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THE PALLADIUM-CATALYSED CONJUGATE ADDITION TYPE REACTION OF ARYLMERCURY COMPOUNDS WITH α,β-UNSATURATED KETONES IN A TWO-PHASE SYSTEM

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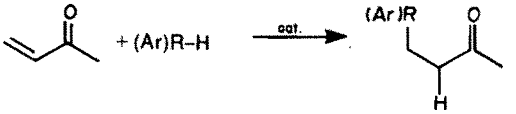
Abstract—Pd-catalysed reaction of arylmercury compounds with α,β-enones in an acidic two-phase system provides a mild and selective way to β-aryl ketones. The present conjugate addition type reaction may accommodate a wide variety of functional groups. Thus, aryl units containing electron-donating and electron-withdrawing substituents such as -Me, -Cl, -CHO, -COMe, -COOMe, -COOH, -OH, -OMe, -NHCOMe and $-NO_2$ were successfully transferred to the β C atom of benzalacetone. A number of α,β-enones were also treated with 3-formylphenyl mercury chloride to give the corresponding β-(3-formylphenyl) derivatives. The main limitation seems to arise from steric hindrance in the starting α,β-enonic system. Substituents in the aryl moiety of the organomercury compounds were found to affect the transmetalation step in the direction expected for a rate determining σ-complex formation.

The formation of C–C bond between the β C atom of an α,β-unsaturated carbonyl system and an unstabilised carbanion according to the eqn (1) is generally achieved through conjugate addition of organocopper reagents[1] or organomagnesium reagents in the presence of catalytic amounts of copper.[1]



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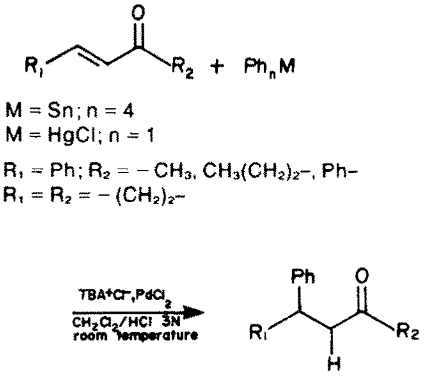
In addition to these largely applied methods, even organoaluminium compounds with[2] or without[3] the presence of nickel as catalyst and organoboron compounds[4] have been reported to undergo conjugate addition to α,β-enones. More recently, a nickel-catalysed conjugate addition of alkenyl zirconium species to α,β-unsaturated ketones has been described.[5]

All these methods allow placement of a variety of hydrocarbons β to a CO function. Regarding ease of preparation of starting materials, stability of reagents, efficiency and specificity of reaction, each procedure has its relative advantages and disadvantages. However, an essentially common limitation can be recognised in what concerns the nature of functional groups tolerated in the carbon framework to be transferred to the enonic β C atom.

Thus, with regard to this last point, the development of a more versatile, alternative procedure would be desirable.

In a previous paper[6] we have reported that unhindered α,β-unsaturated ketones react at room temperature with phenylmercury chloride or tetraphenyltin, catalytic amounts of palladium dichloride and tetrabutylammonium chloride, in an acidic two-phase system to give benzene addition to the olefinic double bond according to eqn (2).



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Very likely, the tetrabutylammonium palladium trichloride salt ($TBA^+PdCl_3^-$) derived *in situ* from tetrabutyl ammonium chloride and palladium dichloride, is the effective catalyst† and the reaction proceeds through the transmetalation of phenyl units from mercury or tin to Pd(II).

As arylmercurials are readily available, stable compounds, and may easily accommodate a wide variety of substituent groups, this Pd-catalysed reaction, formally equivalent to the conjugate additions of organometals described above, seemed to provide us with the desired improvement of the conjugate addition methodology.

