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ALKYLATION REACTIONS WITH ORGANOMETALLIC COMPOUNDS

IV *. THE REACTION OF TRIS(TRIPHENYLPHOSPHINE)METHYLCOBALT WITH DIPHENYLACETYLENE

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Summary

Tris(triphenylphosphine)methylcobalt, $(Ph_3P)_3CoCH_3$, reacts with diphenylacetylene to give α-methylstilbene as the sole addition product. $(Ph_3P)_3CoCH_3$ can be used as an alkylation reagent in ethers or in aromatic solvents.

Introduction

Synthesis involving alkylations of diarylacetylenes are often complicated by the fact that it is usually necessary to produce active organometallic reagents in situ from Grignard reagents, which limits the range of solvents available and may lead to the necessity of using inhomogeneous slurries. An active organometallic compound which can be isolated and characterized is therefore desirable and some such reagents have recently been reported [2—4]. We have found that the cobalt compound $(Ph_3P)_3CoCH_3$ (I) can be isolated and used as an alkylation reagent in ethers or in aromatic solvents.

Results and discussion

Tris(triphenylphosphine)methylcobalt was prepared by a modification of the method used by Yamamoto et al. [5,6]. The procedure is sensitive to slight experimental variations [5,6] and the following details should be noted. (a) $(CH_3)_3Al$ in toluene was used instead of the $(CH_3)_2AlOC_2H_5$ used by Yamamoto [5,6]; this did not give the cobalt compound at temperatures of —5—0°C, but

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* For part III see ref. 1.

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comparatively good yields (30%) were obtained at —30 to —20°C. (b) Higher yields (65%) were obtained when THF was used as a solvent for both the reagent $(CH_3)_3Al$ and the reaction. (c) Molar ratios of $Co(acac)_3/Ph_3P/(CH_3)_3Al$ were 1 : 3 : 1.5 and formation of another compound, viz. $(Ph_3P)_2CoCH_3$ [6], which is reported to decompose in THF was not observed, the complex formed being stable in THF. To confirm the previous evidence [5] for the structure of $(Ph_3P)_3CoCH_3$, it was treated with HCl and with CCl_4 to give $(Ph_3P)_3CoCl$ and $(Ph_3P)_2CoCl_2$, respectively, both of which have been previously prepared [7]. Atomic absorption tests showed the product to contain no aluminum. Tris-(triphenylphosphine)methylcobalt reacted with diphenylacetylene to yield α-methylsilbene as the sole addition product. Part of the alkyne was recovered and some was consumed by side reactions, e.g. cyclisations. The latter occur especially when an excess, sometimes even a slight excess, of cobalt compound is present (Table 1: runs 2 and 3; 5 and 4; 6 and 7; 8 and 9). The presence of oxygen would supress excessive consumption of $PhC{\equiv}CPh$ in such side reactions but would also lead to the formation of other addition products such as α,α'-dimethylstilbene [1]. The side reactions occur at low temperatures while higher temperatures are favorable to triple bond alkylation (runs 1—3). Compared to reagents previously used [8—10] for this reaction, compound I yields the least number of side products of addition. It is of known structure and very reactive even at temperatures below —30°C. The addition product can be separated from the cyclisation products or cobalt complexes by elution with hexane or cyclohexane on silica columns [8b].

The reagent is free of the restrictions of reactions carried out under "Grignard

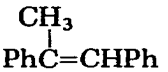
TABLE 1

DISTRIBUTION OF ADDITION PRODUCTS (%) [a] IN REACTIONS OF DIPHENYLACETYLENE WITH $CH_3Co(PPh_3)_3$ at —23°C

Run	Solvent	$CH_3Co(PPh_3)_3$ initial (mmol)	$PhC{\equiv}CPh$ initial (mmol)	α-Methylstilbene		$PhC{\equiv}CPh$ recovered (%)	Yield of addition product (%)
				cis	*trans*		
1	Toluene [b]	1.5	1.48	~1	2	42	3
2	Toluene	1.89	1.75	6.2	3.7	29	10
3	Toluene	4.4	0.87	3.6	5.3	0	12
4	Benzene	1.07	1.06	45	9	trace	24
5	Benzene	0.88	2.26	~15	~1	24	2.5
6	THF	1.42	1.32	3	3	62	6
7	THF	4	2.0	1	7	0	8
8	Diethylether	0.90	0.88	3	10	<1	13
9	Diethylether	4	0.97	1.8	11	0	12.8
10	Chlorobenzene	1.63	1.54	12	18	0	30
11	Pyridine	1.05	0.97	trace	1.8	6	21
12	Cyclohexane	0.72	0.69	3	4	47	7
13	Acetone	1.11	0.71	<1	<1	91	1
14	Chlorobenzene	2.55 [c]	1.72	4.2	17.1	0	21.3

