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FRIEDEL—CRAFTS REACTIONS CATALYZED BY POLYSTYRENETRICARBONYLMOLYBDENUM

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Summary

The heterogeneous catalyst polystyrenetricarbonylmolybdenum, like its homogeneous counterpart, catalyzes Friedel—Crafts reactions. Whereas the polymer-anchored tricarbonylmolybdenum shows decreased activity with respect to the homogeneous system, its selectivity toward *para* substitution is high and it can be reused several times without loss of activity. Exchange and leaching experiments on the catalyst indicate that the tricarbonylmolybdenum group remains attached to the polystyrene support during the course of catalysis. The results are in accord with the contention made for the homogenous system that complete dissociation of the arene ring from molybdenum does not occur in the active form of the catalyst.

Introduction

In a previous publication it was shown that arenetricarbonylmolybdenum is an effective catalyst for Friedel—Crafts reactions [1]. Whereas a detailed mechanism was not offered in that paper, indications were that the arene ring remained attached to the metal during the course of the reaction. In a related work, the polymerization of acetylenes was carried out using arenetricarbonylmolybdenum as the catalyst; the proposed mechanism in that work was based on the contention that the arene ring could function formally as a di- or monodentate ligand, but does not dissociate [2].

It would appear that a study of Friedel—Crafts reactions using polystyrene-bound tricarbonylmolybdenum as the catalyst might provide additional information on the mechanistic aspects of catalysis. In addition, it was of interest to compare results of resin-bound catalysis with those of the homogeneous systems. The feasibility of polystyrene-bound Group VIB carbonyls was demonstrated by Pittman et al., who used polystyrene-anchored tricarbonylchromium as a catalyst for hydrogenation of olefins [3].

Experimental

Starting materials

Aliphatic and acyl chlorides were purchased from either Aldrich or Eastman Chemical Company and used as received. Molybdenum hexacarbonyl was purchased from Pressure Chemical Company. Polystyrene beads (Amberlite XAD-2 type, 20—50 mesh) were obtained as a gift from Rohm and Haas Company.

Physical methods and analyses

Infrared spectra were recorded on a Perkin—Elmer Model 337 Grating Infrared Spectrophotometer using KBr pellets, Nujol mulls or thin films. Nuclear magnetic resonance spectra were obtained on a Varian EM-360 spectrometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

Preparation of polystyrenetricarbonylmolybdenum

Into a 100 ml, three-neck flask equipped with a nitrogen inlet and reflux condenser connected to an oil bubbler were placed 60 ml of freshly distilled heptane, 5 g of polystyrene beads and 2 g of $Mo(CO)_6$. After the system was flushed well with nitrogen, the contents of the flask were heated to reflux with magnetic stirring. After a short induction time, the beads turned yellow and slow gas evolution was observed. The heating was continued for 3 h, whereupon the mixture was filtered hot and washed with hot heptane to remove unreacted $Mo(CO)_6$. The hard, yellow beads were dried and stored in a closed bottle, under nitrogen, in the cold until used.

In a similar manner, a series of reactions were performed at the following reflux times: 1, 2, 6, 9 and 12 h. Whereas the percent by weight of Mo increased slightly with increasing reaction time, the color of the beads took on a greyish appearance, perhaps indicating that some decomposition to the metal occurred. Therefore, we judged that the optimum catalyst was that derived from the 3 h reaction; it was used throughout for all Friedel—Crafts reactions. Elemental analysis for the 3 h preparation gave: C, 89.98; H, 7.96; Mo, 0.95%.

Infrared studies on polystyrenetricarbonylmolybdenum

In order to characterize the catalyst as containing $Mo(CO)_3$ groups π-bonded to the arene rings on polystyrene; infrared spectra were recorded using KBr pellets and Nujol mulls. The catalyst exhibited two bands in the carbonyl stretching region at 1965 and 1880 cm^{-1}. The heptane solution spectrum of toluenetricarbonylmolybdenum showed CO stretching bands at 1970 and 1895 cm^{-1}. Infrared studies were also carried out on the catalyst after its use in promoting Friedel—Crafts reactions. Carbonyl stretching bands in the used, but still active, catalyst appeared at 2010 and 1875 cm^{-1}.

