THE DECARBONYLATION OF AROYL TO ARYL CHLORIDES

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The transformation of aroyl chlorides into aryl chlorides (ArCOCl→ARCl)
is a hardly known reaction, although it would undoubtedly be of some practical
interest. The yields in Hunsdiecker type reactions are unsatisfactory, if aryl
chlorides are desired, and the method of Kochi (1) (lead tetraacetate and lithium
chloride) gives excellent yields, but only in the case of aliphatic acid chlorides.
The observation of Tsuji and co-workers (2) was thus of interest that palladium or
palladium chloride are catalysts both for the decarbonylation of aldehydes - a
fact known for many years (3) - and acyl halides and for the carbonylation of
olefins. However, in the case of aliphatic acid chlorides the decarbonylation is
accompanied by olefin formation, and in the aromatic series the yields are low.

These observations have led us to study a more complex noble metal com-
pound, viz, the recently discovered chlorotris(triphenylphosphine)rhodium (I) (4,5).
This compound decarbonylates aldehydes to hydrocarbons (6), because of its tendency
to form a carbonyl type compound, chlorocarbonylbis(triphenylphosphine)rhodium (II)
(7) with liberation of 1 mole of triphenylphosphine. Indeed, I causes the decar-
bonylation of aroyl chlorides to aryl chlorides in excellent yields at relatively
low temperature. Moreover, at temperatures of 200° and more, it catalyses this re-
action, so that only a small quantity of the metal complex is required. The reason
for this is perhaps because, at this temperature, the carbonyl compound II loses

carbon monoxide and recombines with the liberated triphenylphosphine molecule.

$$RhCl\,[(C_6H_5)_3)P]_3 \qquad RhCl(CO)\,[(C_6H_5)_3P]_2$$

$$\qquad I \qquad\qquad\qquad\qquad\qquad II$$

This second method is, obviously, of particular utility for such high boiling

aroyl and aryl chlorides as those derived from naphthalene. In the following,

three examples for this interesting reaction are presented.

(A)   A mixture of 0.5 ml. of benzoyl chloride, 0.0925 g. of I and 1.5 ml. of
benzene was heated at 80° for 15 mins. The red colour of the solution disappeared,
and a yellowish precipitate of II settled out. The amount of chlorobenzene formed
was determined by comparison with a standard solution of chlorobenzene in benzene
in an F & M Model 720 programmed-temperature gas chromatograph with a 2 ft x 0.25
inch VPC column, filled with 10% Carbowax 20M on 60-80 mesh Chromosorb. The yield
was quantitative: also II could be isolated, by addition of 3 ml. of ethanol to
the reaction mixture, in 90% yield (0.0623 g.), m.p. 195° (dec.) (7). Analogously,
1-naphthoyl chloride gave 1-chloronaphthalene in quantitative yield.

(B)   In a distilling apparatus, protected against humidity, 5 g. of 1-naphthoyl
chloride and 50-100 mg. of I were heated for 5 mins. near to the boiling point of
the chloride. The red solution turned yellow and then red again. Distillation gave
4.1 g. (96%) of 1-chloronaphthalene, b.p. 260-261° , that proved to be analytically
pure by VPC.

(C)   A mixture of 12 g. of benzoyl chloride and 100 mg. of I was refluxed under
anhydrous conditions for 20 hrs. Then, the chlorobenzene formed was distilled off
in a short column and the unchanged benzoyl chloride refluxed again with the same
catalyst until decarbonylation was complete. Thus 8.7 g. (90%) of analytically pure
chlorobenzene was obtained.

        The results of our experiments are summarized in Table I. The last example

in the Table indicates that the method is not necessarily limited to aroyl chlorides :

this point is being further investigated.

TABLE I

No.	Acid Chloride (g)	Method	Product	yield (%), isolated by distillation
1	benzoyl (12)	C	chlorobenzene	90
2	p-chlorobenzoyl (5)	C	p-dichlorobenzene	79
3	o-bromobenzoyl (5)	C	o-bromochlorobenzene	78
4	o-iodobenzoyl (8)	B	o-chloroiodobenzene	38
5	p-iodobenzoyl (3)	B	p-chloroiodobenzene	78
6	2,4-dichlorobenzoyl (30)	C	1,2,4-trichlorobenzene	98
7	1-naphthoyl (5)	B	1-chloronaphthalene	96
8	2-naphthoyl (4)	B	2-chloronaphthalene	94
9	2-methyl-1-naphthoyl (4)	B	1-chloro-2-methylnaphthalene	93
10	1-naphthylacetyl (4)	B	1-(chloromethyl)naphthalene	87[a]

[Note : a) In this case, it is necessary to distil the product _in vacuo_]

The heating time was adjusted to the boiling point : whilst, e.g., No.2 was heated for 8 hrs., the heating period for No. 3 and 6 was 30 mins. In the case of o-iodobenzoyl chloride (No.4), iodine was liberated at 250° during 5 mins.; this decomposition explains the low yield of o-iodochlorobenzene. It is worthy of note that the p-isomer (No.5) does not show this instability and does not liberate iodine during the reaction. Perhaps, a benzyne-type reaction takes place in the case of the _ortho_-isomer.

It is essential to work with pure acyl halides and to avoid contact with humidity, as any free carboxylic acids formed are decarboxylated under the conditions employed here, though slowly.

The mechanism of the new reaction will be studied further; it may be that the primary reaction is the formation of an aroyl rhodium complex from the-planar-compound I (8). In parallel, it has been shown that acyl metal complexes are intermediate stages in the inverse reaction, the carbonylation of aryl halides (9,10).

References

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