Journal of Organometallic Chemistry, C12 (1989) C12–C14
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

JOM 20076PC

Preliminary communication

Conversion of arenes to cyclohexa-1,3-dienes via (*exo*-5-dialkylphosphono-*exo*-6-*R*-η^4-cyclohexadiene) manganese dicarbonylnitrosyl compounds

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(Received March 27th, 1989)

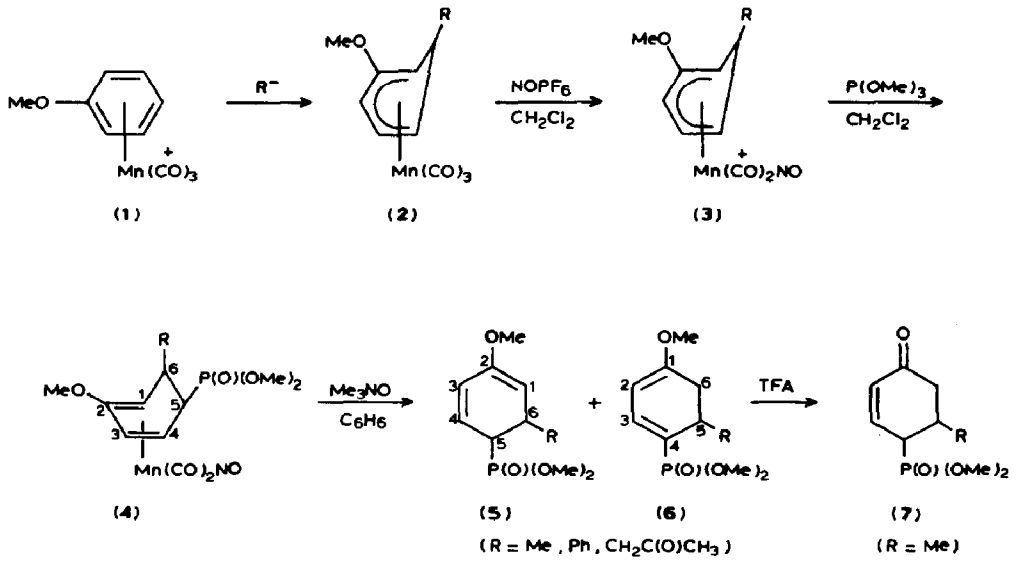
Abstract

(*exo*-5-Dialkylphosphono-*exo*-6-*R*-η^4-cyclohexadiene)$Mn(CO)_2NO$ compounds were prepared by the reaction of (*exo*-6-*R*-η^5-cyclohexadienyl)$Mn(CO)_2NO^+$ with an excess of $P(OMe)_3$. When (*exo*-5-dialkylphosphono-*exo*-6-η^4-*R*-cyclohexadiene) $Mn(CO)_2NO$ compounds are refluxed with Me_3NO in benzene, two kinds of cyclohexadiene compounds are formed depending upon the R group.

The best known reactions of coordinated cyclic π-hydrocarbons involve the addition of a single nucleophile to a coordinated arene or cyclohexadienyl ring to give mono-functionalized products [1]. The addition of two nucleophiles to coordinated rings would be a synthetically useful reaction, particularly if the two nucleophiles could be varied independently. To date, however, few arene complexes have been shown to undergo such double additions [2]. Herein we report the synthesis and demetallation of (*exo*-5-dialkylphosphono-*exo*-6-*R*-η^4-cyclohexadiene)$Mn(CO)_2NO$ (**4**); it is expected that the complexes will provide a general route to 4,5-disubstituted cyclohex-2-enones.

The formation of compound **4** is depicted in Scheme I. The details of the chemistry of compounds **2** and **3** have been published [2]. IR studies show that at room temperature $P(OMe)_3$ reacts with $[(C_6H_6Me)Mn(CO)_2NO]PF_6$ (**3**) to give a mixture of products derived from CO substitution and from addition to the cyclohexadienyl ring. However, treatment of compound **3** in CH_2Cl_2 with an excess of $P(OMe)_3$ ($-20\,^\circ C$, N_2) gives exclusively compound **4** in a reasonable yield after filtration, solvent removal, column chromatography on a neutral alumina column eluting with tetrahydrofuran *. Compound **4** is apparently derived from the spontaneous Michaelis-Arbuzov reaction of the $P(OMe)_3$ adduct [3]. Thus, this reaction provides an easy and viable synthetic route to the phosphonate complexes **4** which are analogues of the (5-dialkylphosphono-cyclohexadiene)$Fe(CO)_3$ [4]. The phos-

0022-328X/89/$03.50



Scheme 1

phonate complexes **4** are moderately stable at room temperature. Many carbon donor nucleophiles, but not $NaCH(CO_2Me)_2$, react with compound **3** by what appears to be a single electron-transfer pathway that ultimately gives a variety of products, including (cyclohexadienyl)$Mn(CO)_3$ [5]. Compound **4** provides one alternative to achieving the double functionalization. If the compound **4** is deprotonated by base, a stabilized-phosphoryl anion is produced. Although phosphonate carbanions are usually used to form carbon bonds by the Horner–Emmons reaction [6], the anions are unsuitable for use with compound **4**.

Compound **4** was demetallated to give a cyclohexadiene compound. The $Mn(CO)_2NO$ group was readily removed by reaction of compound **4** with Me_3NO in benzene under reflux [7]. After demetallation, compound **5** or **6** was isolated as the major product depending upon the R group *. When R = Ph and $CH_2C(O)CH_3$ compound **5** was isolated intact as the major product. When R = Me **6** was obtained as the major product as the result of double-bond migration.