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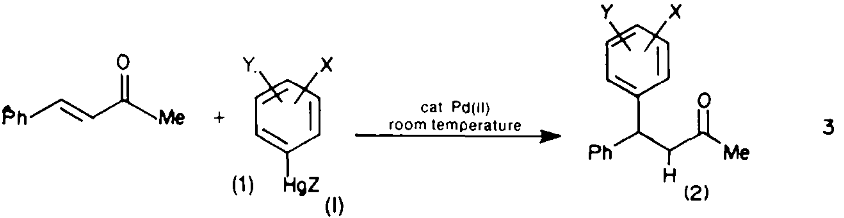
†When benzalacetone was treated with phenylmercury chloride in the presence of 6 mol % of $TBA^+PdCl_3^-$ previously prepared,[6] 4,4-diphenylbutan-2-one was isolated in 86% yield.

RESULTS AND DISCUSSION

Using benzalacetone as substrate, the effectiveness of the reaction has been tested with a number of arylmercury compounds containing a variety of organic functions (eqn. 3).

The following conditions have been found satisfactory in both the reactivity and the selectivity and no attempts were made for optimisation. The reactions were carried out on 0.5–0.6 molar dichloromethane solution of the α,β-enone. The starting α,β-enone (3.4–7.4 mmol) and the arylmercury compound (50 mol % excess) were added to a dichloromethane/aqueous HCl 3N (*ca* 1.6:1 v:v) two-phase system containing $PdCl_2$ (5 mol %) and TBA^+Cl^- (10 mol %). The mixture was stirred at room temperature for an appropriate period (5–24 hr) and worked up. Pure β-arylated ketones were obtained through column chromatography.

As may be seen from the results summarized in Table



(I)

X = H; Y = H[6], 4-Me, 4-OMe, 4-Cl, 3-CHO, 3-COMe, 3-COOH, 3-COOMe, 4-OH, 3-NO_2; Z = Cl

X = H; Y = 4-NHCOMe, 4-NH_2, Z - OAc

X = 5-NO_2; Y = 2-NHCOMe; Z = OAc

X = 3-NO_2; Y = 2-OH; Z - Cl

X = 3-CHO; Y = 4-OH; Z - Cl

Table 1. Palladium catalysed conjugate addition type reaction of organomercury compounds (1) with benzalacetone[a]

Entry	Organomercury compound (1)	Reaction time (h)	Yield of (2) [%][b]
a	PhHgCl	5	85[6]
b	4-Me-C_6H_4-HgCl	4	90
c[7]	4-Cl-C_6H_4-HgCl	12	83[c]
d[8]	3-CHO-C_6H_4-HgCl	5	83
e	3-COMe-C_6H_4-HgCl	24	94
f[8]	3-COOMe-C_6H_4-HgCl	8	84
g[8]	3-COOH-C_6H_4-HgCl	24	[illegible]
h[9]	4-OH-C_6H_4-HgCl	5	89
i[10]	4-OMe-C_6H_4-HgCl	5	98
l	4-NHCOMe-C_6H_4-HgOAc	4	94
m[11]	3-NO_2-C_6H_4-HgCl	15	0[c]
n	"	8	70[d]
o[12]	4-NH_2-C_6H_4-HgOAc	12	0[c]
p[13]	5-NO_2, 2-NHCOMe-C_6H_3-HgOAc	15	0[c]
q[14]	3-NO_2, 2-OH-C_6H_3-HgCl	8	89
r[15]	3-CHO, 4-OH-C_6H_3-HgCl	5[e] (8)[f]	63[e] (86)[f]
s[15]	3-CHO, 2-OH-C_6H_3-HgCl		17[e] (43)[f]

a) Reactions were carried out at room temperature, with a 50 mol % excess of the organomercury compound in the presence of 5 mol % of $PdCl_2$ and 10 mol % of TBA^+Cl^-.

b) Yields are calculated on the starting benzalacetone and are given on pure isolated products.

c) The starting benzalacetone was recovered in almost quantitative yield (GLC analysis).

d) The reaction was carried out in the presence of 20 mol % of palladium salt and 40 mol % of TBA^+Cl^-. Benzalacetone was recovered in 20 % yield.

e) The organomercury compound used in this reaction was a nearly 1:1 mixture of (1r) and (1s) (^1H-NMR analysis). Therefore, the observed 63 % yield raises to about 84 % if the effective amount of (1r) into the reaction mixture is taken into account.

f) The 1:1 mixture of (1r) and (1s) was reacted with a 10 mol % excess of benzalacetone. Yields are based on the organomercury compound.

