REACTIONS OF METHYLTRIS(TRIARYLPHOSPHINE)COBALT

III *. ALDOL CONDENSATION CATALYSED BY METHYLTRIS(TRIPHENYLPHOSPHINE)COBALT, $(Ph_3P)_3CoCH_3$

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Summary

Methyltris(triphenylphosphine)cobalt catalyses the aldol condensation of acetone and ethyl methyl ketone. From acetone mesityl oxide is obtained in ~70% yield, while from ethyl methyl ketone 3-methyl-2-heptene-5-one and 3-methyl-3-heptene-5-one are formed in equal amounts in a total yield of about 100%. The latter products are known to be those of base-catalysed aldol condensation. The corresponding aldols are also observed in small quantities. The reactions mostly take place in the absence of solvent.

In recent publications we described some aspects of the chemistry of $(Ph_3P)_3CoCH_3$ (I) [1,2]. It was inferred that the reactions of I to yield biphenyl and biaryls by decomposition in solutions and by reactions with ArX (X = halides) should be regarded as the result of oxidative addition processes. The more significant properties seemed to result from the strong nucleophilicity of the cobalt atom, which is attached to three donor Ph_3P ligands and σ bonded to a methyl group. Many examples are known of low spin d^8 complexes in which donor ligands and the small volume of the metal atom result in a strong nucleophilic character [3]. The suggestion that other cobalt(I) compounds are strong nucleophiles has certainly been made before. Even supernucleophilicity has been attributed to planar cobaloximes as a result of the presence of a protruding populated d_{z^2} orbital, which is not the same with I [4]. Yet the observation that I dissociates in solution with the loss of Ph_3P ligands suggests that several low spin d^8 forms are present, some even with available coordination sites and less rigidity. The connection between nucleophilicity and the strong tendency of I to be involved in various oxidative additions is reasonable [2,5],

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* For part II see ref. 2.

although the fact that this property of the cobalt complex would dominate its chemistry rather than the presence of the σ-bonded methyl group, which might have been expected to be the major factor [6], is somewhat surprising. However, this feature is more apparent in the study of reactions of I with ketones. The σ-bonded methyl-cobalt complex could have been expected to react with the carbonyl group as do Grignard reagents, but no such reaction was observed. Instead, I catalyses the aldol condensation of acetone and ethyl methyl ketone. No report of a similar reaction is known to us. Only a very few cases of aldol condensations catalysed by transition metal compounds have been described in the literature, and those involve the combined condensation and coordination of the adduct as a π-bonded ligand [7,8,9], thus differing from the classical process of aldol condensation [10,11]. Moreover, classical aldol condensations are carried out in aqueous solution while the reaction now described occurs only in the neat ketone.

Results and discussion

Compound I reacted with acetone in concentrated benzene solution or in neat acetone, and with ethyl methyl ketone only as a neat material but not in solution. No acid or base were present. Although I has been shown to dissociate to free Ph_3P and another complex [1,2], Ph_3P alone did not induce any reaction of these two ketones.

Acetone reacts readily with I at temperatures between -30 to $+10°C$ to yield after a few hours mesityl oxide, $CH_3(CH_3)C=CHCCH_3$ (II) $\sim$ 70%, along with varying amounts of the corresponding aldol, 2-methyl-2-hydroxypentan-4-one (III). To separate the product from inorganic materials, hydrolysis with 8% HCl was carried out. This was not relevant to the formation of II and III, and acetone was not itself affected by the 8% HCl solution. The products II and III were isolated by fractional distillation.

