

the final characterization of products or their derivatives. The α -naphthylurethan derivatives were used for β -phenylethyl alcohol and *o*-tolyl-carbinol. In Table I the chief products in the mixtures are listed in the third column.

Summary

Allylic rearrangement products have been ob-

tained by reaction of benzyl-metallic compounds of zinc, cadmium, mercury and aluminum with formaldehyde, acetyl chloride and carbon dioxide. Such rearrangements now appear to be general with benzyl-metallic types, and the extent of rearrangement generally decreases with the decreasing reactivity of organometallic compounds.

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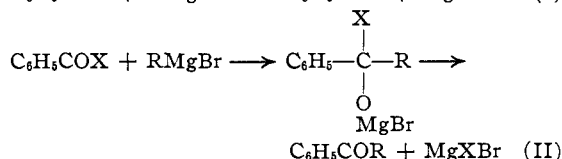
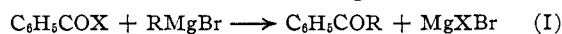
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Relative Reactivities of Organometallic Compounds. XXIV.* Reaction Rates of Benzoyl Halides with Di-*p*-tolylmercury

BY HENRY GILMAN AND JOSEPH F. NELSON

Introduction

There is no direct evidence concerning the mechanism of reaction between acid derivatives and organometallic compounds. For example, the ketones formed by interaction of benzyl halides and Grignard reagents may have resulted from either or both of the following transformations



That is, reaction may have occurred by direct metathesis (I) or by preliminary addition to the carbonyl group (II).

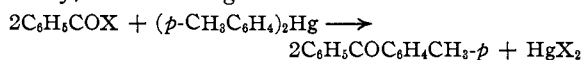
Indirect evidence for Reaction II has been supplied by Entemann and Johnson.¹ These authors have formulated a very useful series of relative reactivities of functional groups. The series, obtained by competitive reactions of a pair of compounds with an insufficient quantity of phenylmagnesium bromide to react with both, is as follows: $-\text{CHO} > -\text{COCH}_3 > -\text{NCO} > -\text{COF} > -\text{COC}_6\text{H}_5, -\text{COCl}, -\text{COBr} > -\text{COOC}_2\text{H}_5 > -\text{C}\equiv\text{N}$. If Reaction I were correct one would expect the acid fluoride to be the least reactive of the three benzoyl halides examined. However, because the acid fluoride was actually found to be the most reactive, it was concluded that reaction occurs through addition to the carbonyl group (II).

This conclusion, we now find, cannot be applied

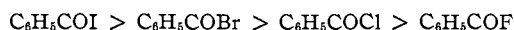
(* Paper XXIII, Gilman and Nelson, *THIS JOURNAL*, **61**, 741 (1939).

(1) Entemann and Johnson, *THIS JOURNAL*, **55**, 2900 (1933).

to some less reactive organometallic compounds like the mercurials. In general, organomercury compounds are unreactive toward most functional groups. They react exceedingly slowly with the carbonyl group in Michler's ketone to give a color test²; slowly with ketenes to give methyl ketones³; with sulfonyl iodides to give sulfones⁴; and with acyl halides, under relatively forced conditions, to give ketones.⁵ For the purposes of the present study, the following reaction was examined



The wide range in reactivity of the benzoyl halides made it desirable to compare the halides in pairs using, for example, relatively moderate conditions when comparing benzoyl iodide with benzoyl bromide and more drastic conditions when comparing benzoyl bromide with benzoyl chloride. Decisive results were obtained when relative reactivities were measured by the yields of pure phenyl *p*-tolyl ketone and the yields of recovered acid halide (determined as benzoic acid). The order of relative reactivities is



This order appears to hold for other mercurials as well as other acid halides like those of acetic acid. Although there is no assurance that the order established with mercurials will be the same with other organometallic compounds of relatively low reactivity, one may predict that no signifi-

(2) Gilman and Schulze, *ibid.*, **47**, 2002 (1925).

(3) Gilman, Woolley and Wright, *ibid.*, **55**, 2609 (1933).

(4) Whitmore and Thurman, *ibid.*, **45**, 1068 (1923).

(5) Otto, *Ber.*, **3**, 197 (1870); Calvery, *THIS JOURNAL*, **48**, 1009 (1926). The reaction with acid halides goes easier with mercurials of thiophene [Steinkopf and Bauermeister *Ann.*, **403**, 59 (1914)], and with mercurials of furan [Gilman and Wright, *THIS JOURNAL*, **55**, 3302 (1933)].

