BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 714—716 (1966)

Organic Syntheses by Means of Noble Metal Compounds. XVIII. Friedel-Crafts Reaction Catalyzed by Rhenium Pentachloride[1]

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(Received July 30, 1965)

Rhenium pentachloride has been found to be a Lewis acid with an efficient Friedel-Crafts catalytic property. Aromatic rings have been alkylated smoothly with olefins or alkyl halides. By the reaction of ethylene with benzene in the presence of rhenium pentachloride, *s*-butylbenzene has been obtained as the main product. In the Friedel-Crafts acylation, a quantitative amount of the catalyst has been consumed in the reaction at a low temperature. On the other hand, the acylation reaction at a high temperature can proceed catalytically. Rhenium pentachloride is also active in the oligomerization of olefins, and in the cyclization and oligomerization of acetylenes.

Numerous metal halide-type Lewis acids, of which aluminum chloride is the most frequently used, are known as Friedel-Crafts catalysts. Until the present time, however, no definite report has appeared on the catalytic activity of group VII metal halides in the Friedel-Crafts reaction.[2] We have found, in the course of our studies of the catalytic activity of noble metal compounds, that rhenium pentachloride is a Lewis acid and that it is an efficient, though mild Friedel-Crafts catalyst, as has already been reported briefly.[3]

Experimental

Gas chromatographic analyses were carried out on a Silicone DC 550 on a Celite column, 2 m. in length, at 180°C or at 100°C. Molecular weights were determined in benzene by using a Mechrolab vapor pressure osmometer. Commercially-available rhenium pentachloride (purchased from Kanto Kagaku) was used without further purification.

Most of the products were purified by preparative gas chromatography and identified by infrared spectra (Hitachi infrared spectrometer, model EPI-S2, in a solution of carbon tetrachloride) and NMR spectra (Varian high resolution spectrometer, models DP 60 and HR 100). The boiling points and melting points were uncorrected.

Alkylation and Acylation.—The reaction conditions and results obtained are summarized in Tables I, III and IV.

The Isomerization of Alkylbenzenes.—The results obtained are summarized in Table II.

Oiligomerization and Cyclization.—The reaction conditions and results are given in Table V.

Results and Discussion

The Alkylation Reaction with Alkenes and Alkyl Halides.

—The alkylation reaction with olefins proceeded smoothly in the presence of a small amount of the catalyst, and in general a mixture of products was obtained, as is shown in Table I. The most characteristic feature of the catalytic action of rhenium pentachloride can be seen in the alkylation with ethylene. At 75°C and at an ethylene pressure of 47 kg./cm^2, a rapid pressure drop was observed, and ethylbenzene, *s*-butylbenzene and hexaethylbenzene were obtained in the ratio of 1 : 2 : 1. It is interesting to notice that *s*-butylbenzene was obtained as the main product, showing that the dimerization of ethylene to form *s*-butyl carbonium ions competes favorably with the direct attack of ethyl carbonium ions on the benzene ring. From anisole, only *p*- and *m*-*s*-butylanisoles were obtained. When a large excess of olefin was used, a considerable amount of the polymer was obtained. This means that the oligomerization of the olefin catalyzed by rhenium pentachloride is quite rapid.

When the reaction of propylene with benzene was carried out at 75°C for 24 hr., a mixed product composed of mono-, di-, tri- and tetraisopropylbenzenes was isolated. On the other hand, when the reaction was carried out with a large excess of benzene, cumene was the main product. It seems likely that some of these products were formed by the isomerization of the initial alkylation products. In order to test the isomerization of alkylbenzene catalyzed by rhenium pentachloride, several alkylbenzenes were heated with a catalytic amount of rhenium pentachloride. Table II indicates that rhenium pentachloride is active in the isomerization, as may be expected for a Friedel-Crafts catalyst.

Alkylation with alkyl halides also proceeded smoothly, as is shown in Table III. Isopropyl bromide gave the same distribution of products as that obtained from propylene.

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[1] Part XVII: J. Tsuji, H. Takahashi and M. Morikawa, *Tetrahedron Letters*, **1965**, 4387.

[2] G. A. Olah, "Friedel-Crafts and Related Reactions," Vol. I, Interscience Pub., New York (1963), p. 201.

[3] J. Tsuji, M. Morikawa and T. Nogi, *Chem. Ind.*, **1964**, 543.

TABLE I. ALKYLATION WITH OLEFIN

Aromatic compound g.	Olefin	Product (g.)
Benzene 45	Ethylene (47 kg./cm^2)	Ethylbenzene (0.8), *s*-Butylbenzene (1.5), Hexaethylbenzene (0.8)
Benzene 25	Propylene 30 ml.	Cumene (5.0), *m*- and *p*-Diisopropylbenzenes (4.0), 1,2,4-, and 1,3,5-Triisopropylbenzenes (3.5), 1,2,4,5-Tetraisopropylbenzene (1.5)
Benzene 25	1-Butene 30 ml.	*s*-Butylbenzene (11.5), *m*- and *p*-Di-*s*-butylbenzenes (5.0), 1,3,5-Tri-*s*-butylbenzene (1.0)
Ethylbenezene 45	Ethylene (50 kg./cm^2)	*m*- and *p*-*s*-Butylethylbenezenes (2.5)
Anisole 25	Ethylene (50 kg./cm^2)	*m*- and *p*-*s*-Butylanisoles (3.0)

The reactions were carried out in the 200 ml. autoclave for 24 hr. at 75°C. 1 g. of $ReCl_5$ was used.