[a] Yields based on diphenylacetylene. Diphenylacetylene was shown to contain small amounts of stilbene observed in the product mixture (~0.2—0.4%). In run 8 *cis* stilbene 6% was found. [b] Reaction performed at —70°C throughout. [c] $CH_3Co(Ph_3P)_2$ was used instead of $CH_3Co(Ph_3P)_3$.

conditions". Indeed, ethereal solvents are shown to be less suitable for this reaction than others. The results in Table 1 indicate that yields fall with increasing donor power of the solvent, i.e. the yields are higher in ether than in THF, a very low yield is obtained with the strong donor pyridine and the best yield with chlorobenzene. (However diphenylacetylene is still used up by other reactions in pyridine.) Acetone probably reacts differently with $(Ph_3P)_3CoCH_3$ so that almost all of the diphenylacetylene is recovered unchanged. Solvents such as CCl_4 and $CHCl_3$ must be avoided as they react with I to yield $(Ph_3P)_3$-CoCl and $(Ph_3P)_2CoCl_2$.

The possibility that the recently reported less saturated compound $(Ph_3P)_2$-$CoCH_3$ [6] would show higher reactivity was tested. This compound gave almost the same yields,of  $\mathrm{Ph\overset{CH_3}{\overset{|}{C}}{=}CHPh}$ in chlorobenzene as the corresponding tris(triphenylphosphine) derivative. It should be noted however, that under the experimental conditions it is difficult to characterize this compound and to ensure absence of dimerisation, or disproportionation of the bis(triphenylphosphine)-methylcobalt, if any is formed, to saturated derivatives.

A comparison of $(Ph_3P)_3CoCH_3$ with the corresponding rhodium compound $(Ph_3P)_3RhCH_3$ [8,11] is informative. While the latter reacts with PhC≡CPh at elevated temperatures (130°C xylene) and forms olefines (stilbenes and α-methylstilbenes) only after hydrolysis, as shown by deuterium incorporation with D_2O and absence of products before hydrolysis [8], the cobalt compound reacts at low temperature and no deuterium whatever is incorporated when D_2O is used for hydrolysis [1]. Hence the formation of α-methylstilbene involves both methyl- and hydrogen-transfer reactions, and under these circumstances the virtual absence of stilbene in the product mixture is somewhat surprising.

Experimental

General

All reactions and operations were performed under dry argon in a 250 ml 3-necked round-bottom flask containing a magnetic stirring bar, fitted with a pressure-equalizing dropping funnel and an argon inlet and outlet through an oil trap. Tris(triphenylphosphine)methyl cobalt was prepared in a double Schlenk tube equipped with a glass filter. All solvents used were dried over sodium. Ether and THF were treated with alumina and dried on sodium, then on $LiAlH_4$ and were freshly distilled before use. Tris(acetylacetonate)cobalt was prepared as previously reported [12]. Trimethylaluminum (Ethyl Corp.) was used in toluene or THF solutions. Triphenylphosphine, diphenylacetylene and biphenyl were used as purchased.

Preparation of tris(triphenylphosphine)methylcobalt

a. Using trimethylaluminum in toluene solution. Cobalt tris(acetylacetonate) [12] (2.2 g, 6 mmol) and triphenylphosphine (4.7 g, 18 mmol) were placed in a Schlenk tube and dissolved in 40 ml dry toluene. The tube was immersed in a —23°C slush bath (CCl_4 /liquid air) and 2 ml of 46% solution of trimethylaluminum (9.5 mmol) in toluene were added dropwise from a syringe. The reaction mixture was stirred at —23°C until a brown slush formed. After allowing this to stand from several minutes to 1 hour, until evolution of gas was no longer observed, the precipitate was filtered and washed several times with cold (—23°C) ether. The region around the glass frit was also maintained at —23°C by saturating an absorbent material placed around this region with CCl_4/liquid-air slush. After washing, the orange precipitate of $(Ph_3P)_3CoCH_3$ was recovered (~1.8 mol, 30% yield).

b. Using trimethylaluminum in THF solution. A considerable amount of heat is evolved when $(CH_3)_3Al$ is dissolved in THF, and the solution obtained is not as sensitive to air as hydrocarbon solutions. The reaction with tris(acetylacetonate)-cobalt and triphenylphosphine was carried out as above but at 0°C. Bubbling occurred immediately and the reaction was stirred at 0°C until no more gas was evolved. The product was filtered and washed with ether at —23°C as in (a), to give 3.8 g (4.4 mmol) of the orange product (65% yield).