1, aromatic rings containing almost all the synthetically significant organic functions were successfully transferred to the enonic *β* C atom.

Biphenyl derivatives, generated by the Pd-catalysed coupling of two aryl units of the arylmercury starting material, are the expected and often observed by-products. For example, 3,3′-diformylbiphenyl was isolated in about 4% yield (80% yield based on Pd) from the reaction of 3-formylphenylmercury chloride with cyclopent-2-en-1-one (see Table 3). Clearly, as the reduced Pd species cannot be recycled into the conjugate addition type process, the Pd-catalysed copulation must occur only to a limited extent in the presence of the enonic system.

Only with some mercurials containing the nitro and the amino groups the reaction failed (see entries *m*, *o*, *p*, Table 1) and benzalacetone was recovered in almost quantitative yield. For example, benzalacetone was recovered in 93% isolated yield (98% glc yield) after 20 hr from the reaction with 3-nitrophenylmercury chloride under our standard conditions.

Two reasonable explanations for these failures appeared possible: (1) the addition of arylpalladium intermediates containing strongly electron-withdrawing substituents to the olefinic double bond was too slow to compete with the alternative reaction pathways such as coupling; and (2) the presence of a strongly electron-withdrawing substituent in the aromatic ring affected negatively the transmetalation step. These observations also apply to amino group, as under the acidic two-phase reaction conditions only its protonated form is present. Moreover, protonation of nitrogen can affect even the solubility of the organomercury compound in the organic phase.

We have not had evidence for the first possibility as no

Table 2. Characterization of addition products (2)

