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ALKYLATION REACTIONS WITH ORGANOMETALLIC COMPOUNDS

I. THE REACTION OF METHYLTRIS(TRIPHENYLPHOSPHINE)RHODIUM WITH DIPHENYLACETYLENE*

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SUMMARY

The reaction of diphenylacetylene with $(Ph_3P)_3RhCH_3$ was studied in order to clarify the role of the organometallic compound as an alkylating reagent. *Trans*-α-methylstilbene was the main product of addition to the alkyne. The reaction is mostly an insertion process as concluded from studies with D_2O. It was compared with the reaction of diphenylacetylene with the systems $(Ph_3P)_3RhBr/CH_3MgBr$, and $RhBr_3 \cdot 3H_2O/CH_3MgBr$. With the first system mainly *trans*-α-methylstilbene was formed. In this reaction however, $(Ph_3P)_3RhCH_3$ is shown not to be an active intermediate. With the second system, *cis*-addition was observed with a high degree of stereospecificity *cis*-α-methylstilbene being the main product. Condensation of diphenylacetylene to products like 1,2,3-triphenylnaphthalene, 1,2,3,4-tetraphenylbutadiene and 1,2,3,4-tetraphenylcyclopentadiene was also observed.

INTRODUCTION

Salts of transition metals have been shown to affect the alkylation reactions of organic molecules by organometallic compounds, *e.g.* the effect of cupric salts on Grignard reactions[1], the effect of metallic halides on the reactivity of organomercury compounds[2] and on alkylations of diphenylacetylene by Grignard reagents[3,4]. Although alkyl derivatives of transition metals have been postulated as active intermediates, no specific alkylmetallic compound has been marked as such. We therefore set out with the intention first of using an actual methyl compound of a transition metal as an alkylating agent and secondly of comparing its reactivity with other systems in one of which the organometallic compound is formed *in situ*. The results with methyltris(triphenylphosphine)rhodium[5] and with two related systems are reported.

RESULTS

Three different alkylating systems were used with diphenylacetylene: methyltris(triphenylphosphine)rhodium, $(Ph_3P)_3RhCH_3$ (I); a mixture of bromotris(tri-

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phenylphosphine)rhodium, $(Ph_3P)_3RhBr$, and methylmagnesium bromide (II); and a mixture of rhodium tribromide, $RhBr_3 \cdot 3H_2O$, and methylmagnesium bromide (III). The reaction conditions were different in each case, but essentially the same products (after hydrolysis) were obtained. The results are summarized in Scheme 1:

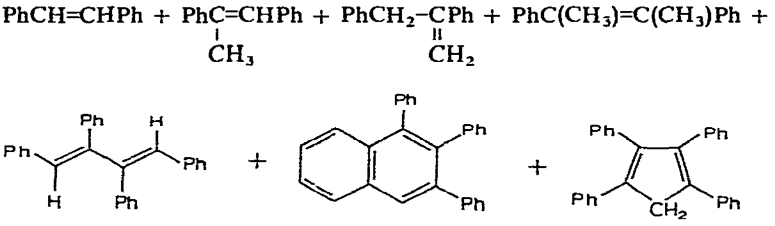
SCHEME 1

$PhC{\equiv}CPh$ + $(Ph_3P)_3RhCH_3$ (I)

$PhC{\equiv}CPh$ + $(Ph_3P)_3RhBr/CH_3MgBr$ (II)

$PhC{\equiv}CPh$ + $RhBr_3 \cdot 3H_2O/CH_3MgBr$ (III)

Products:



$$PhCH{=}CHPh + \underset{\displaystyle CH_3}{PhC}{=}CHPh + PhCH_2{-}\underset{\displaystyle \| \atop CH_2}{CPh} + PhC(CH_3){=}C(CH_3)Ph +$$

α-Methylstilbene is the main component among the addition products, but the formation of stilbene shows that hydrogen transfer occurs as well. Condensation products, such as 1,2,3,4-tetraphenylbutadiene, 1,2,3-triphenylnaphthalene, 1,2,3,4-tetraphenylcyclopentadiene and some polymethylene of low molecular weight [the last with system (I) only] were formed as well. The yields and distribution of the various addition products are given in Table 1.