The relative amounts of III were small and varied from run to run, II being the main product. Phorone IV (b.p. 198°C) and isophorone V, products of double alkylation, were not found in the highest boiling distillate nor in the residue.
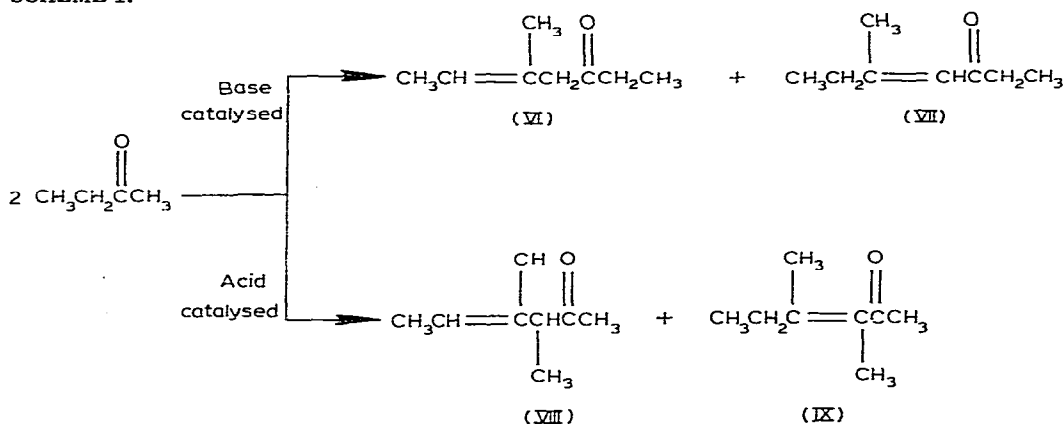
SCHEME 1.

TABLE 1

MASS SPECTRA OF PRODUCTS OF CONDENSATION OF $C_2H_5\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}CH_3$ ON $(Ph_3P)_3CoCH_3$

Peak (m/e)	Relative intensity (% of base peak)		Assignment
	$CH_3CH_2\overset{CH_3}{\overset{\|}{C}}{=}CH\overset{O}{\overset{\|}{C}}CH_2CH_3$	$CH_3CH{=}\overset{CH_3}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}CH_2CH_3$	
126	18	11.1	
97	90	100	$M{-}(C_2H_5)$
69	24	26.3	$M{-}(C_2H_5CO)$
57	100	23.7	$C_2H_5CO^+$
55	12.8	13.15	
43	36.2	23.68	
41	72.5	92.1	

The reaction of I with ethyl methyl ketone is even more revealing. Aldol condensation of ethyl methyl ketone is known to yield one set of products, VI and VII, under basic catalysis and another set, VIII and IX in the presence of acids (Scheme 1) [11,12].

Reaction of I with ethyl methyl ketone gave VI and VII in 1 : 1 ratio, and with a combined high yield (~100%) based on cobalt. This ratio was observed in all runs. The products were separated and identified by NMR (300 MHz) and by GC-MS. The mass spectra of the products is presented in Table 1. The predominance of fragments such as m/e 97 $[M - CH_2CH_3]$; 69 $[M - \overset{O}{\overset{\|}{C}}CH_2CH_3]$; 57 $[M{=}\overset{O}{\overset{\|}{C}}CH_2CH_3]$ is very clear. The observation that with VI the ratio of m/e 41/43 is larger than in VII is also in accord with expectation. VIII and IX on the other hand, give a very different mass spectrum.

The title compound did not react with more bulky ketones such as benzyl methyl ketone and acetophenone. The latter was, in fact, arylated by I, as will be discussed elsewhere [5].

Aldol condensations are known to involve protonation (acid catalysed) or proton abstractions (base catalysed), and are mostly carried out in aqueous solutions. The reaction we describe is unusual in that it takes place in a non-protic media. Hydrogen transfer reactions with I in aprotic solvents have been observed before [2,6], but the nature of the migrating hydrogen atom, whether hydride, free radical or proton, has not been established, and may depend on the specific process involved. However, the products of aldol condensation of ethyl methyl ketone as catalysed by I are like those obtained under basic catalysis, e.g. by a mechanism of proton abstraction followed by ketol formation in the first stage:

$$CH_3\overset{O}{\overset{\|}{C}}CH_2CH_3 + B \rightarrow BH^+ + [CH_2\overset{O}{\overset{\|}{C}}CH_2CH_3]^-$$
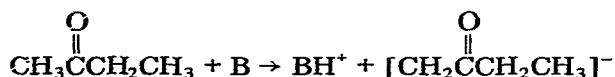
It is more than likely that the same is true for the condensation of acetone. It is

not at all clear whether the condensation actually involves proton abstraction, since complex I is a nucleophile rather than a base and the reaction takes place in aprotic solvent. The analogy with base-catalysed aldolisation is therefore partial at best. In discussing the reaction with ethyl methyl ketone it is important to notice that the difference between the routes in Scheme 1 is generally considered as a distinction between two different mechanisms of catalysis [11]. Ingold has suggested [13] that the two routes differ in the kinetic control of the ionisation step. Inductive effects play the dominant role in the base catalysed deprotonation of the methyl group, while with acids resonance and hyperconjugation cause preferred attack on the carbonyl oxygen followed by deprotonation of the methylene group. In his discussion he describes these effects as Hoffman-like and Saytzeff-like control [13a,13b], respectively.

Because of the differences in the conditions, reaction media and type of catalyst between our reaction and classical aldol condensations, it is difficult to judge as to how much diagnostic value should be attributed to the fact that ethyl methyl ketone yields only VI and VII. It is interesting, however, to consider the possible implications. Evidence for the nucleophilicity of complexes such as I is based on intrinsic structural features such as orbital symmetry and types of ligands [4]. Their reactions, especially oxidative additions with halides such as RX or ArX, are often considered as a reflection of their nucleophilicity [14]. While this is most likely so, the phenomenon of oxidative addition is itself defined in terms of products rather than mechanisms, more than one of which could explain the formation of a single set of products [14,5]. Aldol condensation such as that of ethyl methyl ketone with I, perhaps offers independent evidence for the nucleophilicity of the metal complex as based on the type of product. Whether this is so will be further studied.

It is also not clear why the dehydrated product predominates. The reaction conditions are too mild for thermal dehydration of the aldol. Coordination of the ketone or its derivative with I at some stage of the reaction is very likely, since little or no biphenyl is formed and experience shows that the characteristic autodecomposition of I in solutions to yield biphenyl [1,2] is blocked whenever an interfering, ligating agent is present. Unlike the two reported cases of metal-catalysed condensation [8,9] we have no direct evidence for such complexation. Another feature of the reaction, the sharp decrease in yield in the presence of a non-polar solvent (C_6H_6, C_6H_5Cl), indicates a strong dependence on the polarity of the medium.

Experimental

The preparation of $(Ph_3P)_3CoCH_3$ (I) as a dry powder has been described [6].

Reaction of I with acetone

To 3.5 g (4.1 mmol) in I in the form of dry powder, acetone (12 ml, 163 mmole) was added at $-23°C$. After mixing, the slurry was allowed to warm to 25°C. The colour changed from red to dark brown and a brown precipitate formed. The reaction was kept under a slow stream of Ar. After 24 h, when the volume of liquid was reduced to 5.5 ml, the mixture was hydrolysed with aq.

TABLE 2

FRACTIONAL DISTILLATION OF PRODUCTS FROM REACTION OF I WITH ACETONE

Fract. No.	Temp. (°C)	Quantity [a]	Condensation Products (g × 10⁻³) [b]
1	67—69	10 ml	—
2	72—74	3.4 g	40
3	74	2.5 g	55
4	74	1.1 g	53
5	76	0.3 g	11
residue	—	0.25 ml	182

[a] Containing CCl_4. [b] Determined by NMR and comparison with CCl_4 solutions of known concentrations. Condensation products are mesityl oxide and diacetone alcohol.