Substituted cyclohex-2-enones are important in natural product synthesis owing to their widespread occurrence in nature. In general, positions 4 and 5 (especially 5)

* *Compound* **4** (R = Ph): IR ν(CO) 2042, 1984cm^{-1} ν(NO) 1742 cm^{-1}, ^{13}C NMR($CDCl_3$) C^1 52.76, C^3 68.94, C^4 62.57, OMe 55.01, $P(OMe)_2$ 48.03, 51.74, Ph 127.06, 127.93, 129.81, 129.83, CO 220.92, 224.50 ppm. EI-MS, *m/z*, 379($M^+ - 2CO - NO$), 294($M^+ - 2CO - NO - Mn$).
Compound **4** (R = Me): IR ν(CO) 2038, 1979cm^{-1} ν(NO) 1739cm^{-1}. ^{13}C NMR($CDCl_3$) C^1 54.76, C^3 68.9, C^4 65.75, C^5 38.93, OMe 54.70, $P(OMe)_2$ 52.14, Me 22.32, CO 221.15, 224.22 ppm. EI-MS, *m/z*, 345 ($M^+ - CO$), 317 ($M^+ - 2CO$), 287 ($M^+ - 2CO - NO$), 232 ($M^+ - 2CO - NO - Mn$).
Compound **4** (R = $CH_2C(O)CH_3$): IR ν(CO) 2041, 1983, 1715cm^{-1} ν(NO) 1740cm^{-1}. ^{13}C NMR ($CDCl_3$) C^1 48.98, C^3 67.47, C^4 62.52, OMe (54.37), $P(OMe)_2$ 51.82, CH_2 35.50, C(O) 206.0, CH_3 29.85, CO 220.40, 223.50 ppm. EI-MS, *m/z*, 359 ($M^+ - 2CO$), 271 ($M^+ - 2CO - NO - CHC(O)CH_3$), 217 ($M^+ - 2CO - NO - CH_2C(O)CH_3 - Mn$).

are difficult to functionalize by standard procedures. Compounds **5** and **6** show promise as good intermediates in the route to 4,5-disubstituted cyclohex-2-enones. When compounds **5** and **6** were acid-hydrolyzed in trifluoroacetic acid (TFA) at room temperature, the 4,5-disubstituted cyclohex-2-enone (**7**), was obtained as one of the major compounds *. The reaction conditions have not yet been optimized. The elimination of phosphonate occurs rapidly under mild conditions for the phosphonate compound **7**. The ultimate product that is obtained after the Horner-Emmons reaction are 4,5-disubstituted cyclohex-2-enones.

We have shown that the arenes can be converted into cyclohexadienes via (*exo*-5-dialkylphosphono-*exo*-6-*R*-cyclohexadiene)$Mn(CO)_2NO$. A study of the acid-hydrolysis and the Horner–Emmons reaction is in progress and future work will be directed at exploring the range of the substituted anisole and related complexes available using $P(OMe)_3$.

Acknowledgement. This work was supported by a Dae Woo Research Fund for Natural Sciences Grant to the Seoul National University.

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* *Compound* **5** (R = Ph) ^1H NMR ($CDCl_3$) H^1 3.66, H^3 5.14(d, 6HZ), H^4 3.44(m), H^5 2.28(d, $J(P-H) = 18$ Hz), H^6 2.97(m), OMe 3.52(s), $P(OMe)_2$ 3.17(d, 10.5HZ), 3.54(d, 10.5HZ), Ph 7.07–7.32 ppm. ^{13}C NMR ($CDCl_3$) C^1 129.0, C^2 129.00, C^3 162.35, C^4 141.66, C^5 35.59, C^6 38.56, OMe 54.92, $P(OMe)_2$ 51.70, Ph 126–129 ppm. EI-MS, m/z, 294(M^+), 217($M^+ - Ph$), 185($M^+ - P(O)(OMe)_2$).
Compound **6** (R = Me): ^1H NMR ($CDCl_3$) H^2 5.05(d, 6 Hz), H^3 6.85 (dd,19.6 Hz) H^5 2.73(m), H^{6exo} 2.19(m), H^{6endo} 2.73(m), Me 1.06 (d,6.7 Hz), OMe 3.65(s), $P(OMe)_2$ 3.74(d,14.7 Hz) ppm. ^{13}C NMR ($CDCl_3$) C^1 150.87(d,2.73 Hz), C^2 139.79(d,10.3 Hz), C^3 97.65 (d,14 Hz), C^4 129.46(d,154 Hz), C^5 29.47(d,17.2 Hz), C^6 31.45 (d,12 Hz), OMe 53.22, $P(OMe)_2$ 51.88(d,9.5 Hz), Me 21.96 ppm. EI-MS, m/z, 232(M^+), 217($M^+ - Me$), 123($M^+ - P(O)(OMe)_2$).
Compound **5** (R = $CH_2C(O)CH_3$) ^1H NMR ($CDCl_3$) H^1 4.72(m), H^3 5.24 H^4 2.88(m), H^5 3.19(d,13 Hz), H^6 2.88(m), CH_2 2.16(d,6 Hz), $-C(O)CH_3$ 2.06(s), OMe 3.58(s), $P(OMe)_2$ 3.76(d,11.8 Hz) ppm. EI-MS, m/z, 274(M^+), 217($M^+ - CH_2C(O)CH_3$), 165($M^+ - P(O)(OMe)_2$).
Compound **7** (R = Me): IR ν(CO) 1680cm^{-1}, ^1H NMR ($CDCl_3$) $H^{2,3}$ 6.91, 6.20, $H^{4,5,6}$ 3.0–2.0, CH_3 1.20(d, 6 Hz), $P(OMe)_2$ 3.77(d,11 Hz).