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A simple route to (η^6-arene)tricarbonylchromium complexes and a systematic study of different catalysts for complexation of arenes with $Cr(CO)_6$

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Abstract

A systematic investigation was made of the catalytic effect of different substances on complexation of toluene with $Cr(CO)_6$. 1–3 molar equivalents of butyl acetate in refluxing decalin was found to be the best catalyst, providing that the complexation was carried out in a special apparatus described earlier. Comparable yields were obtained also in butyl acetate as a solvent, but the reaction time was more than doubled. The utility of the method was verified by complexation of 7 different benzene derivatives.

Introduction

Several methods of complexation of arenes with $Cr(CO)_6$ are known, and as catalysts there have been used THF [1], α-picoline [2], and pyridine [3]. The last method gives very good results but the reaction has to be carried out in an autoclave, and CO evolved must be discharged at the pressure of 6–8 atm. The catalytic effect of acetone and benzene on either internal or external ligand exchange reaction of (η^6-arene)tricarbonylchromium complexes has been described [4–6] but no one, to the best of our knowledge, has examined the possibility of using ketones or esters as catalysts for the complexation of arenes. Exploring a new method for the synthesis of (η^6-arene)tricarbonylchromium complexes, we noticed [7] unusually rapid complexation of benzophenone, methyl benzoate, methyl phenylacetate and *N,N*-dimethylbenzamide. These findings prompted us to investigate thoroughly the catalytic effect of different additives upon complexation of toluene with $Cr(CO)_6$ in refluxing decalin. For the above reasons esters (ethyl and butyl acetate, butyl formate) a ketone (butanone, due to its higher boiling point than that of acetone) and *N,N*-dimethylacetamide were chosen as additives. As $Cr(CO)_3(CH_3CN)_3$ is well known as a good complexation agent [8], acetonitrile was also included.

Results and discussion

Toluene was selected as a standard arene for complexation due to the fact that it gave at best a 34% yield of the complex even in a special apparatus [7]. All

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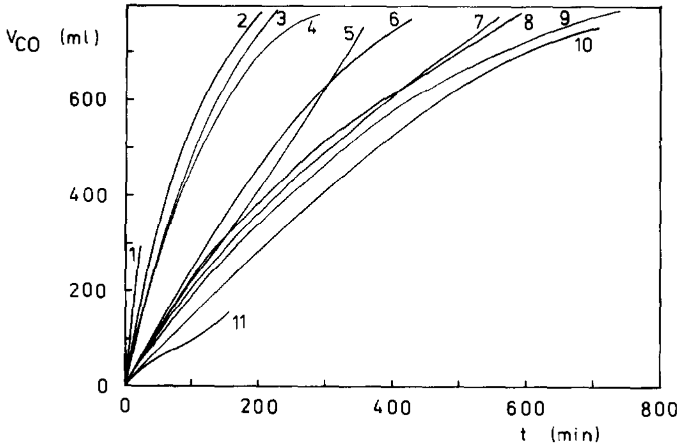

Fig. 1. Complexation of toluene with $Cr(CO)_6$. Dependence of CO evolved at different conditions (catalyst). (1) 2.9 ml of *N*,*N*-dimethylacetamide (reaction interrupted due to decomposition), (2) 8.2 ml of butyl acetate, (3) 4.1 ml of butyl acetate, (4) 16.4 ml of butyl acetate, (5) 2.8 ml of butanone, (6) 3 ml of ethyl acetate, (7) 5.6 ml of butanone, (8) 3.3 ml of acetonitrile, (9) 6 ml of ethyl acetate or 3.5 mol of butyl formate, (10) 100 ml of butyl acetate. (11) no catalyst (reaction interrupted due to decomposition.

experiments were executed with 2 g (9 mmol) of $Cr(CO)_6$, 31 mmol of an arene and the total volume of the solvent was 100 ml. The course of complexation was followed volumetrically by measuring the volume of CO evolved. For a quantitative reaction about 750 ml of CO should be evolved.