8% HCl for 30 min, and the organic material extracted with CCl_4 (10 ml). Table 2 summarizes a typical run.

The total quantity of condensation products was 0.341 g (67% yield based on molar quantity of I). The fractions in Table 2 contained, respectively, (Fraction No.): (1) Acetone, CCl_4 and residues of ether and THF from I; (2) Acetone, diacetone alcohol, CCl_4; (3) Diacetone alcohol and CCl_4; (4) Diacetone alcohol and mesityl oxide; (5) Mesityl oxide; (Residue) Mesityl oxide.

Mesityl oxide was identified by NMR and GC-MS. Diacetone alcohol was identified by NMR. Quantities of the latter were usually small and varied from run to run.

Reaction of I with ethyl methyl ketone

Ethyl methyl ketone (6 ml, 70 mmol) was added to I (1.3 g, 1.5 mmol) at 23°C. No colour change was observed. The mixture was allowed to warm to 25°C, the colour slowly turning to brown, but no precipitate was formed. After 24 h the mixture was hydrolysed with aq. 8% HCl for 30 min, and the organic layer was separated with benzene, dried and fractionated. A typical run is shown in Table 3.

Reaction of I with acetone and ethyl methyl ketone in solvents

The reaction of ethyl methyl ketone (8 mmol) with I (4 mmol) in chlorobenzene (10 ml) under otherwise identical conditions yielded only a trace of condensation products (~1.5%). Other products were biphenyl and $(Ph_3P)_3CoCl$ which I forms with chlorobenzene [2]. With THF and benzene as solvent, only biphenyl [2] was found, and no condensation products.

TABLE 3

FRACTIONATION OF PRODUCTS FROM REACTION OF I WITH ETHYL METHYL KETONE

Fract. No.	Temp. (°C)	Quantity (ml)	GC analysis
1	70—74	3	ethyl methyl ketone, benzene
2	74	1	ethyl methyl ketone, benzene
3	70	1	ethyl methyl ketone, benzene, toluene
4	160	0.3	ethyl methyl ketone, biphenyl, C.P. [a]
5	165/18 mm	0.3	ethyl methyl ketone, biphenyl, C.P. + aldol.

[a] C.P. = condensation product: 3 methyl-2-heptene-5-one and 3 methyl-3-heptene-5-one, in 1 : 1 ratio. Toluene and biphenyl in small amounts.

Acetone gave a 5% yield of condensation products in THF.

Control experiments

1. Acetone or ethyl methyl ketone (10 ml) were mixed with aqueous 8% HCl (10 ml) at 25°C for 2 h *. The organic layer was separated and dried. No condensation products were detected using high sensitivity NMR tests or mass spectrometry.

2. Acetone or ethyl methyl ketone (1 mol) were mixed with Ph_3P (3 mol) at 25°C for 48 h. Tests were taken after 27 h and 48 h, after and before hydrolysis with 8% HCl. No condensation or any other products were detected (NMR at high sensitivities or mass spectrometry).

3. A mixture of the ketone (10 ml) and cobalt acetylacetonate $Co(acac)_3$ (0.5 g) was left for 24 h, hydrolysed by 8% HCl and tested as above. No condensation was detected.

Attempted reaction with other ketones

I did not react under the conditions described with benzyl methyl ketone, $PhCH_2COCH_3$. There was a reaction with acetophenone, but this was not a condensation. This reaction will be discussed elsewhere [5].

Instrumentation

Analyses by GC-MS were taken with a Varian MAT 11 model with E.I. ionization chamber, NMR spectra with T-60 and Bruker WHZ 300 MHz instruments, and mass spectra with a Varian MAT 311 spectrometer.

Note added in proof.

While this work was in press our attention was drawn to the work of K. Irie and K. Watanabe [15] describing aldol condensations in polar aprotic solvents, in which a combination of metal ion, conjugate anions and nucleophilic ligands influence catalysis.

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* The reaction time was 0.5 h.