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Preliminary communication

Reactions of *ortho*-manganated aryl-ketones, aldehydes and amides with alkynes; a new synthesis of inden-1-ols and indenones

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Abstract

η^2-(2-Acetylphenyl)tetracarbonylmanganese reacts directly in benzene with diphenylacetylene to give 2,3-diphenyl-1-methylinden-1-ol in 97% yield, while *ortho*-manganated *N,N*-dimethylbenzamide or *p*-dimethylaminobenzaldehyde react similarly to give the corresponding indenones. Other alkynes give analogous products.

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ortho-Manganated aryl ketones, aldehydes, amides, and esters are readily prepared [1], and show promise in a variety of synthetic applications. We have reported previously on reactions of these species with halogens [2], with mercuric chloride [3], and with vinyl reagents (in the presence of Pd^{II}) [4]. We now report that reactions of *ortho*-manganated aryl carbonyl compounds with alkynes in the absence of Pd^{II} provide an efficient route to indenols and indenones.

η^2-(2-Acetylphenyl)tetracarbonylmanganese (**1**) reacts with diphenylacetylene (1 mol) in benzene under reflux for 8 h to form 2,3-diphenyl-1-methylinden-1-ol (**4a**) in 97% yield [5*]. A similar reaction in methanol also gave **4a** in 51% yield together with demetallated acetophenone (22%), while in heptane under aprotic conditions no **4a** could be isolated although all the starting material was consumed. Reaction of **1** with acetylene in benzene gave unsubstituted **4b** in 60% yield, while the bulky alkyne $Me_3SiC{\equiv}CSiMe_3$ gave only 8% of **4c** under the same conditions. With the unsymmetrical alkyne phenylacetylene 43% of **4d** results; this isomer is indicated by a two-dimensional NMR COSY experiment, the four-bond coupling of the alkenyl H(3) to aryl H(4) being clearly visible.

The reaction of the *ortho*-manganated *N,N*-dimethylbenzamide (**2**) with diphenylacetylene under the same conditions gives the indenone **5** in 56% yield. The bright red indenone **6** results similarly from *ortho*-manganated *p*-dimethylaminobenzalde-

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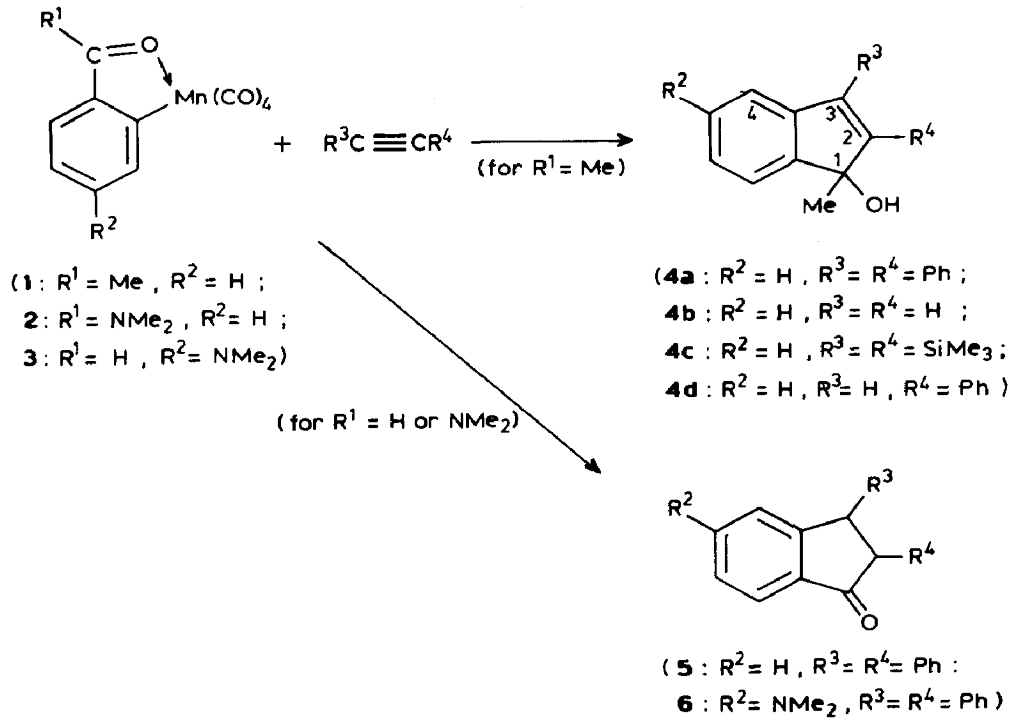
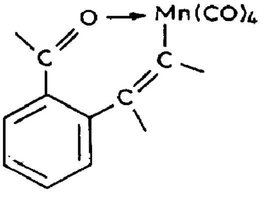
* Reference numbers with asterisks indicate notes in the list of references.



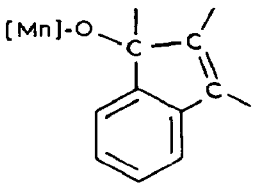
($\mathbf{1}$: R^1 = Me, R^2 = H;
$\mathbf{2}$: R^1 = NMe_2, R^2 = H;
$\mathbf{3}$: R^1 = H, R^2 = NMe_2)

($\mathbf{4a}$: R^2 = H, R^3 = R^4 = Ph;
$\mathbf{4b}$: R^2 = H, R^3 = R^4 = H;
$\mathbf{4c}$: R^2 = H, R^3 = R^4 = $SiMe_3$;
$\mathbf{4d}$: R^2 = H, R^3 = H, R^4 = Ph)

($\mathbf{5}$: R^2 = H, R^3 = R^4 = Ph:
$\mathbf{6}$: R^2 = NMe_2, R^3 = R^4 = Ph)



(**7**)



(**8**)

hyde (3) in 46% yield; for this it seems likely that the corresponding indenol is first formed, as for the ketone precursors, but is then oxidised to the indenone.

The mechanism of these reactions has yet to be established but a reasonable sequence can be proposed. Initial insertion of the alkyne into the Mn–C bond (cf. ref. 7) would give the seven-membered ring species **7**. Intramolecular addition across C=O would give **8**, which in the case of ketone or aldehyde would generate an inden-1-ol product on protonolysis by adventitious water. In the case of the amide, **8** would lead to the acyl substitution product, the indenone, a reaction that is also likely for *ortho*-manganated esters.

The full scope of the reaction is being explored with other *ortho*-manganated arenes, and with other alkynes, but the results already available suggest this new route will provide a useful general synthesis of inden-1-ols and indenones.

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5 Reactions were worked up by filtering the mixture through a short column of alumina followed by evaporation. Pure products were isolated by radial chromatography on silica plates (Chromatotron), with petroleum spirit/ CH_2Cl_2 as eluant. **5** was identified from reported properties [6], while other products were characterised by ^1H and ^{13}C NMR and mass spectroscopy, by elemental analysis, and by single crystal X-ray crystallography for **4a**.

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