TABLE 1

DISTRIBUTION OF ADDITION PRODUCTS (%), IN THE REACTION OF DIPHENYLACETYLENE WITH ORGANORHODIUM REAGENTS

System	Temp. (°C)	α,α'-Dimethylstilbene		α-Methylstilbene		Stilbene		α-Benzylstyrene	Combined addition products (%) in total products[a]
		Cis	*Trans*	*Cis*	*Trans*	*Cis*	*Trans*		
(I)	134		1.7	14.6	62	3.4	9.4	9	35
(II)	10			18	74	4.8	4.8		90
(III)	10			58.6		26	12.5	3	55

[a] Yields based on rhodium compounds. Other products were condensation products, and an amorphous material analysing as polymethylene, the latter, only with (I). Distribution of condensation products was not analyzed in detail.

Reaction of $(Ph_3P)_3RhCH_3$ with diphenylacetylene in boiling p-xylene was practically complete after 30 min and no change in product ratios was observed when the mixture was kept boiling for 8 h. There was no reaction in ether at 10–30° and only low yields (< 5%) were obtained in boiling benzene or dioxane.

In the reaction of (I) in xylene, the combined yield of addition products was ca. 35% of the total. No unreacted diphenylacetylene was detected. The rhodium was recovered after reaction, mainly as $(Ph_3P)_2\overline{RhC_6H_4PPh_2}$ (IV) (50%), which has previously been reported[5] as the decomposition product of (I).

When the anhydrous product mixture from the reaction of $(Ph_3P)_3RhCH_3$ and diphenylacetylene was injected into a gas chromatograph before hydrolysis, no volatile products were observed except for a small quantity of stilbene and polymethylene. Using D_2O for hydrolysis, the isolated products showed the presence of deuterium in the vinylic positions of the stilbene derivatives. The IR spectrum of *cis*- and *trans*-α-methylstilbene exhibited a sharp absorption at 2240 cm^{-1}, indicating a vinylic C–D stretching. In the NMR spectra of these compounds, the resonance band of the vinylic proton had about 35% of the intensity expected for the vinylic C–H compound, *i.e.*, showing the presence of 65% of vinylic C–D. Mass spectrometric analysis of *cis*-α-methylstilbene showed it to be 68% singly D-labelled and 32% unlabelled. The *trans* isomer was 78% singly D-labelled and 22% unlabelled. The mass spectrum of *cis*-stilbene showed the presence of 11% unlabelled, 79% singly D-labelled and 10% doubly D-labelled compound.

The effect of traces of residual inorganic salts was studied by preparing (I) with either CH_3Li (I"Li"), or CH_3MgBr (I"Mg"). The following differences in product distribution were observed. The yield of *trans*-dimethylstilbene was 5% using (I"Li"), against 1.7% with (I"Mg"). The corresponding *cis*-isomer (4%), was formed only with (I"Li") and not at all with (I"Mg"). *Trans/cis* ratios for α-methylstilbene were 4.3 and for stilbenes 3 with (I"Mg"), against ratios of 3, and 1 respectively for (I"Li"). Polymethylene was less than 5% with (I"Mg") against 25% with (I"Li").

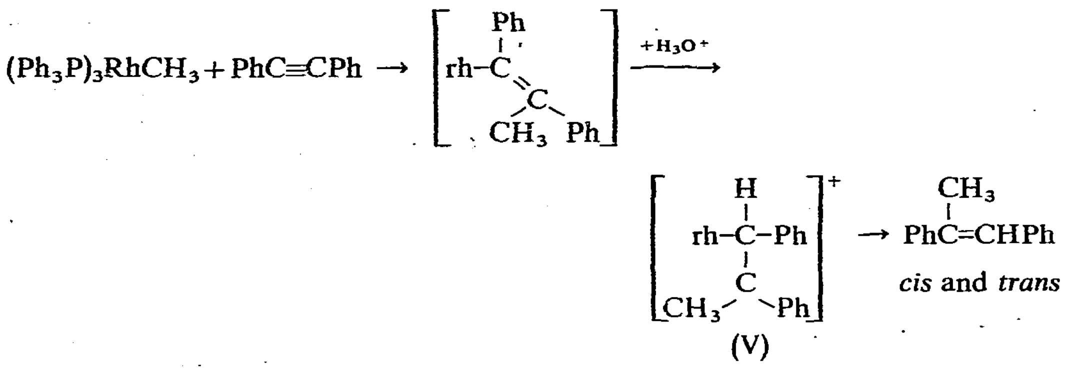
In contrast to (I), $(Ph_3P)_3RhBr$ and CH_3MgBr [system (II)] reacted with diphenylacetylene in ether at room temperatures. After 24 h the yield of transmethylation and hydrogenation products was 90%, the rest being condensation products.