Addition product	Mp (°C)	Molecular formula[a]	IR ν (cm^{-1})	^{1}H-NMR (CDCl$_3$) δ (ppm)	MS m/e:M$^+$ (rel.int.), Parent Ion
2b	119–120[b]	$C_{17}H_{18}O$ (238.3)	1715[c]	7.10–7.00 (m, 9H), 4.46 (t, 6.75 Hz, 1H), 3.03 (d, 6.75 Hz, 2H), 2.20 (s, 3H), 1.93 (s, 3H)	238 (17.4), 181
2c	129–130[b]	$C_{16}H_{15}OCl$ (258.7)	1715, 1490, 750, 700[c]	7.30–7.10 (m, 9H), 4.55 (t, 7.5 Hz, 1H), 3.10 (d, 7.5 Hz, 2H), 2.00 (s, 3H)	438 (1.1), 440 (0.4)[e], 201[b]
2d	81–82	$C_{17}H_{16}O_2$ (252.3)	2740, 1710, 1690[d]	9.90 (s, 1H), 7.70–7.10 (m, 9H), 4.62 (t, 7.5 Hz, 1H), 3.16 (d, 7.5 Hz, 2H), 2.02 (s, 3H)	252 (51.6), 209
2e	55–56	$C_{18}H_{18}O_2$ (256.3)	1710, 1675, 1360, 1270[c]	7.90–7.00 (m, 9H), 4.64 (t, 7.5 Hz, 1H), 3.17 (d, 7.5 Hz, 2H), 2.44 (s, 3H), 2.00 (s, 3H)	256 (28.3), 43
2f	142–143[b]	$C_{18}H_{18}O_3$ (282.3)	1720, 1290, 750, 705[c]	8.00–7.20 (m, 9H), 4.64 (t, 7.5 Hz, 1H), 3.77 (s, 3H), 3.15 (d, 7.5 Hz, 2H), 1.97 (s, 3H)	462 (0.4)[e], 225[b]
2g	128–129	$C_{17}H_{16}O_3$ (268,3)	1710, 1680[d]	12.1 (s, 1H), 8.00–7.00 (m, 9H), 4.60 (t, 6.75 Hz, 1H), 3.17 (d, 6.75 Hz, 2H), 2.05 (s, 3H)	268 (3.4), 84
2h	98–99	$C_{16}H_{16}O_2$ (240,3)	3360, 1700[d]	7.23 (m, 5H), 6.90 (AA′BB′, 8.4 Hz, 4H), 6.27 (bs, 1H), 4.52 (t, 7.5 Hz, 1H), 3.15 (d, 7.5 Hz, 2H), 2.07 (s, 3H)	240 (23.0), 183
2i	93–94[b]	$C_{17}H_{18}O_2$ (254.3)	2830, 1720, 1245 1130, 830[c]	7.6–6.57 (m, 9H), 4.52 (t, 7.5 Hz, 1H), 3.65 (s, 3H), 3.09 (d, 7.5 Hz, 2H), 1.97 (s, 3H)	254 (36.4), 197
2l	113–114	$C_{18}H_{19}O_2N$ (281.3)	3280, 3250, 3180, 3120, 1705, 1660[d]	8.37 (bs, 1H), 7.27 (AA′BB′, 8.1 Hz, 4H), 7.20 (bs, 5H), 4.53 (t, 7.5 Hz, 1H), 3.13 (d, 7.5 Hz, 2H), 2.03 (s, 3H), 2.02 (s, 3H)	281 (23.3), 182
2m	138–139[b]	$C_{16}H_{15}O_3N$ (269.3)	1710, 1525, 1350[c]	8.33–7.00 (m, 9H), 4.70 (t, 7.5 Hz, 1H), 3.24 (d, 7.5 Hz, 2H), 2.07 (s, 3H)	269 (1.3)[e], 209
2q	186–187[b]	$C_{16}H_{15}O_4N$ (285.3)	3200, 1710, 1535, 1450, 1355[c]	7.91 (q, 8.6 Hz, 1.5 Hz, 1H), 7.50 (q, 7.5 Hz, 1.5 Hz, 1H), 7.26 (m, 5H), 6.88 (q, 8.6 Hz, 7.5 Hz, 1H), 5.07 (t, 7.6 Hz, 1H), 3.22 (d, 7.6 Hz, 1H), 2.10 (s, 3H)	225
2r	87–88	$C_{17}H_{16}O_3$ (268,3)	3200, 2740, 1710, 1655[c]	10.87 (s, 1H), 9.77 (s, 1H), 7.4–7.2 (m, 7H), 6.87 (d, 10 Hz, 1H), 4.59 (t, 7.5 Hz, 1H), 3.15 (d, 7.5 Hz, 2H), 2.07 (s, 3H)	268 (43.3), 211
2s	220–221[b]	$C_{17}H_{16}O_3$ (268.3)	3200, 2745, 1720, 1650[c]	11.48 (s, 1H), 9.75 (s, 1H), 7.53–6.67 (m, 8H), 5.00 (t, 7.5 Hz, 1H), 3.19 (d, 7.5 Hz, 2H), 2.07 (s, 3H)	268 (0.8)[e], 231

a) All products gave satisfactory microanalyses (C, ± 0.38; H, ± 0.17; N, ± 0.37).

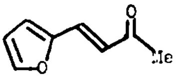
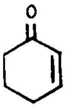
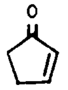
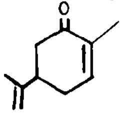
b) As the 2,4-dinitrophenylhydrazone derivative. All 2,4-dinitrophenylhydrazones gave analytical and spectroscopic data in agreement with the proposed structures.

c) Liquid film.

d) Nujol.

e) The molecular ion was confirmed recording the mass spectrum in chemical ionization (CH_4).

