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## The Effect of Ferric Chloride on the Cadmium Reaction

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eral symmetrical molecules which appeared to have appreciable dipole moments (4). For example, 4,4'-dinitrobiphenyl was reported to have a dipole moment of 0.7 to 1.0 debyes (5). From dielectric loss measurements DiCarlo and Smyth illustrated that this compound, if polar, could not have a permanent dipole moment greater than 0.20 D, and thus they concluded that a large atomic polarization exists in the molecule. We have encountered similar cases in our work with *para-beta*-disubstituted styrenes. Consider a molecule in which the same group is substituted in both the *para* and *beta* positions of styrene. If the groups are *trans* to each other the molecule would be expected to have a dipole moment equal approximately to that of styrene, since the groups will act equally but in opposite directions. We have found *trans-p*,  $\beta$ -dinitrostyrene to have a dipole moment of 0.83 D, and *trans-p*,  $\beta$ -dicyanostyrene a dipole moment of 1.01 D. Each of these is much greater than the value which we have presented for styrene in this article. It is possible that these relatively large values are due, at least in part, to abnormally large atomic polarizations.

#### ACKNOWLEDGMENT

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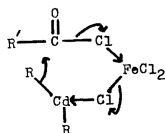
## The Effect of Ferric Chloride on the Cadmium Reaction

RICHARD BOGAN, JOSEPH PLAMONDON and KENNETH W. KRAUS<sup>1</sup>

*Abstract.* The reaction of di-*n*-butylcadmium with either capryl chloride or benzoyl chloride at  $-10^{\circ}$  in the presence of ferric chloride yields 50% of the expected ketone. The reactions of the same acid chlorides with diphenylcadmium are hampered by coupling of the aromatic cadmium reagent in the presence of the ferric chloride. A yield of 20-30% of ketone can be obtained, however, if the ferric chloride is added to the precooled acid chloride followed by the addition of the diphenylcadmium.

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It has been reported that the reaction of an organocadmium reagent with the ester acid chloride of an unsymmetrical dibasic acid at  $-10^\circ$  in the presence of ferric chloride results in no rearrangement (1). These authors have taken this result, plus the fact that the reaction is subject to steric hindrance, as indication of a concerted mechanism.



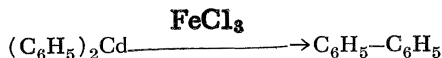
This low temperature, catalyzed reaction would seem to have considerable synthetic application to those reactions with acid chlorides which lead to rearranged products when the ordinary cadmium reaction is used, as described by several authors (2, 3, 4, 5). The rearrangement in the ordinary cadmium reaction has been attributed by Cason (6) to the formation of an intermediate acylonium ion which can rearrange in certain instances.

Since the only reported example of a low temperature, catalyzed cadmium reaction (1) involved the use of an aliphatic cadmium reagent and an aliphatic acid chloride, it was considered useful to check the general application of the reaction by using both simple aliphatic and aromatic acid chlorides with both aliphatic and aromatic cadmium reagents as a preliminary step to reactions with the more complex acid chlorides. The results of these reactions are summarized in Table I.

The reaction of di-*n*-butylcadmium with benzoyl chloride (B) gave results (This result was taken from the unpublished work of Richard M. Weier and Kenneth W. Kraus) very similar to those previously reported (A) for the reaction of di-*n*-butylcadmium with capryl chloride (1).

In both of these reactions, A and B, the ferric chloride was added to the precooled cadmium reagent followed by addition of the acid chloride. However, when this was attempted with diphenylcadmium, a vigorous exothermic reaction took place when the ferric chloride was added to the cadmium reagent. The addition of benzoyl chloride apparently caused no further reaction since the workup yielded a large amount of biphenyl, but essentially no ketone.

Apparently diphenylcadmium gives a very facile reaction with ferric chloride similar to that reported for the Grignard reagent



(7). In any case, it was obvious that the coupling completely interfered with the desired reaction by destroying both the cad-

mium reagent and the ferric chloride before a reaction with the acid chloride could take place.

TABLE I

Reactions of Organocadmium Reagents with Acid Chlorides at  $-10^\circ$  in the Presence of Ferric Chloride

Reaction	Acid Chloride	Cadmium Reagent	Mole % <sup>a</sup> FeCl <sub>3</sub>	% Yield of Ketone
A	capryl	<i>n</i> -butyl	6	50
B	benzoyl	<i>n</i> -butyl	6	50
C <sup>b</sup>	benzoyl	phenyl	18	30
D <sup>b</sup>	capryl	phenyl	18	20

<sup>a</sup> Mole per cent of ferric chloride is based on moles of acid chloride.

<sup>b</sup> In runs C and D approximately 20% of the bromobenzene used turned up as biphenyl.

In an effort to circumvent this difficulty a reaction (C) was run in which the ferric chloride was added to the precooled benzoyl chloride followed by the addition of diphenylcadmium. Run C gave a 30% yield of benzophenone plus some biphenyl, which demonstrated that this method allowed the desired reaction to compete with the coupling. The same method of adding the diphenyl cadmium to a precooled mixture of capryl chloride and ferric chloride (D) was successful in giving a 20% yield of nonyl phenyl ketone.

About three times as much ferric chloride was used in reactions C and D with the aromatic cadmium reagent since it was obviously being consumed by reaction with diphenylcadmium, however, no exhaustive study has yet been made to determine the optimum amount of ferric chloride that should be used.

#### CONCLUSION

It can be seen from the results that an aliphatic cadmium reagent can be used successfully with either an aliphatic or aromatic acid chloride in the low temperature, catalyzed reaction, but the use of an aromatic cadmium reagent is limited both by rather poor yields and also by the formation of biphenyl from which the desired ketone must be separated.

However, it may be desirable to tolerate these limitations in those instances in which the ordinary cadmium reaction leads to rearranged products. In view of reports by Cason and co-workers (1,8), it should be pointed out that the method of adding ferric chloride to the cooled acid chloride before the addition of the cadmium reagent could conceivably lead to rearrangement in those instances where cyclization is possible. Therefore, in any attempt to use the reaction in this manner, the possibility of rearrangement will have to be considered.

It is our intention to apply these reactions, in the near future, to some complex acid chlorides that could potentially rearrange.

## EXPERIMENTAL

*Acid chlorides.* Capryl chloride, prepared by use of thionyl chloride and capric acid as has been reported (9), had  $n_D^{25}$  1.4393 after a vacuum distillation; literature  $n_D^{25}$  1.4393 (9). Reagent grade benzoyl chloride was used.

*General Procedure for Organocadmium Reactions in the Presence of Ferric Chloride.* The cadmium reactions were run according to the method described by Cason and Kraus (1), except that, after the workup the ketone was isolated by vacuum distillation. The cadmium reagent in each case was prepared by way of the Grignard reagent from 0.45 mole of butyl bromide or bromobenzene. All of the reactions were run on 0.15 mole of the acid chloride.

The procedure was modified for runs C and D by adding the ferric chloride to the precooled acid chloride followed by the addition of the diphenylcadmium.

*Ketone Products.* The nonyl phenyl ketone had b.p. 147-148° (3 mm.), m.p. 36°, 2,4-dinitrophenylhydrazone m.p. 107-108°, and phenylhydrazone m.p. 107-108°; literature b.p. 142-146° (2 mm.), m.p. 33-33.5° (10). The benzophenone had b.p. 151.5° (9 mm.) and m.p. 48°; literature m.p. 48° (11). The valerophenone was vacuum distilled and gave a semicarbazone, m.p. 165°; literature 166° (12).

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