CHEMISTRY LETTERS, pp. 535-538, 1978. Published by the Chemical Society of Japan

RHODIUM CARBONYL CLUSTER CATALYZED ADDITION OF ARENES TO DIPHENYLKETENE AND ARYL ISOCYANATES

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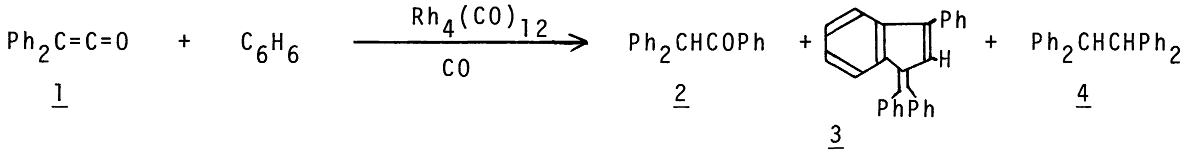
Under pressure of carbon monoxide, rhodium carbonyl clusters catalyze a novel addition of benzene and monosubstituted benzenes to diphenylketene and aryl isocyanates to give benzene-adducts, diphenylmethyl arylketone and N-aryl benzamides, respectively.

Recently there has been much interest in the homogeneous catalytic activation of carbon-hydrogen bonds of aromatic hydrocarbons and its application to organic synthesis.1) As such examples are known the arylation of olefins by palladium salts2) and the H-D exchange of arenes by a variety of transition-metal complexes.1)3) Previously we reported that under pressure of carbon monoxide $Co_2(CO)_8$ catalyzes the deoxygenation of diphenylketene to give 1-(diphenylmethylene)-2-(diphenylacetoxy)-3-phenylindene,4) while under a nitrogen atmosphere it catalyzes the decarbonylation of the ketene.5) In the course of the comparative study of catalytic behavior of rhodium carbonyls with that of the cobalt carbonyl for the ketene, we found a novel addition of a carbon-hydrogen bond of benzene used as a solvent to the carbon-carbon double bond of the ketene. We now wish to report the catalytic addition of a carbon-hydrogen bond of arenes to the unsaturated bond of diphenylketene and aryl isocyanates by rhodium carbonyl clusters.

When a mixture of diphenylketene (1, 1g, 5.2mmol), $Rh_4(CO)_{12}$ (20mg, 0.027mmol) and benzene (30ml) was heated at 200°C for 5hr under 30Kg/cm^2 pressure of carbon monoxide, a benzene-adduct, 2,2-diphenylacetophenone (2, mp. 138-139°C, lit. 139°C[6]) was obtained as the main product (68%, ca.144 catalytic turnovers per $Rh_4(CO)_{12}$), together with small amounts of 1-(diphenylmethylene)-3-phenylindene (3, 4%) and tetraphenylethane (4, 3%), which are also obtained as by-products in the deoxygenation of 1 by $Co_2(CO)_8$.[4]



The yield of the benzene-adduct 2 depends on the pressures of carbon monoxide, as shown in Table 1. Under the lower pressures the yields were very low. This result shows that a moderate pressure of carbon monoxide (at least 10Kg/cm^2) is necessary for good catalytic cycles of the addition. As the catalyst, $Rh_6(CO)_{16}$ could be also used.

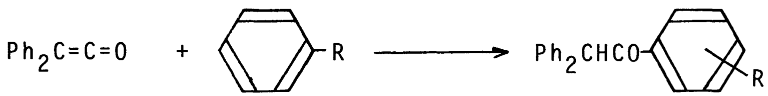
With this catalytic system, monosubstituted benzenes such as toluene, anisole, and fluorobenzene also reacted with 1 to give diphenylmethyl arylketones in good yields. The products were consisted of three isomers (ortho, meta, and para) and the isomer ratio was affected by the substituents, as shown in Table 2. In the case of toluene addition, the formation of the meta-isomer was predominant, but in either case of anisole or fluorobenzene, the yields of the isomers decreased as following order, ortho > meta > para, indicating an importance of the inductive effect of the substituents. The addition of the benzenes was favored

Table 1. Dependence of the yield of 2 on the pressures of carbon monoxide.

