

Reactions of Organocadmium Compounds with Carbonic Acid Chlorides

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It is well known that organocadmium compounds react with acyl halides to give ketones.^{1,2} The reaction is catalysed by magnesium salts.³ To our knowledge, the corresponding reactions of carbonic acid chlorides, phosgene and alkyl or aryl chloroformates, have only been investigated by Tatibouët and Fréon⁴ who obtained the symmetric ketone $R_2C=O$ from phosgene and the organocadmium compound R_2Cd , the yield being less than 20 % of theory.

The organocadmium compounds were synthesized from Grignard reagents and anhydrous cadmium chloride in diethyl ether^{1,2} or tetrahydrofuran.⁵ Their reactions with acyl chlorides were carried out under a nitrogen atmosphere in benzene or toluene after removal of the ether or in tetrahydrofuran using in most cases a mole ratio of acyl chloride to alkyl or aryl halide of 0.4. After a reaction period varying from 3 h to several days, often at reflux temperature, the mixture was usually treated with cold hydrogen chloride solution and the organic layer was separated and dried. The reaction products were usually not isolated but the solution was analysed, sometimes after a crude distillation, by gas-liquid chromatography and infra-red and proton magnetic resonance spectroscopy using authentic samples for comparison.

Phosgene and diphenylcadmium were allowed to react in a molar ratio of 2:1 in toluene. The main product was found to be benzophenone rather than benzoyl chloride. This indicates that benzoyl chloride, which is evidently formed as an intermediate, reacts with the organocadmium compound more rapidly than phosgene.

The reactions of organocadmium compounds with *alkyl* and *aryl chloroformates* should lead to the formation of the corresponding alkyl and aryl esters of carboxylic acids, if the reactions take place analogously as with ordinary acyl halides. The reactions of *dialkylcadmiums* and chloro-

formates (dimethylcadmium + methyl chloroformate, diethylcadmium + methyl chloroformate, diethylcadmium + ethyl chloroformate, diethylcadmium + phenyl chloroformate) yielded no ester at all or only traces (in the most favourable case, ester amounted to less than 3 % of the amount of unreacted chloroformate after 3 days). On the other hand, the reactions of *diphenylcadmium* and chloroformates (diphenylcadmium + ethyl chloroformate = ethyl benzoate, diphenylcadmium + phenyl chloroformate = phenyl benzoate) led mainly to the expected ester at a high rate (the yields did not increase after 20 h). The reaction is not, however, of any practical significance for the preparation of ordinary esters. The results show that, as in solvolytic reactions, chloroformates are less reactive than ordinary acyl chlorides toward organocadmium compounds. It can be mentioned for comparison that 48 % of the theoretical amount of ethyl methyl ketone was obtained from diethylcadmium and acetyl chloride in the present study (lit.² 46 %).

One purpose of the present investigation was to determine whether trichloromethyl esters can be prepared with the aid of organocadmium compounds. *Trichloromethyl chloroformate* (diphosgene) was allowed to react with dimethyl-, diethyl-, diisopropyl-, and diphenylcadmium for this purpose. Because the expected trichloromethyl esters are unknown and probably decompose easily at elevated temperatures, they could not be isolated or detected with certainty. Some indications of their formation were, however, found in the IR spectra (carbonyl peaks at about 1800 cm^{-1}), NMR spectra (a quartet at $\delta = 2.2$ ppm to TMS for $\text{CH}_3\text{CH}_2\text{C}(=\text{O})-$ in the case of $(\text{CH}_3\text{CH}_2)_2\text{Cd} + \text{ClCOOCCl}_3$), gas-liquid chromatograms (peak for benzoyl chloride, the probable decomposition product of trichloromethyl benzoate, in the case of $(\text{C}_6\text{H}_5)_2\text{Cd} + \text{ClCOOCCl}_3$; biphenyl was, however, the main product in this case), and in kinetic experiments with the reaction mixtures.

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The Dehydration of Triterpenoid Ring A ϵ -Lactams

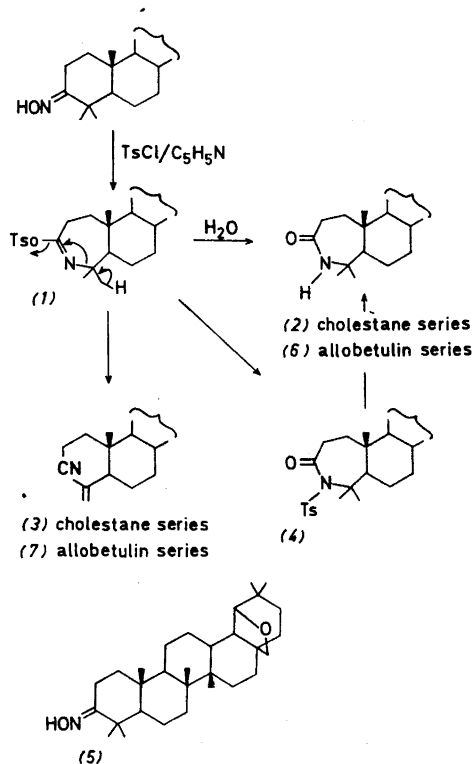
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In a recent communication¹ the mechanism of the "abnormal" Beckmann rearrangement² of triterpenoid oximes was discussed. In that particular case a mixture of the ϵ -lactam (2) and the seconitrile (3) was obtained by the treatment of 4,4-dimethyl-5 α -cholestan-3-one oxime with tosyl chloride in pyridine. It was proposed that the reactions involve the initial formation of the tosyloxy-imine (1) in agreement with the generally accepted mechanism of the "normal" Beckman rearrangement.³ (1) on hydrolysis gives the ϵ -lactam (2) either directly¹ or via the *N*-tosyl lactam (4),³ or eliminates tosic acid in the manner indicated to give (3). (1) and (4) must be interconvertible since prolonged reaction times favour the (presumably irreversible) formation of (3) at the expense of (2).

The failure of isolated (2) to provide (3) under the same conditions was considered further to support the mechanism given.¹ However, it is probable that this observation has no bearing on the mechanism as it merely indicates that (2) is not tosylated under the conditions. The use of more forcing conditions in the tosylation of (2) to give (1) or (4)* should result in the formation of (3) if the mechanism of the seconitrile formation is correct.

The treatment of *allobetulone* oxime (5),** m.p. 262°C (decomp.), with tosyl



chloride in pyridine gave, after one week at room temperature, 37% of the ϵ -lactam (6), m.p. 322°C, and 48% of the seconitrile (7), m.p. 256°C, with no starting material or *allobetulone* being recovered. Two days at room temperature gave 81% of (6) whereas two days at 90°C gave 59% of (7) and no (6) from (5). The ϵ -lactam (6) yielded, after 11 days at room temperature, in the presence of tosyl chloride in pyridine, only starting material, whereas (6) was converted to (7) in three days in 36% yield by the same reagent at 90°C.

Similarly, the ϵ -lactam obtained by the Beckmann rearrangement of methyl 18 β -H-3-oxoglycyrrhetate oxime is reported⁵ to yield 50% of the corresponding seconitrile on heating in pyridine in the presence of tosyl chloride.

The results are in agreement with the mechanism given¹ and clarify the role of the ϵ -lactam.

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* Dehydration of prim. amides by tosyl chloride in pyridine to give nitriles⁴ is thought to involve *O*-tosylation.

** All new compounds have been characterized by the usual spectroscopic methods and satisfactory elemental analysis.