The effect of these catalysts on the complexation of toluene is demonstrated in Fig. 1 and Table 1. With the given molar ratio of the catalyst and toluene was observed the following order of catalytic activity: Butyl acetate > ethyl acetate ≈ butyl formate > butanone > acetonitrile ⋙ *N*,*N*-dimethylacetamide. In the last case it is difficult to say whether or not it is a suitable catalyst. The rate of the reaction in its presence is high, but unfortunately a rapid decomposition of the complex takes place very soon — approximately after 10% of conversion.

The linear part of the curves describing the amount added of butyl acetate was used to calculate approximate rate constants for an individual reaction. These rate

Table 1

The complexation of toluene under different conditions

Entry	Catalyst	ml/mol	Time (h)	Yield (%)
1	$CH_3COOC_2H_5$	3/0.03	8.5	92
2	$CH_3COOC_2H_5$	6/0.06	12	98.5
3	$CH_3COCH_2CH_3$	2.8/0.03	6	72.5
4	$CH_3COCH_2CH_3$	5.6/0.06	6.5	68
5	CH_3CN	3.3/0.06	9	80.5
6	$CH_3CON(CH_3)_2$	2.9/0.03		0
7	$CH_3COOC_4H_9$	4.1/0.03	4.5	97.5
8	$CH_3COOC_4H_9$	8.2/0.06	4	98
9	$CH_3COOC_4H_9$	16.4/0.124	4.5	94
10	$CH_3COOC_4H_9$	100	11.5	90
11	$HCOOC_4H_9$	3.6/0.03	9.5	94

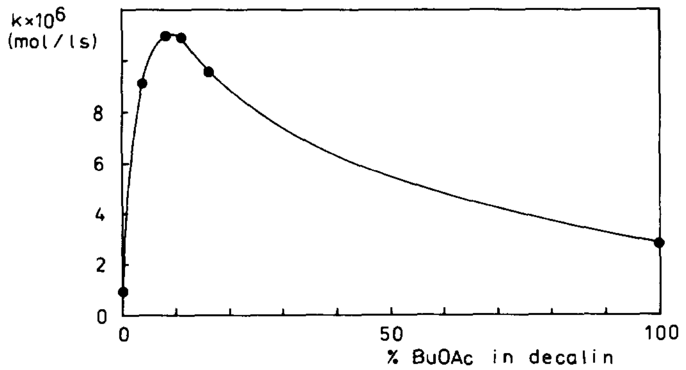

Fig. 2. Complexation of toluene with $Cr(CO)_6$. Dependence of the approximate rate constants on the amount of butyl acetate.

constants were used to optimize the reaction conditions. As can be seen from Fig. 2, the optimum is attained when two molar equivalents of butyl acetate (calculated on toluene) were used. The rate of complexation is much slower in pure butyl acetate, probably due to its lower b.p. (124–126 °C) in comparison with that of decalin (187–194 °C).

The method was tested on a set of 6 other benzene derivatives, and the results are shown in Table 2. It was proved that complexation in the presence of one molar excess of butyl acetate gives in all cases excellent yields of the desired product in a very short time (3–6 h). The lowest yields were obtained with chlorobenzene (57.5%). Nevertheless, such a yield represents a remarkable improvement in comparision with the yield of the reaction without a catalyst (1%). Twelve per cent of (η^6-benzene)tricarbonylchromium as a by-product was isolated in this case too. The complexation of benzoic acid deserves a comment. It has been stated several times