TABLE II. ISOMERIZATION REACTION

Aromatic compound g.	$ReCl_5$ g.	Product (%)
Cumene (5)	1	Benzene (44), Cumene (44), Diisopropylbenzene (10), Triisopropylbenzene (2)
1,2,4-Triisopropylbenzene (2)	0.5	Benzene (25), Cumene (30), Diisopropylbenzene (20), Triisopropylbenzene (25)
1,2,4-Triisopropylbenzene (2) and Benzene (10)	1	Cumene (85), Di- and Tri-isopropylbenzene (15)
o-Diethylbenzene (2)	0.5	Benzene (10), Ethylbenzene (20), Diethylbenzene (60), Triethylbenzene (10)

The reactions were carried out at 50°C for 8 hr.

TABLE III. ALKYLATION WITH ALKYL HALIDE

Aromatic compound g.	Alkyl halide ml.	Product (g.)
Benzene 12	Ethyl bromide 30	Ethylbenzene (2.5), *m*- and *p*-Diethylbenzenes (1.5)
Benzene 12	Isopropyl bromide 30	Cumene (3.0), *m*- and *p*-Diisopropylbenzene (2.0), 1,2,4- and 1,3,5-Triisopropylbenzenes (2.0), 1,2,4,5-Tetraisopropylbenzene (0.5)
Benzene 12	Cyclohexyl bromide 30	Cyclohexylbenzene (8.0), *p*-Dicyclohexylbenzene (2.5)
Benzene 25	Benzyl bromide 40	Diphenylmethane (21.0)

The reactions carried out at 50°C for 8 hr. 1 g. of $ReCl_5$ was used.

Acylation Reaction.—In the Friedel-Crafts acylation, it is generally known that an amount of catalyst equivalent to acyl halide is consumed as a result of the formation of a complex of metal halide with a ketonic compound formed by the acylation. The stability of the complex seems to vary with the kind of metal halide used. If the complex can be dissociated under certain conditions, especially by heating, then it might be possible to carry out the acylation reaction as a catalytic reaction. Actually this has been proved to be possible. For example, the benzoylation of toluene was found to be carried out in the presence of a catalytic amount of ferric chloride when the reaction temperature was kept between 135 and 150°C.4) From this standpoint, the catalytic activity at a rather high temperature was compared by using chlorides of aluminum, iron(III), molybdenum and rhenium; the results are shown in Table IV.

TABLE IV. BENZOYLATION OF TOLUENE

Cayalyst	Temp.a)	Yield 1b)%	Yield 2c)%
$ReCl_5$	125	850	10.5
$MoCl_5$	135	2300	29.0
$FeCl_3$	150	5000	60.0
$AlCl_3$	127	600	7.7

a) Maximum temperature, reached at the end of the reaction.
b) mol. %, based on the amount of the catalyst.
c) Based on benzoyl chloride.

As is apparent from the table, ferric chloride was the most efficient catalyst from this standpoint. As for rhenium pentachloride, the catalyst can not be recycled at 80°C; it then gives only 85%

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4) A. Noguchi, T. Ikawa and Y. Shimada, *J. Soc. Org. Syn. Chem. Japan*, **21**, 377 (1963).

TABLE V. OLIGOMERIZATION AND CYCLIZATION

Olefin	Solvent ml.	Reaction Temp., °C	Reaction Time, hr.	Product (g.)
Ethylene 50 kg./cm^2	Cyclohexane 30	70	20	C_4 olefins (1.5), C_6 (0.5), Higher than C_8 (0.5)
Propylene 20 ml.	Cyclohexane 20	70	20	C_6 olefin (2.0), C_9 olefin (4.5), C_{12} olefin (3.0), Higher olefins (2.0)
1-Butene 20 ml.	Cyclohexane 20	70	20	C_8-olefin (3.0), Higher olefins (2.0)
Propyne 20 ml.	*n*-Pentane 30	80	24	1,2,4- and 1,3,5-Trimethylbenezenes (1.0)

The reactions were carried out in the 200 ml. autoclave. 1 g. of $ReCl_5$ was used.

of the acylation product (based on rhenium chloride). On the other hand, a yield of 850% was obtained in the reaction carried out at 120—125°C. These results clearly show that the dissociation of the complex formed from certain metal halides and ketonic products is temperature-dependent, that at higher temperatures it is possible to carry out the acylation reaction in the presence of a catalytic amount of the metal halides.

The Oligomerization of Olefins and Acetylene.—It is known that Lewis acids can catalyze the oligomerization of olefins; rhenium chloride was tested for this activity. As is shown in Table V, a mixture of oligomers was obtained, but no selectivity was observed under the reaction conditions adopted. Therefore, no further studies were carried out. Acetylenes were found to be cyclized to form benzene derivatives in addition to a certain quantity of linear oligomers. For example, 1, 2, 4- and 1, 3, 5-trimethylbenzenes were obtained from propyne heated with rhenium pentachloride.