Table 3. Palladium catalysed conjugate addition type reaction of 3-formylphenylmercury chloride with α,β-unsaturated ketones (3)[a]

Entry	α,β-Unsaturated ketone (3)	Reaction time (h)	Yield of (4) [%][b]
a[17]	$PhCH{=}CHCOC_6H_4\text{-}2\text{-}OCH_2Ph$	4	92
b	$CH_2{=}CHCOMe$	3	89[c]
c[18]	$PhCH{=}CHCOCH_2Ph$	3	93
d[19]		10	87
e		4	84
f		5	71
g[20]	$PhCH{=}CHCOPh$	5	85
h[21]	$PhCH{=}CHCOCH{=}CHPh$	4	65[d]
i[22]	$PhCH{=}CHCOC_6H_4\text{-}2\text{-}NO_2$	5	91
l		12	0

a) Reactions were carried out at room temperature with a 50 mol % excess of the organomercury compound in the presence of 5 mol % of $PdCl_2$ and 10 mol % of TBA^+Cl^-.

b) Yields are calculated on the starting α,β-unsaturated ketones and are given on pure, isolated products.

c) The reaction was carried out at 0°C.

d) Compound (5) was isolated in 17 % yield.

3,3′-dinitrobiphenyl derived from Pd-catalysed copulation of 3-nitrophenyl units was recovered from the mixture even when the Pd/α,β-enone molar ratio was raised to reach a more easily detectable amount of the likely formed copulation product. [Presumably the substituents affect the formation of the diarylpalladium species in a way similar to that we propose for the transmetalation step (*vide supra*)].

On the contrary, we have found that raising the Pd/α,β-enone molar ratio allows the formation of addition products even with arylmercury compounds containing a strongly electron withdrawing substituent such as the nitro group. Thus, 4-(3-nitrophenyl), 4-phenylbutan-2-one was obtained in 75% glc yield when the reaction was carried out in the presence of 20 mol % of $PdCl_2$ and 40 mol % of TBA^+Cl^- (see entry n, Table 1).

In the presence of an equimolar amount of the Pd salt, 4-(3-nitrophenyl), 4-phenylbutan-2-one was isolated in 86% yield after 4 hr.

In addition, treatment of 3-nitrophenylmercury chloride with TBA^+Cl^- and $PdCl_2$ (1.5 : 1 : 1 molar ratio; 6 hr) followed by treatment with benzalacetone (Pd(II)/benzalacetone 1 : 1 molar ratio; 8 hr) gave a mixture from which 3,3′-dinitrobiphenyl was isolated in only 17% yield (based on Pd). The addition product was isolated in 76% yield.

It may be of interest to report here that a casual check of a run carried out with 5 mol % of Pd salt and allowed to stand for about 3 months revealed the formation of 4-(3-nitrophenyl), 4-phenylbutan-2-one in 74% isolated yield.

The results obtained suggest that the formation of the arylpalladium intermediate is the rate limiting step and that, in the presence of the α,β-enonic system, the addition of arylpalladium to the olefinic double bond and the acid-catalysed elimination of the Pd(II) species from the α-Pd(II) intermediate[6] are faster than any other reaction pathway.

We have not thoroughly examined the mechanism of the transmetalation step but nevertheless a rough correlation may be found between our observations and the reaction pathway reported in the following scheme.

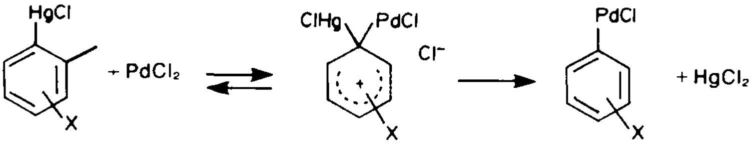


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Table 4. Characterization of addition products (4)