Reaction of $RhBr_3 \cdot 3H_2O$ and CH_3MgBr [system (III)] with diphenylacetylene occurred at low (−50°) as well as at room temperature. With (III) stereospecificity was high but unlike cases (I) and (II) mainly *cis* products were formed. Of the total, 55% were addition products and 45% condensation products, after a reaction time of 24 h.

DISCUSSION

The results show that methyltris(triphenylphosphine)rhodium (I) transfers a methyl group to diphenylacetylene. This rhodium compound is sensitive and difficult to purify but has, nonetheless, been well characterized[5]. The reagent $(Ph_3P)_3RhBr/CH_3MgBr$ (II) yields the same products. Since CH_3MgBr alone does not react with diphenylacetylene and (I) is prepared from the constituents of system (II), it would seem plausible to assume that (I) is an intermediate responsible for the alkylation. The results, however, indicate that such is not the case. System (II) reacts in much higher yields and at lower temperatures than (I). Furthermore, with (I) condensations are the more important reactions while with system (II) additions are predominant.

We believe that the alkylation of diphenylacetylene by (I) takes place by insertion of the two-carbon acetylenic unit into the Rh–C bond. The test with D_2O shows that the final products are liberated from strongly bonded complexes only in the final hydrolysis step:



The formation of stilbene presumably occurs similarly by the insertion of diphenylacetylene into intermediate rhodium hydrides. This is inferred from the fact that 80% of the stilbene has only one of the vinylic hydrogen atoms labelled by deuterium. Hydrides may form during intramolecular rearrangements of phosphine transition-metal complexes[7] and it was shown that the decomposition of (I) involves such rearrangements[5]. The results with D_2O also imply that hydrogen from the methyl group is not involved in the reaction, indicating that the present case differs significantly from that of chromium systems where methyl groups and not $H_2O(D_2O)$ account for the vinylic hydrogen[3c]. The presence of unlabelled stilbene and α-methylstilbene, as well as doubly D-labelled stilbene suggests that to some extent, alternative reaction pathways are operative.

Stereochemically, an overall *cis* addition would be expected with (I) since the insertion of the alkyne is best envisaged as a *cis* addition and the subsequent hydrolysis would be expected to proceed with retention of configuration[8]. The high *trans/cis* ratio can however be explained if a protonated intermediate (intermediate as defined by Ingold[9]) is envisaged, (V), which would account for *cis/trans* isomerization. Admittedly, distinct processes leading independently to *cis* or *trans* adducts cannot be ruled out; *e.g.*, *trans* additions to alkynes have been observed with lithium aluminium hydride[10] and with platinum compounds[11].

The reasons for the influence of inorganic salts such as LiBr or $MgBr_2$ on the pattern of products distribution are not clear, but similar phenomena have been reported with other reactions of organometallic reagents[12].

The different stereochemistry in the reaction system (III), as well as the larger extent of hydrogen transfer reactions and condensation at low temperatures, suggests that this case is similar to other reactions of transition metal salts which bear no ligands *e.g.* chromium compounds[3], where a concerted addition of hydrogen and methyl groups to the alkyne has been proposed to explain the *cis* orientation of the process.