Atomic absorption analysis of acetic acid, aqueous solutions of this compound (pH 3—4), showed that samples containing 55 ppm of cobalt contained no trace of aluminum.

Reaction of $(Ph_3P)_3CoCH_3$ with HCl, CCl_4 and $CHCl_3$

Addition of aqueous concentrated HCl to the orange $(Ph_3P)_3CoCH_3$, either dry or in the presence of THF or ether caused evolution of gas and formation of a green precipitate, which was filtered off under argon. It could be kept for several days but on exposure to air it eventually became tourquouse. The green precipitate was shown to be $(Ph_3P)_3CoCl$ [7], (I.R. spectrum) melting at 170—176°C [m.p. of $(Ph_3P)_3CoCl$; 177°C) [7], with traces of the blue oxidized material m.p. 210—255°C [13].

Upon addition of CCl_4 or $CHCl_3$ to $(Ph_3)_3CoCH_3$, the orange complex turned green and eventually blue, yielding a mixture of $(Ph_3P)_3CoCl$ and $(Ph_3P)_2CoCl_2$ (m.p. 225°C) [13].

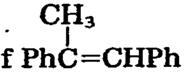
Reaction of tris(triphenylphosphine)methylcobalt with diphenylacetylene

In all the reactions, biphenyl was added along with the diphenylacetylene to serve as an internal standard for GC analysis of the products.

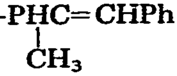
a. Reaction in chlorobenzene. After being washed with ether, the orange cobalt complex was transferred to a weighed 250 ml 3-neck flask fitted with an argon inlet and outlet. The complex was dried under argon with an occasional stirring and crushing. The flask was reweighed and the number of mmol of complex calculated. To the dry $(PPh_3)_3CoCH_3$ (1.4 g, 1.6 mmol), 25 ml chlorobenzene was added at —23°C. Diphenylacetylene (0.27 g, 1.5 mmol) in ca. 50 ml chlorobenzene was then added. The mixture was stirred at —23°C for ~1 h after which it was allowed to warm to room temperature. After stirring for ~16 h, the mixture was hydrolyzed with water for 24 h, extracted with hexane and analyzed by gas chromatography. Reactions in other solvents were performed similarly.

Benzene and cyclohexane solutions of $(Ph_3P)_3CoCH_3$ froze quickly at —23°C, but solutions of PhC≡CPh stayed liquid long enough to enable mixing. After mixing the reactions were worked up as above.

Reaction of $(Ph_3P)_2CoCH_3$

This compound was prepared as described in ref. 6 by use of small quantitites of triphenylphosphine. The cobalt compound (2.55 mmol) was allowed to react with $PhC{\equiv}CPh$ (1.72 mmol) in chlorobenzene. The procedure was the same as for $(Ph_3P)_3CoCH_3$. Lower yields of  $\mathrm{Ph\overset{CH_3}{\overset{|}{C}}=CHPh}$ (viz. 4.2% *cis* and 17.2% *trans* isomer) were observed.

Product analysis

Products were analysed by GLC on SE-30 silicone columns [8], by use of authentic compounds and of GCMS analysis. On SE-30 columns, *trans*- $\mathrm{P\underset{CH_3}{\underset{|}{H}}C=CHPh}$ and *trans* PhCH=CHPh were not separated, but a detailed GCMS analysis of the relevant GC peak showed it to consist exclusively of α-methylstilbene.

The accuracy of gas chromatography measurements was tested on the actual columns and instruments used in this work, by analysing known mixtures. This showed that the detector response to the different compounds involved is the same to within less than 10%. Reaction mixtures were also examined by NMR with Varian T-60 and HR100 instruments. α-Methylstilbene was the only addition product detected.

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