Addition product	Mp (°C)	Molecular formula[a]	IR ν (cm^{-1})	^{1}H-NMR (CDCl$_3$) δ (ppm)	MS m/e:X$^+$ (rel.int.), Parent Ion
4a	86–87	$C_{28}H_{24}O_3$ (420.5)	2730, 1695, 1670, 1235[d]	9.83 (s, 1H), 7.70–6.70 (m, 18H), 5.03 (s, 2H), 4.80 (t, 7.5 Hz, 1H), 3.79 (d, 7.5 Hz, 2H)	420 (0.2)[e], 121
4b	64–65	$C_{11}H_{12}O_2$ (176.2)	2730, 1700[c]	9.98 (s, 1H), 7.8–7.4 (m, 4H), 3.15–2.62 (m, 4H), 2.15 (s, 3H)	176 (14.8), 43
4c	138–140[b]	$C_{23}H_{20}O_2$ (328.4)	2740, 1690[c]	9.87 (s, 1H), 7.70–7.00 (m, 14H), 4.67 (t, 7.5 Hz, 1H), 3.57 (s, 2H), 3.20 (d, 7.5 Hz, 2H)	508 (2.3), 28[b]
4d	168–170[b]	$C_{15}H_{14}O_3$ (242.3)	2740, 1700[c]	9.98 (s, 1H), 7.83–6.05 (m, 7H), 4.70 (t, 7.5 Hz, 1H), 3.33 (q, 7.5 Hz, 17.2 Hz, 1H), 3.05 (q, 7.5 Hz, 17.2 Hz, 1H), 2.05 (s, 3H)	422 (40.3), 43[b]
4e	223–224[b]	$C_{13}H_{14}O_2$ (202.4)	2730, 1700[c]	10.05 (s, 1H), 8.10–7.20 (m, 4H) 3.10 (m, $W_{1/2}$ = 21 Hz, 1H), 2.67–1.50 (m, 8H)	202 (87.8), 131
4f	222–224[b]	$C_{12}H_{12}O_2$ (188.2)	2730, 1740, 1690[c]	10.06 (s, 1H), 8.10–7.30 (m, 4H) 3.53 (m, $W_{1/2}$ = 24 Hz, 1H), 2.95–1.70 (m, 6H)	368 (28.8), 183[b]
4g	108–109	$C_{22}H_{18}O_2$ (314.4)	2730, 1690, 1675[d]	9.93 (s, 1H), 8.05–7.10 (m, 14H), 4.92 (t, 7.5 Hz, 1H), 3.75 (d, 7.5 Hz, 2H)	314 (20.0), 105
4h	93–94	$C_{24}H_{20}O_2$ (340.4)	2730, 1695, 1640[d]	9.93 (s, 1H), 7.22 (AB, 16.5 Hz, 2H) 7.75–7.05 (m, 14H), 4.83 (t, 7.5 Hz, 1H), 3.45 (d, 7.5 Hz, 2H)	340 (11.5), 131
4i	105–106	$C_{22}H_{17}O_4N$ (359.4)	2740, 1700, 1530, 1350[d]	9.95 (s, 1H), 8.10–6.93 (m, 13H), 4.82 (t, 7.5 Hz, 1H), 3.65 (d, 7.5 Hz, 2H)	359 (1.4)[c], 151

a) All products gave satisfactory microanalyses (C, ± 0.33; H, ± 0.12; N, ± 0.27).

b) As 2,4-dinitrophenylhydrazone derivative. All 2,4-dinitrophenylhydrazones gave analytical and spectroscopic data in agreement with the proposed structures.

c) Liquid film.

d) Nujol.

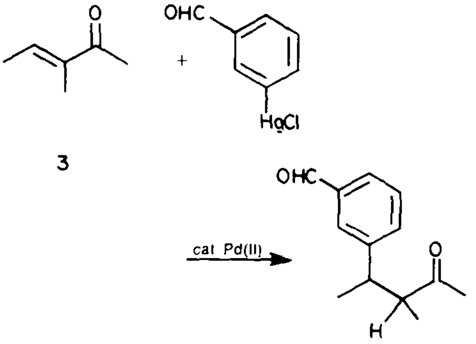
e) The molecular ion was confirmed recording the mass spectrum in chemical ionization.