As for system (II), it has been shown that diphenylacetylene displaces one phosphine ligand of $(Ph_3P)_3RhBr$ to form $(PhC{\equiv}CPh)(Ph_3P)_2RhBr$[13] under conditions such as ours. Generally, π-bond formation enhances nucleophilic attacks on olefins and alkynes[14], alkynes being more susceptible to nucleophilic attacks than olefins[15]. It is likely that with (II) attack of the Grignard reagent or its methyl moiety on the alkyne is made possible, when the latter is bonded as a ligand to rhodium. Such a reaction pathway need not involve methylrhodium compounds. Attack on the alkyne from the outside such as this, is consistent with the high percentage of *trans* addition and with the observation that (I) is not an intermediate. It is also noteworthy that with system (II) little condensation of the alkyne is observed while with system (III) in which the competing phosphine ligands are absent, it is appreciable. Condensations apparently require the coordination of more than one alkyne molecule and even partial blocking of coordination sites is expected to affect this type of reaction.

EXPERIMENTAL

Preparation of reagents and reactions were all carried out under dry argon. Solvents were dried by reflux over sodium and THF was further refluxed and kept over $LiAlH_4$.

Methyltris(triphenylphosphine)rhodium, $(Ph_3P)_3RhCH_3$

The reaction of $(Ph_3P)_3RhBr$ with CH_3MgBr[5] was carried out at 4° for 24–36 h in a double Schlenck tube equipped with a glass filter. The solution was filtered and the product isolated by repeated precipitations from the concentrated ethereal solution (or THF solution), by adding hexane and cooling. Methyllithium in ether could be used instead of methylmagnesium bromide, giving a much faster reaction (3 h), but seperation of lithium bromide from the product was difficult.

The product, m.p. 120° (decompn.), [lit.[5] 120–140° (decompn.)] was soluble in THF, benzene, xylene and ether. The NMR spectrum showed a broad multiplet resonance band at 0.3–0.5 ppm (in C_6D_6 or octadeuterotoluene, with dioxane as reference), attributed to the CH_3–Rh group[5].

Reaction of $(Ph_3P)_3RhCH_3$ with diphenylacetylene

In all these reactions biphenyl was added together with diphenylacetylene and used as an internal standard for VPC analysis of the products, by comparing its quantity (unchanged during reaction) with that of diphenylacetylene and addition products.

A. Reaction in diethyl ether. (I) (500 mg, 0.55 mmole) and diphenylacetylene (130 mg, 0.73 mmole), were dissolved in ether (50 ml). There was no change after 6 h at room temperature, nor after 2 additional h of reflux. The solution was hydrolysed with 25 ml of water for 24 h and the organic phase analysed by VPC for addition products. Only diphenylacetylene was detected (90% recovered).

B. Reaction in benzene or dioxane. The same amounts of reactants were refluxed for 3 h. After hydrolysis small amounts of stilbene and α-methylstilbene were detected by VPC. Most of the alkyne was recovered (75%). Yields in dioxane were somewhat higher.

C. Reaction in refluxing p-xylene. Using amounts as above, samples of 10 ml were hydrolysed and checked for products after 15, 35, 95 min and 3.6 and 8 h. Results were reported in Table 1. There was practically no difference in distribution of products after different reaction times.

D. Control experiment. Tests by VPC for the presence of reaction products were carried out on samples from xylene reaction, both before and after hydrolysis. Except for small quantities of stilbene and polymethylene, no products were observed by VPC in samples which had not been hydrolysed. Hydrolysed samples from the same batch, contained the expected quantities of products.

E. Hydrolysis with D_2O. Reactions were carried out with $(Ph_3P)_3RhCH_3$ and diphenylacetylene in boiling xylene by the standard procedure and hydrolysed with D_2O. Products were then separated by preparative VPC. They were analysed by NMR, IR and mass spectra. Mass spectrometric analysis was carried out according to a procedure recommended by Biemann[16], by running spectra of unlabelled compounds at low energies until $(M-1)^+$ ions were no more observable and running the spectra of the labelled compounds for determination of the $M/(M+1)$ ratios. The electron beam energies were in the order of 10 eV for stilbene and the corresponding derivatives.