Reactions catalyzed by polystyrenetricarbonylmolybdenum

The procedures for alkylation, acylation and polymerization are similar, and the conditions of all reactions carried out are summarized in Tables 1 and 2. Therefore, detailed descriptions are given for one of each type of reaction. All reactions involving the carbonyl catalyst were carried out under an atmosphere of dry nitrogen in apparatus similar to that described under the preparation of

TABLE 1

ALKYLATION REACTIONS

Aromatic substrate (ml)	Organic halide (g)	Amount of catalyst (g)	Reflux time (h)	Yield (%)	Products and comments
Anisole (100)	t-Butyl chloride (19.7)	0.4	0.75	41.7	*p*-t-Butylanisole
Anisole (100)	Benzyl chloride (10.2)	0.3	0.5	89.3	Tolylphenylmethane and polybenzyl
Toluene (50)	Benzyl chloride (13.2)	0.4	30	68.3	*p*-Methoxydiphenylmethane (60%), *o*-Methoxydiphenylmethane (40%), and polybenzyl
Toluene (50)	t-Butyl chloride (8.3)	0.5	20	4.1	*p*-t-Butyltoluene
t-Butylbenzene (100)	Benzyl chloride (18.1)	0.5	44	51.0	*p*-t-Butyldiphenylmethane and polybenzyl
Phenyl ether (80)	t-Butyl chloride (8.4)	0.3	0.42	—	Alkylated products obtained [a]
t-Butylbenzene (50)	t-Butyl chloride (8.2)	0.7	22	0	No reaction
Anisole (100)	Cyclohexyl chloride (10.7)	0.5	6	0	No reaction
Benzyl chloride (50)	Neat	0.2	1.5	100	Polybenzyl

[a] Yield and isomer distributions were not determined.

TABLE 2

ACYLATION REACTIONS

Aromatic substrate (ml)	Organic halide (g)	Amount of catalyst (g)	Reflux time (h)	Yield (%)	Products and comments
Anisole (100)	Benzoyl chloride (6.6)	0.5	16	56	Catalyst added in two portions. *p*-Methoxybenzophenone
Anisole (50)	Phenylacetyl chloride (4.7)	0.3	2	81	*p*-Phenylacetylanisole
Anisole (50)	Hexanoyl chloride (9.9)	0.4	12	38	p-Hexanoylanisole
Anisole (100)	Acetyl chloride (12.2)	0.5	24	30	Catalyst added in 3 portions. 91.5% *p*-Methoxyacetophenone, 8.5% *o*-methoxyacetophenone
Anisole (120)	Trimethylacetyl chloride (12.9)	0.4	1.5	17.6	*p*-Trimethylacetylanisole
Toluene (100)	Benzoyl chloride (6.1)	0.3	24	0	No reaction

the catalyst. All solvents and reagents were deoxygenated prior to use by purging with nitrogen.

Bulk polymerization of benzyl chloride

Into the flask were placed 50 ml of benzyl chloride and 0.2 g of the catalyst. The contents were heated to reflux and stirred magnetically. Voluminous amounts of HCl gas evolved from the flask and the reaction mixture became increasingly more viscous. After evolution of HCl ceased (ca. 1.5 h), heating was discontinued and the contents were allowed to cool to room temperature. The resulting solid was dissolved in benzene, filtered from the catalyst and the benzene was removed by rotary evaporation. The resulting polybenzyl showed a melting point of 72—80° C, and represented a 100% yield.