For example, the competition reaction of phenylmercury chloride and 3-formylphenylmercury chloride with benzal acetone revealed that the former reacted 1.86 times faster than the latter. However, in the competition reaction of phenylmercury chloride and 4-methylphenylmercury chloride, the latter reacted 1.6 times faster than the former.

The substituents effects are not very large, but are in the direction required if this reaction follows the pathway proposed in the eqn (4) with the rate limiting step lying on the way of the σ-complex. This fact is in agreement with the known poor influence of substituents in the reactivity of monosubstituted benzene toward palladium acetate as compared with typical electrophilic aromatic substitution reactions.[16] Only in the presence of strongly electron-withdrawing groups such as $-NO_2$ and $-\overset{+}{N}H_3$, the formation of the σ-complex is so difficult to slow significantly the reaction rate under our standard conditions. However, if the deactivating effect of the nitro group is balanced by the introduction of a strongly electron-donating group, and protonation of the amino group is prevented through acetylation, the addition products can be isolated in 89% and 94% yield respectively (see entries *q* and *l*, Table 1).

It must be pointed out that in the competition reaction of phenylmercury chloride and the strongly activated 4-methoxyphenylmercury chloride with benzalacetone, phenylmercury chloride was found to react faster than 4-methoxyphenylmercury chloride. Presumably, this anomalous result may be ascribed to reversible protonation and/or coordination with an electrophilic species of the oxygen of 4-methoxyphenylmercury chloride. This equilibrium lowers the concentration of 4-methoxyphenylmercury chloride promoting the reaction of phenylmercury chloride in the competitive reaction. When no phenylmercury chloride is added, benzalacetone perturbes effectively the equilibrium between 4-methoxyphenylmercury chloride and its O-bonded species and 4-(4-methoxyphenyl), 4-phenylbutan-2-one is obtained in 96% yield after 5 hr.

The efficiency of this route to β-arylated ketones was also tested with a variety of α,β-enones selecting 3-formylphenylmercury chloride as the organomercury compound (eqn 5).



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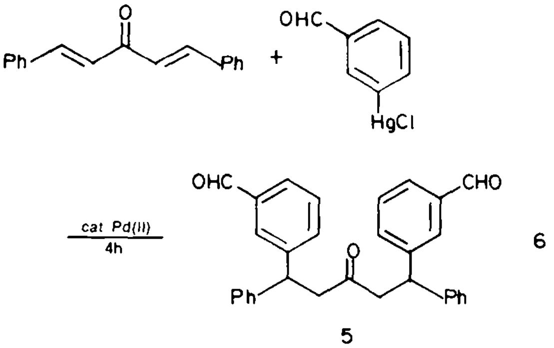
The results are summarised in the Table 3.

As expected, the results obtained with 5,5-diphenyl-penta-1,4-dien-3-one (see entry h, Table 3) are strongly dependent from the amount of the organomercury compound. Thus, treatment of 5,5-diphenyl-penta-1,4-dien-3-one with a 300 mol % excess of 3-formylphenylmercury chloride gave the di-addition product (5)[†] in 86% yield as a diastereoisomeric mixture.



The main limitation in the choise of the α,β-enonic system seems to arise from steric effects. We have recovered in almost quantitative yield the starting ketones when we tested cholest-4-en-3-one,[6] 3,5,5-trimethyl-cyclohex-2-en-1-one[6] and 2-methyl-5-i-propenyl-cyclohex-2-en-1-one (see entry *l*, Table 3). However, when substrates with no strict steric demands are used as starting material, this multi-step reaction works well and may be a valuable, mild method for the selective synthesis of β-aryl ketones from α,β-unsaturated ketones.