Reaction of diphenylacetylene with $(Ph_3P)_3RhBr$ and CH_3MgBr [system (II)]

Into a suspension of tris(triphenylphosphine)rhodium bromide (2.2 g, 2.27 mmole), in 50 ml ether at −50°, a solution of 1 *N* CH_3MgBr in ether (20 ml) was slowly added, followed by 25 ml of an ethereal solution of diphenylacetylene (360 mg, 2.02 mmole) and biphenyl (180 mg). The mixture was allowed to warm to room temperature, stirred for 24 h, and worked up by the standard procedure.

Reaction of diphenylacetylene with $RhBr_3 \cdot 3H_2O$ and CH_3MgBr [system (III)]

Methylmagnesium bromide in ether (25 ml of 1.5 *N* solution), was added to an ethereal solution (50 ml) of rhodium salt (400 mg, 1 mmole), at −50°. A black suspension formed, to which diphenylacetylene (360 mg, 2.02 mmole) and biphenyl (180 mg) in 25 ml ether was added. The suspension was warmed up to room temperature, stirred for 24 h and treated as below.

Analysis of products

Hydrolysis in all cases was carried out by stirring with excess of water for 24 h. Stilbene derivatives were extracted with cold hexane or diethyl ether, while some of the least soluble condensation products were separated by filtration. After evaporation, the residue of the hexane or ethereal solution was extracted with CCl_4 for NMR and IR analysis, or with hexane for analysis and separation by VPC. VPC was carried out on $6' \times \frac{1}{8}''$ columns ($\frac{1}{4}''$ for preparative work), loaded with 10% SE-30 silicone or 15% XF-1150 cyanosilicone on chromosorb P. Separation temperature was 180–190°. Order of elution: polymethylene, biphenyl, *cis*-stilbene*, *cis*-α-methylstilbene*, benzylstyrene, *cis*-α,α′-dimethylstilbene[17], *trans*-α,α′-dimethylstilbene[17], diphenylacetylene, *trans*-α-methylstilbene, *trans*-stilbene.

The separated products were identified by NMR and IR spectra and compared with authentic compounds[3,17]. Condensation products were identified by thin layer chromatography on (250 μ) Kieselgel G on glass plates by comparison to authentic samples[3b]. 1,2,3-Triphenylnaphthalene was identified with the use of a 4/6 (v/v) mixture of $CHCl_3$ and CCl_4 as a developer. 1,2,3,4-Tetraphenylbutadiene (m.p. 180°), $(Ph_3P)_2RhC_6H_4PPh_2$, and 1,2,3,4-tetraphenylcyclopentadiene were separated with a mixture of $CHCl_3$/dioxane 50/1 (v/v). The last compound was also recognized by the typical NMR band at τ 6.06. Iodine vapour and UV light were used for detection.

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* Not separated on XF-1150.

Polymethylene was isolated as follows. After extraction of addition products with cold hexane, a syrupy residue remained which was extracted with boiling hexane, which does not dissolve the condensation products. The extracted material was soluble in benzene, ether and acetone. This material or some fraction of it could be eluted by gas chromatography (see above). The IR spectrum (in CCl_4) consisted of absorptions at 2950, 2920, 2860, 1440, 1380 and 700 cm^{-1}. The NMR spectrum showed a complicated but narrow band at δ 1.15 ppm. The mass spectrum was as expected from an aliphatic hydrocarbon. Masses as high as 270 and 280 were observed.

Thermal decomposition of $(Ph_3P)_3RhCH_3$ in boiling xylene

From $(Ph_3P)_3RhCH_3$ (200 mg, 0.22 mmole), after 30 min of reflux in *p*-xylene (15 ml), a dark yellow precipitate was obtained and identified as $(Ph_3P)_2\overline{RhC_6H_4P}Ph_2$ m.p. 110–115° (decompn.)[5]. The resulting mixture was also analysed by NMR, before and after hydrolysis. There was no evidence for any reaction with the solvent.

Instrumentation

IR spectra were taken with the Perkin–Elmer model 337 spectrophotometer. NMR analyses were carried out with Varian T-60 and HR-100 instruments. Gas chromatography analyses were carried out on a Wilkens Aerograph Hi-Fi model 600 equipped with hydrogen flame detector, and preparative separations were carried out with the Wilkens model A-700 having a thermal conductivity detector. For mass spectrometry a Hitachi–Perkin–Elmer model RMU-6 was used.

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