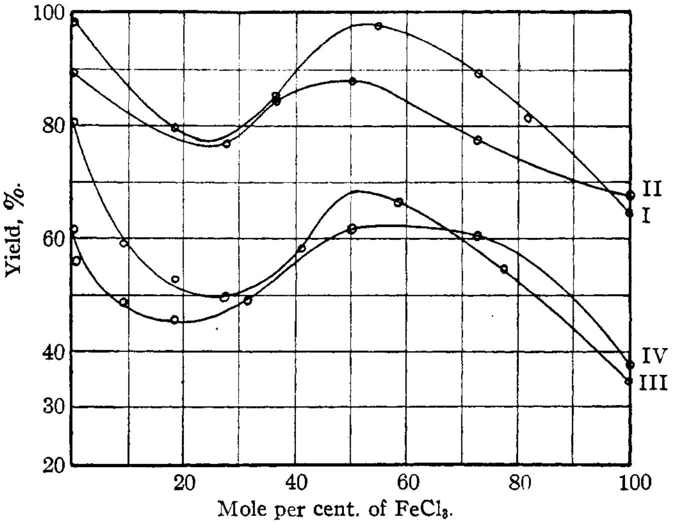

Fig. 2.—Reactions requiring 2 moles of catalyst: I, *n*-butyrophenone from *n*-butyric anhydride and benzene; II, benzophenone from benzoic anhydride and benzene; III, *n*-propiophenone from *n*-propionic anhydride and benzene; IV, acetophenone from acetic anhydride and benzene.

In the curves, the percentage yield is plotted against the mole per cent. of ferric chloride. It is readily seen that the curves are in general of two types: (1) those in which the yield is decreased in proportion to the amount of ferric chloride present[5] and (2) those in which the yield decreases rapidly

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[5] Most of these curves show an initial rapid drop, a point which was discussed in the previous paper. The rapid drop as pure ferric chloride is approached is without doubt due to the difficulty of working up the reaction mixture because of the increased amount of tarry by-products.

to a minimum, then rises to a maximum and finally falls off to the value obtained with pure ferric chloride. To the first group belong the reactions of all the carboxylic acid chlorides with benzene and of benzene with an excess of carbon tetrachloride. In the latter case the ferric chloride is entirely non-reactive, probably because of the low temperature at which the reaction is carried out, and the curve is essentially the same as that obtained when pure aluminum chloride is used and the amount of catalyst is decreased. To the second group belong the reactions of all the acid anhydrides, of *p*-toluene sulfonyl chloride and of carbon tetrachloride with excess benzene.

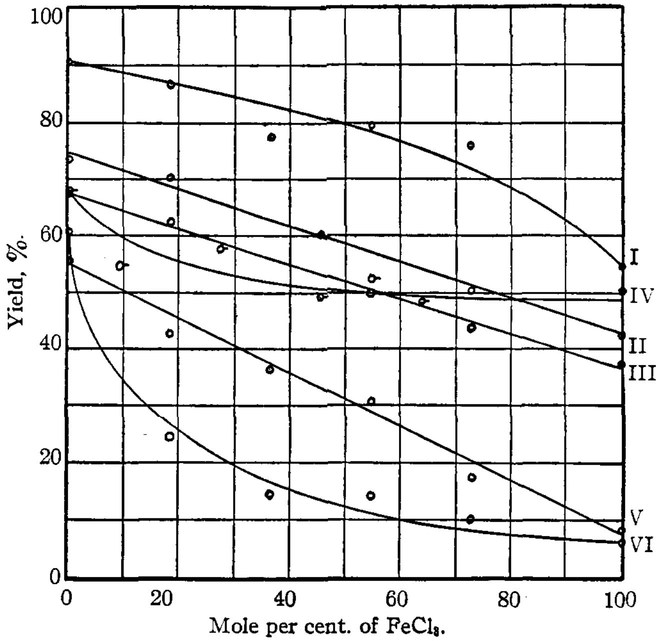

Fig. 3.—Reactions run in carbon disulfide: I, *p*-methoxyacetophenone from acetic anhydride and anisole; II, *p*-methoxyacetophenone from acetyl chloride and anisole; III, acetophenone from acetyl chloride and benzene; IV, acetophenone from acetic anhydride and benzene; V, *p*-bromoacetophenone from acetyl chloride and bromobenzene; VI, *p*-bromoacetophenone from acetic anhydride and bromobenzene.

It is quite difficult to explain the curves of the second type. In the first place this type occurs whether one or two moles of catalyst is required per mole of reactant. While we have found no exceptions to the rule that carboxylic acid chlorides give curves of the first type and acid anhydrides give curves of the second type, *p*-toluene sulfonyl chloride is an acid chloride and carbon tetrachloride is not an anhydride and yet both give curves of the second type. The maximum in the curves of the second type appears to come in the majority of cases at fifty mole per cent. of ferric chloride and in most cases is almost equal to the yield obtained with pure aluminum chloride. In the case of carbon tetrachloride with excess benzene, however, the maximum comes at about thirty-five mole per cent. The maximum is quite sharp in all cases except that of acetic anhydride, where it is rather flat with little variation in yield while the amount of ferric chloride changes from fifty to seventy mole per cent. The minimum in the curves is in the neighborhood of twenty-five mole per cent. of ferric chloride and is always somewhat higher than the yield with pure ferric chloride.

If compound formation between the aluminum and ferric chlorides is to be considered as a possible explanation of the above results, it is almost necessary to assume the formation of two compounds, one composed of twenty-five mole per cent. of ferric chloride, which gives rather poor yields of product, and one composed of fifty mole per cent. of ferric chloride which gives yields almost as good as pure ferric chloride. This does not seem to be a very plausible assumption. Moreover, attempts were made to determine by the fusion point method whether compound formation between ferric and aluminum chlorides takes place and no evidence for it could be obtained. These results obtained at relatively high temperatures do not of course entirely eliminate the possibility of compound formation at the temperatures at which the Friedel and Crafts reaction takes place.

The results obtained when carbon disulfide was used as a solvent appear to further complicate the situation. These experiments, which were undertaken to determine the behavior of aromatic compounds other than benzene, show that in carbon disulfide solution neither acid chlorides nor acid anhydrides give the typical minimum–maximum curve within the limits of experimental error.

Summary

The yields of product in a number of typical Friedel and Crafts reactions have been determined for various mixtures of anhydrous ferric chloride and aluminum chloride as catalysts. It was found that when excess benzene is used as a solvent, the reactions are of two types: (1) those in which the decrease in yield is proportional to the amount of ferric chloride added and (2) those in which the yield first decreased, then rose to a maximum at about fifty mole per cent. ferric chloride and then decreased to the yield with pure ferric chloride. It was further found that all reactions appear to be of the first type when run in carbon disulfide.

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