Table 2

Complexation of different arenes under the selected conditions

Entry	Arene	Catalyst	ml/mol	Time (h)	M.p. (°C)	Yield (%)
1	toluene	–		4.5	83–85	34
2	toluene	$CH_3COOC_4H_9$	8.2/0.06	4	83–85	98
3	benzene	$CH_3COOC_4H_9$	8.2/0.06	5.5	168–69	93.5
4	benzene	$CH_3COOC_4H_9$	100	11	168–69	92.5
5	benzene	–		4	168–69	0.5
6	*o*-xylene	$CH_3COOC_4H_9$	8.2/0.06	3	97–98	98
7	*o*-xylene	$CH_3COOC_4H_9$	100	10	94–96	96
8	chlorobenzene	$CH_3COOC_4H_9$	8.2/0.06	6	99–105	57.5
9	chlorobenzene	–		7	99–105	1
10	methyl benzoate	$CH_3COOC_4H_9$	8.2/0.06	6	98–100	89
11	methyl benzoate	–		6.5	98–100	84
12	methyl phenylacetate	$CH_3COOC_4H_9$	8.2/0.06	2.5	76.5–78	96
13	methyl phenylacetate	–		5	76.5–78	83
14	benzoic acid	–		0.1		0
15	benzoic acid	$CH_3COOC_4H_9$	8.2/0.06	1.5	215 dec.	27

[9,10] that direct complexation of this substance is impossible. We came to the same conclusion after performing the reaction in pure decalin (entry 5). After 2–3 min of heating the reaction mixture became cloudy and after 50 min of reflux a yellow-brown material was isolated (most probably $(PhCO_2)_2Cr$) which was immediately oxidized by air to the mixture of Cr_2O_3, and $(PhCO_2)_3Cr$. However, complexation in the presence of butyl acetate yielded 27% of the stable complex (entry 15).

Table 2 clearly demonstrates how in all cases examined complexation is much slower when butyl acetate is used as a solvent. However, the yields are comparable with the yields achieved in decalin with butyl acetate as a catalyst.

Conclusion

The complexation of 7 different arenes with $Cr(CO)_6$ proceeds much faster in boiling decalin if 2 molar equivalents of butyl acetate (calculated on an arene) are present. The same reaction performed in butyl acetate is much slower. The isolation of the product, on the other hand, is much easier in the latter case (see Experimental). It seems worthwhile to try and compare methods for the preparation of new complexes. The mechanism and the scope of this reaction is under study in our laboratory.

Experimental

All solvents, as well as catalysts were carefully purified and dried. Special attention was paid to the purification of decalin [7], and $Cr(CO)_6$ was sublimed prior to use. All reactions were carried out in atmosphere of pure Ar.

General procedure for complexation

1. The complexation in pure decalin was carried out as described earlier [7]. The reaction mixture which consisted of 0.031 mol of arene, and 2g (0.009 mol) of $Cr(CO)_6$ was refluxed in 100 ml of decalin for the time given in Tables 1 and 2.

2. Complexation with the addition of catalyst. The arene (0.031 mol), 2 g (0.009 mol) of $Cr(CO)_6$, 0.03 or 0.06 mol of a catalyst in decalin (the total volume of decalin and the catalyst was 100 ml in all cases) was refluxed for the time given in Tables 1 and 2. After the reaction was over, the reaction mixture was cooled to 20 ° C and filtered through Kieselguhr. The catalyst was evaporated under reduced pressure, and the decalin solution was chromatographed on a SiO_2 column. The slurry of SiO_2 in petroleum ether (b.p. appr. 60 ° C) was used for column preparation. Decalin was eluted with petroleum ether. The product was eluted either with benzene or with benzene–ethyl acetate mixture. The solvent was evaporated and the product was crystallized from the benzene–petroleum ether mixture at -18 ° C.

In the case of benzoic acid, the reaction mixture was extracted with 5% NaOH solution and the complex was precipitated from the aqueous solution by addition of 20% H_3PO_4.

3. Complexation in pure butyl acetate. The reaction was carried out as described above, and 100 ml of butyl acetate was used as the solvent. After the reaction the mixture was cooled to 20 ° C and the solution filtered through Kieselguhr. The solvent was evaporated at reduced pressure, petroleum ether was added, and the mixture was left for crystallization at -18 ° C. The product was filtered off and the

mother liquor was filtered through Kieselguhr again. The solution was concentrated, petroleum ether was added and the second crop of the product was collected after crystallization at −18 °C.

The results of the complexation are given in Tables 1 and 2. The yields given in the Tables are calculated from the amount of $Cr(CO)_6$ taken into reaction.

All products had correct elemental analyses, and ^{1}H-NMR spectra.

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