Alkylation of anisole with benzyl chloride

In a 250 ml, three-neck flask were mixed 100 ml of anisole, 10.2 g (0.08 mol) of benzyl chloride, and 0.3 g of polystyrenetricarbonylmolybdenum. The mixture was refluxed and after an induction period of about 5 min, rapid HCl evolution, which lasted for about 0.5 h, was observed. After gas evolution ceased the mixture was allowed to cool to room temperature, filtered from the catalyst, and the anisole removed on a rotary evaporator. The viscous residue was distilled at 117—119° C (0.5 Torr); the distillate was identified by IR and NMR spectroscopy to be a mixture of 40% *o*- and 60% *p*-methoxydiphenylmethane (14.2 g, 89.3% yield). The remaining residue was identified as polybenzyl.

Acylation of anisole with phenylacetyl chloride

A mixture composed of 50 ml of anisole, 4.7 g (0.03 mol) of phenylacetyl chloride, and 0.3 g of the catalyst, was refluxed until the evolution of HCl ceased (ca. 2 h). The mixture was allowed to cool to room temperature, filtered from the solid catalyst, and anisole removed by rotary evaporation. The residue was taken up in 50 : 50 (v/v) acetone/water and refluxed for 20 min. The solvent was stripped, the resulting solid was taken up in ether and extracted with 5% NaOH solution. The ether layer was separated and after removal of the solvent, the resulting solid was recrystallized. The product, which weighed 5.6 g (81% yield) was identified as *p*-phenylacetylanisole.

Experiments on leached catalyst

1. A mixture of 1.01 g of polystyrenetricarbonylmolybdenum and 50 ml of toluene was refluxed under nitrogen for 2 h. The toluene solution, which was now light yellow, was filtered from the beads and evaporated to dryness. A very small amount (4.2 mg) of a yellow material was obtained which by its IR spectrum was identified as toluenetricarbonylmolybdenum. This represents about 0.15% exchange of $Mo(CO)_3$ groups from polystyrene to toluene.

2. A mixture of 50 ml of anisole and 10.1 g of polystyrenetricarbonylmolybdenum was placed in a three-neck vessel equipped with a nitrogen inlet and condenser. The third neck was fitted with a glass tube containing a glass sinter disc leading to another flask equipped as the original. The heterogeneous mixture was refluxed for 2 h and then, while hot, filtered through the frit into the second flask. The solvent was evaporated to dryness, and the residue weighed 3.6 mg.

This represents an exchange of $Mo(CO)_3$ groups from polystyrene to anisole of about 0.12%.

3. A mixture of 80 ml of anisole and 1 g of the polystyrene-anchored catalyst were placed in the apparatus described under 2 above. The mixture was refluxed for 1 h, and then filtered into the second vessel. 10 ml of t-butyl chloride were injected, and the pale yellow solution was refluxed for 1 h. Gas evolution was not observed, indicating that an alkylation reaction had not occurred. After that time 0.3 g of polystyrenetricarbonylmolybdenum was added to the anisole-t-butyl chloride system, and HCl evolution commenced after an induction period of about 3 min. After HCl evolution ceased, the final product was identified as *p*-t-butylanisole.

Alkylations with recycled catalyst

A mixture of 50 ml anisole, 5 ml t-butyl chloride and 0.2 g of the catalyst was refluxed until the evolution of HCl ceased. The catalyst beads were recovered and transferred to a second flask containing anisole and t-butyl chloride. This procedure was repeated six times, and in each case, the catalyst showed uniform activity.

Results

A summary of the alkylation and acylation reactions are shown in Tables 1 and 2, respectively.

Discussion

The first point of interest is a comparison of the relative catalytic activities of polystyrenetricarbonylmolybdenum with its homogeneous counterpart, toluenetricarbonylmolybdenum, toward alkylation reactions. In general, the polystyrene-anchored system is sluggish, promoting alkylation reactions at slower rates and in lower yields when compared to the homogeneous catalyst system. For example, toluenetricarbonylmolybdenum promoted certain alkylation reactions on toluene in the 80—90% range in 1—12 h [1] where the same reaction required 20—30 h with the homogeneous catalyst to yield considerably lower amounts of products. A similar decrease in activity was noted for polystyrenetricarbonylmolybdenum in hydrogenation reactions when compared to homogeneous tricarbonylchromium catalysts [3].

