ortho-Functionalisation of Aryl Ketones with Alkenes; Synthesis of 3-Methylindene-2-carboxylates and 3-Substituted-2-acetylthiophenes from η^2-(*o*-Acetylaryl)tetracarbonylmanganese Compounds with Alkenes in the Presence of Palladium(II)

Louie H. P. Gommans, Lyndsay Main,* and Brian K. Nicholson*

School of Science, University of Waikato, Hamilton, New Zealand

η^2-(*o*-Acetylaryl)tetracarbonylmanganese compounds in the presence of Pd^{II} undergo new synthetically valuable coupling reactions with methyl acrylate, methyl vinyl ketone, acrylaldehyde, allyl alcohol, and acrylonitrile.

Palladium(II) reagents promote an extensive range of synthetically valuable coupling reactions of alkenes at aryl-carbon substituted by mercury[1] or halogens.[2] Some similar reactions of aryl–thallium,[3] –tin,[1,4] and –lead[1,4] compounds are also known. We report now related reactions involving replacement of manganese *ortho* to aryl ketone functions, *i.e.* at a site not accessible *via* mercuration or halogenation of ketones. For some alkenes the carbon function introduced differs from that expected from the previous results[1] for mercury and the yields generally are high.

η^2-(2-Acetyl-5-methoxyphenyl)tetracarbonylmanganese (**1**)† reacts with methyl acrylate (8 mol), $PdCl_2$ (1 mol), and LiCl (3 mol) in MeCN under reflux over 3 hours to form methyl 3-methyl-6-methoxyindene-2-carboxylate (**2**) (76%).‡ Similarly formed from the appropriate *ortho*-manganated ketones are the methyl esters of 3-methyl-4,5,6- and 3-methyl-5,6,7-trimethoxyindene-2-carboxylic acid in yields of 66% and 89%, respectively. The *ortho*-manganated derivative (**3**) of 3-acetyl-2,5-dimethylthiophene reacts similarly over 5 hours to form (**4**) (34%) but the major product in this case is the arylated acrylate ester (**5**) (56%).

Coupling products of the latter arylated alkene type are generally formed readily under nitrogen at room temperature using methanol as solvent in place of acetonitrile. Thus, η^2-(2-acetyl-3-thienyl)tetracarbonylmanganese [**6**; R = $Mn(CO)_4$] reacts instantly with methyl acrylate (5 mol) and Li_2PdCl_4 (1 mol) to form methyl (*E*)-3-(2-acetyl-3-thienyl)acrylate (**6**; R = $CH{=}CHCO_2Me$) (64%),§ while η^2-(2-acetylphenyl)tetracarbonylmanganese similarly yields methyl (*E*)-3-(2-acetylphenyl)acrylate[2] (75%).

Such arylalkene products are expected by analogy with the Pd^{II}-promoted coupling of aryl–mercury compounds[1] with methyl acrylate but with some other alkenes in methanol unexpected alternative coupling products are formed. Thus, methyl vinyl ketone with [**6**; R = $Mn(CO)_4$] and Li_2PdCl_4 gives the aryl-substituted *saturated* ketone 4-(2-acetyl-3-

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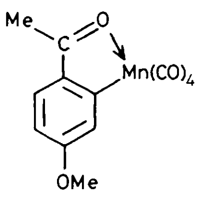
† All *ortho*-manganated ketones reported here were prepared from the parent ketones by reaction[5] with $PhCH_2Mn(CO)_5$ in refluxing heptane under N_2, and have been characterised by ^1H and ^{13}C n.m.r., i.r., and mass spectroscopy.

‡ This and other products were obtained by filtering the reaction product mixture through a short column of silica gel, removing solvent and excess of alkene under reduced pressure, and chromatographing the residue on a silica gel plate using ethyl acetate–light petroleum as eluant. To our knowledge none of the products reported here has been previously synthesised. Structures were assigned by ^1H and ^{13}C n.m.r. and mass spectroscopy, and are already confirmed in most cases by elemental analysis.

§ Much of our initial study has been concentrated on thiophene because routes to its 2,3-disubstituted derivatives are rare (ref. 6).



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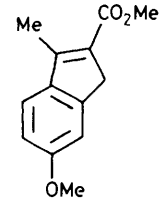

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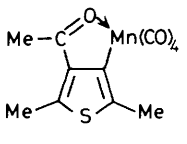

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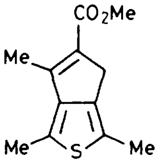

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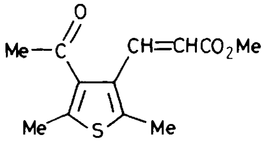

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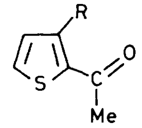

(6)

thienyl)butan-2-one [**6**; R = $(CH_2)_2COMe$] (97%) rather than the α,β-unsaturated ketone, and in similar fashion acrylaldehyde gives the saturated aldehyde 3-(2-acetyl-3-thienyl) propanal as its dimethyl acetal [**6**; R = $(CH_2)_2CH(OMe)_2$] (85%).

Another difference shows up in the case of allyl alcohol which, with the *ortho*-manganated substrate [**6**; R = $Mn(CO)_4$] in MeOH, gives 2-acetyl-3-prop-2-enylthiophene [**6**; R = $CH_2CH{=}CH_2$] (60%) by introducing the propenyl group instead of the aldehyde group expected[1] with an aryl–mercury precursor.

The most unexpected product of all is methyl 2-(2-acetyl-3-thienyl)ethanoate (**6**; R = CH_2CO_2Me) (29%) the major product from the very sluggish reaction of [**6**; R = $Mn(CO)_4$] with acrylonitrile; aryl–mercury compounds give simple arylation of this alkene.[1a]

Although mechanisms of these reactions are unknown, it is possible, as proposed[1] for the coupling of aryl–mercury compounds with alkenes, that the initial step is transmetallation to form aryl–palladium derivatives, which then initiate coupling by adding to the alkene double bond. However, the different product types of the aryl–manganese as compared with aryl–mercury compounds suggest more intimate metal involvement than that involved in simple stepwise transmetallation. Further mechanistic speculation must await the more detailed studies underway.

Given that transmetallation by Pd^{II} may be involved, it is worthy noting that direct *ortho*-palladiation is not known for ketones. Therefore, the reactions reported here may provide the simplest routes to some of the compound classes represented above. They add to the synthetic utility of *ortho*-manganated ketones previously reported.[5]

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