Acylation of the Nucleus of Aromatic Compounds in the Presence of Metals

1958

SovietRxiv

Abstract

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Chemistry

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(Presented by Academician A. A. Balandin, February 5, 1958)

As early as in older works connected with the study of the Friedel–Crafts reaction, several attempts were described to acylate aromatic hydrocarbons with acid chlorides in the presence of zinc dust and iron ([1–4]). Good yields were obtained only in the benzoylation of naphthalene. This reaction was recently proposed in a patent for the synthesis of 1,5-dibenzoylnaphthalene ([5]).

It should be noted, however, that the benzoylation of naphthalene, diphenyl, and anthracene proceeds rather readily even without catalysts, as a thermal reaction ([6]).

Indian authors, studying the activity of metals (uranium, cerium, titanium, chromium) in various condensations, obtained small yields of ketones from acetyl chloride and benzoyl chloride and benzene ([7]).

On the basis of our work on homolytic alkylation of the aromatic nucleus ([8–10]), we tested the possibility of acylation reactions in the presence of various metals. The experiments were carried out by heating (90–150°), in a flask with a reflux condenser, a mixture of the acid chloride and the aromatic compound with powders of copper, tungsten, and molybdenum, taken in amounts of 0.05–0.01 g-at. per 1 g-mol of acid chloride. The condensations proceed with vigorous evolution of hydrogen chloride, which ceases after 4-16 hr. (at the same time the odor of the acid chloride disappears from the mixture).

The mixture was decanted from the catalyst and, after washing with water, was fractionated. When copper is used, some amount of Cu_2Cl_2 is formed; the other metals do not change noticeably and can be used in repeated experiments.

The results of acylation under these conditions depend on the boiling point of the acid chloride and on the mobility of the hydrogens of the aromatic nucleus. The benzoylation of anisole and *m*-xylene is accomplished most readily; the yields of ketones in this case are close to theoretical. Control experiments on benzoylation without catalyst under the same conditions gave no ketones.

With toluene, 50% *p*-methylbenzophenone was obtained; with benzene, 20% benzophenone; with chlorobenzene, only traces of ketone. In the last three reactions, much unreacted benzoyl chloride is recovered.

Acetylation of benzene and toluene was unsuccessful; with *m*-xylene, 20% 2,4-dimethylacetophenone was obtained; with anisole, 30% 4-methoxyacetophenone. Reactions proceed somewhat better with butyryl chloride, and still better with caproyl chloride (60% 4-methoxycaprophenone). Evidently, for reactions with low-boiling acid chlorides it is necessary to select other conditions.

We believe that this method of acylation of aromatic compounds has advantages in comparison with reactions in the presence of aluminum chloride.

Table 1

Reagents	Catalyst	Temperature, °C	Reaction time, h	Main reaction product	Yield, % of theoretical: total	Yield, % of theoretical: based on the acid chloride reacted	B.p., °C/mm Hg	M.p., °C	Derivative (m.p.)
Benzoyl chloride, benzene	Copper	90	15	Benzophenone	20	60	156—158/10	46—47	Oxime (141—142°)
Benzoyl chloride, toluene	Copper, molybdenum	110—120	16	4-Methylbenzophenone	50	80	164—166/10	58	Semicarbazone (221°)
Benzoyl chloride, *m*-xylene	Molybdenum, tungsten	120—140	4—6	2,4-Dimethylbenzophenone	97	—	142—144/4	—	Dinitro derivative (144°)
Benzoyl chloride, anisole	Copper, molybdenum, tungsten	150; 90; 90	4; 8; 8	4-Methoxybenzophenone	94	—	160—162/3	60—61	2,4-Dinitrophenylhydrazone (178—180°)

Reagents	Catalyst	Temperature, °C	Reaction time, h	Main reaction product	Yield, % of theoretical: total	Yield, % of theoretical: based on the acid chloride reacted	B.p., °C/mm Hg	M.p., °C	Derivative (m.p.)
Caproyl chloride, anisole	Molybdenum	90	10	4-Methoxycaprophenone	60	80	141—142/5	41	2,4-Dinitrophenylhydrazone (141°)
Butyryl chloride, *m*-xylene	Copper	90	20	2,4-Dimethylbutyrophenone	30	80	130—131/13	—	2,4-Dinitrophenylhydrazone (169°)
Butyryl chloride, anisole	Molybdenum, copper	90	8; 20	4-Methoxybutyrophenone	45	80	159—160/20	—	Semicarbazone (183°)
Acetyl chloride, *m*-xylene	Molybdenum	90	10	2,4-Dimethylacetophenone	20	—	104—106/10	—	Semicarbazone (185—186°)
Acetyl chloride, anisole	Copper	90	10	4-Methoxyacetophenone	30	—	130—132/12	38	Semicarbazone (195—196°)

Table 1 gives the results of several reactions. The constants of the substances listed in the table and their derivatives correspond to the literature data.

Conclusions: 1. The possibility has been shown of acylating the aromatic nucleus with acid chlorides in the presence of powders of copper, molybdenum, and tungsten.

2. High yields were obtained: 4-methoxybenzophenone (95%), 2,4-dimethylbenzophenone (97%), 4-methoxycaprophenone (60%).

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Received
4 II 1958

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