The homogeneous catalyst was shown to promote alkylations on several aromatic systems with a variety of alkyl chlorides; the corresponding polystyrene-anchored $Mo(CO)_3$ system is only effective where tertiary or stabilized carbonium ions can be generated. Furthermore, the nature of the aromatic host plays an important role. Anisole, which is more susceptible to electrophilic attack than toluene, alkylates with t-butyl chloride at faster rates and in higher yields than toluene. In fact, the heterogeneous catalyst promoted alkylation on anisole in reasonable yields in less than 1 h reaction time. Rates and yields are comparable for the two catalyst systems in the polymerization of benzyl chloride to polybenzyl.

Acylation reactions promoted by the heterogeneous system on anisole are somewhat comparable to those of the homogeneous catalyst. The homogeneous catalyst promotes reactions on anisole with acetyl and benzoyl chloride in 70% yields where the polymer-anchored system catalyzes those reactions in 30—56% yields. However, acylation reactions on toluene, promoted by the heterogeneous catalyst, are ineffective.

One of the features of Friedel—Crafts reactions promoted by arenetricarbonylmolybdenum is that in substitution reactions on aromatic systems containing *ortho-para*-directing substituents, the product is predominantly the *para* isomer [1]. In the same reactions promoted by the heterogeneous catalyst, the high selectively toward substitution in the *para* position is generally retained.

Of significant interest is the fact that polystyrenetricarbonylmolybdenum retains uniform activity after repeated use. This indicates that the $Mo(CO)_3$ group remains attached to the polystyrene during the course of catalysis; otherwise, exchange with the aromatic solvent would occur, and the activity of the beads would decrease rapidly in run to run. This observation is in accord with the mechanistic speculation proposed for the homogeneous catalyst [1].

Infrared studies on the catalyst system also indicate that the catalyst remains on the support. The freshly-prepared catalyst shows two carbonyl bands at 1965 and 1880 cm^{-1}. Whereas the catalyst remains active for several runs, the infrared spectrum of the used catalyst still shows the expected two carbonyl bands, but the 1965 cm^{-1} absorption is now shifted to 2010 cm^{-1}. The reason for this shift of 45 cm^{-1} to higher wavenumbers is not clear, but might indicate that catalysis occurs by way of an expanded coordination number on molybdenum.

In order to obtain additional information on the active site of the catalyst, leaching experiments were carried out on the heterogeneous system. When polystyrenetricarbonylmolybdenum was refluxed in toluene, it was found that a small amount of exchange occurred, as evidenced by the recovery of 4.2 mg of toluenetricarbonylmolybdenum, identified by IR spectroscopy.

In the alkylation of anisole by t-butyl chloride, the catalyst was first leached by refluxing in anisole. The solution was then separated from the beads and treated with t-butyl chloride; this mixture was inactive toward alkylation. This same solution became active, however, upon addition of the heterogeneous catalyst.

These results clearly show that the catalyst beads are active, and that the amount of catalyst in solution resulting from exchange with the solvent is at concentrations below the active level. It is safe to conclude, therefore, that in Friedel—Crafts reactions promoted by arenetricarbonylmolybdenum, the active form of the catalyst retains the arene ring and that any free or exchanged $Mo(CO)_3$ groups are present only in negligible amounts. This conclusion is similar to that proposed by Cais and Rejoan for hydrogenation reactions catalyzed by arenetricarbonylchromium [4]. In that paper, a mechanism was advanced in which a partial, but not complete, dissociation of the arene ring from chromium occurred.

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