Run No.	Catalyst	CO (Kg/cm^2)	Yield of 2 (%)
1	$Rh_4(CO)_{12}$	1	3
2	$Rh_4(CO)_{12}$	5	11
3	$Rh_4(CO)_{12}$	10	47
4	$Rh_4(CO)_{12}$	20	59
5	$Rh_4(CO)_{12}$	30	68
6	$Rh_6(CO)_{16}$	25	69

* The reactions were carried out with 1 (1g), C_6H_6 (30ml), and the catalyst (20mg) at 200°C for 5hr.

Table 2. The addition of monosubstituted benzenes to 1



C_6H_5R	Product[a)]	Yield (%)	Isomer ratio[b)] ortho	meta	para	Relative rate[c)]
C_6H_6	$Ph_2CHCOC_6H_5$ (2)	68	-	-	-	1
$C_6H_5CH_3$	$Ph_2CHCOC_6H_4CH_3$ (6)	57	6	62	32	0.5
$C_6H_5OCH_3$	$Ph_2CHCOC_6H_4OCH_3$ (7)	56	55	31	14	1.5
C_6H_5F	$Ph_2CHCOC_6H_4F$ (8)	53	60	27	13	1.6

a) All products except for ortho-6 were isolated by column chromatography on silica, and their structures were identified by comparison of their m.p.[10)] and spectroscopic data with those of authentic samples prepared from the reaction of 1 with the corresponding aryl Grignard reagents, followed by hydrolysis.

b) The isomer ratio was estimated by G.L.C. (conditions: 1.5% OV-17 on Shimalite W; 230°C) or N.M.R.

c) The relative rates were determined from competitive reactions with benzene; C_6H_6(0.3mol), C_6H_5R(0.3mol), 1(1g), $Rh_4(CO)_{16}$(20mg), CO(30Kg/cm^2), 200°C, 5hr.

by electron-withdrawing substituents as shown in the order of the relative rate, $C_6H_5CH_3 < C_6H_6 < C_6H_5OCH_3 \approx C_6H_5F$, which was determined from competitive experiments with benzene. However, the range of the rates was very small, less than a factor of 4. Such effect of the substituents on the orientation and reactivity is similar to that in the H-D exchange reaction with base catalysts[7)] rather than those in general electrophilic aromatic substitution[8)] and in palldium catalyzed arylation of olefins.[2)9)] This reaction thus is suggested to be nucleophilic in nature. Hence it seems that the cleavage of a carbon-hydrogen bond of the benzenes occurs by nucleophilic attack on the aromatic ring by a low-valent electron-rich rhodium carbonyl cluster even though there is no direct evidence for retention of high nuclearity of the cluster. The insertion of 1 into the resulting aryl- or hydrogen-metal bond and the subsequent reductive elimination give the products. The carbon monoxide may play an important role in facilitating catalyst regeneration and in keeping good catalytic cycles.

We also found the addition of benzene to aryl isocyanates (9) such as phenyl, p-tolyl, p-chlorophenyl, and α-naphthyl isocyanate to yield N-aryl benzamides (10, ca. 35-95 turnovers per $Rh_4(CO)_{12}$). For example, phenyl isocyanate reacted with benzene in the presence of $Rh_4(CO)_{12}$ under 25Kg/cm^2 pressure of carbon monoxide at 220°C for 6hr to give benzanilide (42%).

$$\underset{\underline{9}}{RN{=}C{=}O} \quad + \quad C_6H_6 \quad \xrightarrow[CO]{Rh_4(CO)_{12}} \quad \underset{\underline{10}}{RNHCOC_6H_5}$$

R= Ph, p-$CH_3C_6H_4$, p-ClC_6H_4, and α-$C_{10}H_7$

Study on the detailed mechanism and the application to other unsaturated compounds of this catalytic system are in progress.

Reference and notes

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10) All products are colorless crystals, and their melting points are following.

$Ph_2CHCOC_6H_4R$	M.p. (°C) [Lit.]		
	ortho	meta	para
6 (R= CH_3)	not isolated	98-98.5	101-102 [101-102][11]
7 (R= OCH_3)	102-103	105-106	129-130 [130-131][12]
8 (R= F)	79-81	104-105	135-136 [136][13]

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(Received March 10, 1978)