EXPERIMENTAL

M. ps are uncorrected and were determined with a Büchi apparatus. The starting ketones **3b**, **3e**, **3f**, **3l**, are commerically available and were used without further purfication. Ketones **3a**, **3c**, **3d**, **3g**, **3h**, **3i** were prepared according to cited refs. Organomercury compounds **1b** and **1l** were from City Chem. Corp. and from Aldrich respectively and were used as such. Compound **1e** was prepared according to the method described by Heck[8] for the mercuration of benzophenone: m.p. = 188–192°. ^{1}H NMR analysis in DMSO-d_6 or $(CD_3)_2CO$/LiCl and subsequent addition confirmed that the obtained mercurial contained at least substantial amounts of the expected product. All the other organomercury compounds were prepared according to cited refs. Tetrabutylammonium chloride and $PdCl_2$ were purchased from Fluka and used as such. The products were purified on silica gel open columns (SiO_2–60, 70–230 mesh, Merck) eluting with n-hexane/EtOAc mixtures.

^{1}H NMR and MS spectra were recorded with a Varian EM 390 spectrometer (TMS internal standard) and a Hewlett-Packard HP 5980A spectrometer equipped with a Data System 5934A.

General procedure of synthesis of β-aryl ketones. This is exemplified by the reaction of 4-chlorophenylmercury chloride and benzalacetone (entry c, Table 1). To a stirred soln of benzalacetone (0.5 g, 3.42 mmol) in CH_2Cl_2 (6.5 ml) were added a 3N HCl (4.0 ml), TBA^+Cl^- (0.095 g, 0.34 mmol), $PdCl_2$ (0.030 g, 0.17 mmol) and 4-chlorophenylmercury chloride (1.78 g, 5.13 mmol). This mixture was stirred for 12 hr at room temp, the organic layer was separated, washed with a 10% thiosulphate soln and water, dried (Na_2SO_4) and concentrated under reduced pressure. The residue was chromatographed on silica gel. Elution with a 85/15 cyclohexane/EtOAc gave 4-(4-chlorophenyl), 4-phenylbutan-2-one (0.73 g).

General procedure for competitive reactions of phenylmercury chloride with arylmercury chlorides. Phenylmercury chloride (3.42 mmol) and the arylmercury chloride (3.42 mmol) were reacted with benzalacetone (3.42 mmol) in a CH_2Cl_2 (6.5 ml)/3N HCl (4 ml) two-phase system at room temp in the presence of $PdCl_2$ (0.17 mmol) and TBA^+Cl^- (0.34 mmol). Then, aliquots were sampled at an interval of 15 min and immediately after each sampling the samples were subjected to glc analyses (OV-1, 2 m, program: from 50 to 270°, N_2). The relative reactivity of phenylmercury chloride to the arylmercury chloride was determined from the relative intensities of β-aryl ketones for the first 5 aliquots.

3-*Nitrophenylmercury chloride coupling.* A mixture of $PdCl_2$ (0.486 g, 2.74 mmol) and TBA^+Cl^- (0.76 g, 2.74 mmol) in CH_2Cl_2 (5.2 ml) and 3N HCl (3.2 ml) was stirred for 0.5 hr at room temp. Then, 3-nitrophenylmercury chloride (1.47 g, 4.11 mmol) was added and the heterogeneous system was stirred for 6 hr during which time precipitation of metallic Pd and formation of 3,3′-dinitrobiphenyl (tlc) were observed. Benzalacetone was added and stirring was continued. After 8 hr the mixture was worked-up as described. Pure products were obtained through open column chromatography on silica gel. Elution with a 85/15 cyclohexane/EtOAc mixture gave benzalacetone (0.073 g), 4-(3-nitrophenyl), 4-phenylbutan-2-one (0.56 g), and 3,3′-dinitrobiphenyl (0.115 g; m.p. 199–201°, lit.[23] m.p. = 201–202°).

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[†] δ TMS $CDCl_3$ 9.90 (s, 2H), 8.00–7.00 (m, 18H), 4.62 (bt, 2H, 7.5 Hz), 3.16 (bd, 4H, 7.5 Hz); ν_{nujol}^{max} 2730, 1680.