TABLE I
 REACTION OF BENZOYL HALIDES WITH DI-*p*-TOLYLMERCURY

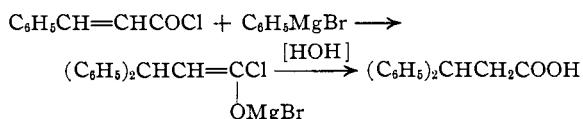
Acyl halide	Temp., °C.	Time	% yield C ₆ H ₅ COC ₆ H ₄ (CH ₃) ₂ - <i>p</i>	% recovery ^a C ₆ H ₅ COX	% recovery mercury comps.
C ₆ H ₅ COI	Reflux in C ₆ H ₆	10 hours	29		0.7
C ₆ H ₅ COBr	Reflux in C ₆ H ₆	12 hours	0 ^b	93	81.0
C ₆ H ₅ COBr	140–160	45 min.	36	0	0.0 ^c
C ₆ H ₅ COCl	140–160	105 min.	14	78	66.7
C ₆ H ₅ COCl	120	35 hours	32	49	9.2
C ₆ H ₅ COF	120	35 hours	2 ^d	94	73.2

^a The percentage recovery of benzoyl halide is based in each case on the recovery of benzoic acid, making due allowance for the excess benzoyl halide used. ^b Three-tenths gram of a yellow oil was isolated. No oxime could be isolated when the oil was treated with hydroxylamine. ^c Seven and one-half grams of tars was formed. In the other experiments where mercury compounds were recovered, no attempts were made to separate the mixtures. ^d In this experiment, the phenyl *p*-tolyl ketone was isolated as the oxime.

cant variations will be found with organometallic compounds of zinc, cadmium, tin, lead and bismuth.

The mechanism of reaction, therefore, of acid halides with mercurials appears to be a direct metathesis (I) rather than addition to the carbonyl linkage (II). This is essentially what might have been predicted because it has long been known that mercurials do not add at any significant rate to the carbonyl group in the highly reactive aldehydes. It should be pointed out, however, that even with mercurials an initial coördination complex may involve the carbonyl group. For example, in the benzoyl iodide reaction carried out in benzene, mercuric iodide does not separate during the reaction; but upon hydrolysis with iced water, heat is evolved and much red mercuric iodide is precipitated.

What may be supporting evidence for the preliminary addition of Grignard reagents to the carbonyl group of acid halides is to be found in the extensive studies by Kohler and co-workers on conjugated systems. Phenylmagnesium bromide and cinnamoyl chloride give a mixture of β,β -diphenylpropiophenone and β,β -diphenylpropionic acid.⁶ Both products are due undoubtedly to 1,4-additions, and the formation of β,β -diphenylpropionic acid



indicates preliminary addition of part of the Grignard reagent to the carbonyl group of an acid halide. The possibility that there might have been a metathesis involving removal of chlorine and formation of magnesium halide and a ketene (which with water would give the β,β -diphenyl-

(6) Kohler and Heritage, *Am. Chem. J.*, **33**, 21 (1905).

propionic acid) is ruled out. This is so because the intermediate having an —OMgBr linkage reacted with cinnamoyl chloride to give the corresponding ester. If such evidence has any merit, it can be extended to other conjugated systems having acid groupings, like esters and amides, which also undergo 1,4-addition.⁷

Experimental Part

Benzoyl iodide was prepared essentially in accordance with the method of Staudinger,⁸ and benzoyl fluoride by Johnson's procedure.¹

In the benzoyl iodide-benzoyl bromide experiments, 0.02 mole of R₂Hg compound and 0.045 mole of benzoyl halide were used. In the benzoyl bromide-benzoyl chloride and benzoyl chloride-benzoyl fluoride experiments, no solvent was used, and 0.02 mole of R₂Hg compound was treated with 0.125 mole of benzoyl halide. A solvent (benzene) was needed in the benzoyl iodide experiments to moderate the vigorous reaction.

The satisfactory yields of ketones in some of the reactions suggests that the synthesis may prove to be of preparative value when optimal conditions have been established. The conditions followed were purely arbitrary, the only objective being to get reasonable bases of comparison.

Summary

The relative reactivities of benzoyl halides in their reactions with di-*p*-tolylmercury to give phenyl *p*-tolyl ketone are as follows: C₆H₅COI > C₆H₅COBr > C₆H₅COCl > C₆H₅COF.

The mechanism of reaction of mercurials and acid halides is very probably direct metathesis and not preliminary addition to the carbonyl linkage.

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(7) The mechanism suggested may be related to the principle of vinylogy. See Fuson, *Chem. Rev.*, **16**, 1 (1933).

(8) Staudinger and Anthes, *Ber.*, **46**, 1423 (1913).