(1973).
10. A F. Corsmit, H. E. Hoefdraad and G. Blasse, *J. Inorg. Nucl. Chem.*, **34**, 3401 (1972).
11. N. Ramadas, J. Gopalakrishanan and M.V.C. Sastri, *J. Inorg. Nucl. Chem.*, **40**, 1453 (1978).
12. J. T. Last, *Phys. Rev.*, **105**, 1740 (1957).
13. E. W. Kaleveld, D. J. Bruntinck, J. P. Dotman and G. Blasse, *J. Inorg. Nucl. Chem.*, **35**, 3928 (1973).
14. P. W. Selwood, "Magnetochemistry" 2nd Ed., Chap. 5, Interscience, New York (1956).

Nucleophilic Addition of Phosphate to Coordinated (Arene)manganes Tricarbonyl Cations

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$[(Benzene)Mn(CO)_3]^+$ reacts with $NaP(O)(OR)_2$ (R = Me, Et, Ph) to give the phosphonate compound 1. Compound 1 reacts with R'Li (R = Me, Ph, ^{n}Bu, ^{t}Bu) to yield the isomerized compound 2 and the alkylated compound 3. $[(Toluene)Mn(CO)_3]^+$ reacts with $NaP(O)(OMe)_2$ to give the phosphonate complexes 1-A and 1-B. Treatment of 1-A with ^{t}BuLi in THF affords complexes 3-A and 3-B with the later major. With 1-B only the complex 3-C is formed. $[(Anisole)Mn(CO)_3]^+$ reacts with $NaP(O)(OMe)_2$ to give the phosphate complex 1-C, which on treatment with ^{t}BuLi and then H_2O yields compound 3-D. After demetallation of compound 3-D, meta-tertbutyl-anisole is obtained in a reasonable yield.

Introduction

Activation of aromatic compounds toward nucleophilic attack represents an attractive method for the synthesis of polyfunctionalized derivatives. The use of arene chromium complex is now fairly well established[1], but these compounds undergo carbon-carbon bond formation only with very reactive nucleophiles[2], thereby limiting the degree to which deactivating substituents (-OR, $-NR_2$, etc.) may be attached to the ring.

(Arene) mangananese tricarbonyl cations have been and continue to be the topics of extensive investigation. This is due in part to the rich chemistry associated with nucleophilic attack at the aromatic ring leading to the formation of cyclohexadienyl manganese tricarbonyl compounds[3].

The reaction of aldehydes and ketones with phosphonium salts to produce olefins was developed in 1953 by Wittig and Geissler[4]. Since then the Wittig reaction has been widely used as a convenient high-yield synthesis of olefins, especially in the field of natural products[5]. Recently, much interest has been centered on the use of organometallic species in the synthesis of organic compounds not readily available otherwise. The use of the Wittig reaction in organometallic chemistry has been used successfully in preparing new derivatives of (benzene)dicarbonyl chromium[6], ferrocene[7], and six- and seven-membered ring dienyl complexes of $Fe(CO)_3$[8].

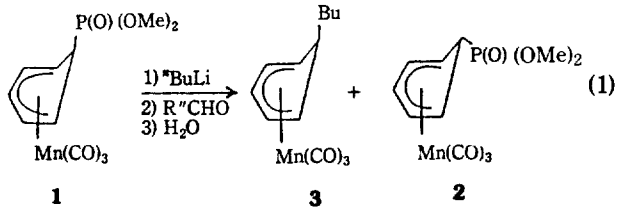
$[(Arene)Mn(CO)_3]^+$ has a low electrophilicity and cannot react with triphenylphosphine to yield a phosphonium salt. A very useful alternative method for the preparation of resonance stabilized phosphoranes for use in the Witting reaction proceeds from phosphonate esters[9]. So we tried to make organometallic phosphonate compounds.

We recently reported on the use of phosphate as a nucleophile to the $[(C_6H_6)Mn(CO)_3]^+$ cation[10]. To our knowledge there are no reports on the use of phosphate as a nucleophile to the π-coordinated ring. Our previous communication revealed that $[exo\text{-}(RO)_2P(O)\text{-}\eta^5\text{-}C_6H_6]Mn(CO)_3$ which on treatment with ^{n}BuLi and H_2O underwent stereospecific rearrangement to $[endo\text{-}(RO)_2P(O)\text{-}\eta^5\text{-}C_6H_6]Mn(CO)_3$. In this report we describe the reaction of [exo-(RO)$_2$P(O)-n^5-cyclohexadienyl]$Mn(CO)_3$ with R'Li (R' = Me, ^{n}Bu, ^{t}Bu, Ph) and related reactions.

Results and Discussion

(Exo-phosphonate-η^5-cyclohexadienyl) manganese tricarbonyl compounds were synthesized as previously described[10]. The compounds are soluble in organic solvent and stable in the air. The formation of the cyclohexadienyl compounds can be followed by checking the CO stretching bands and the reaction went completely within 30 min.

To do the Horner-Emmons reaction with compound 1, compound 1 was treated with ^{n}BuLi and aldehyde. After work-up, two compounds were obtained, one was butylated compound and the other isomerized phosphonate compound (eq. 1).



(1)

When the above reaction was carried without using aldehyde, the same reaction products were obtained. After deprotonation by ^{n}BuLi, the carbon which has a negative

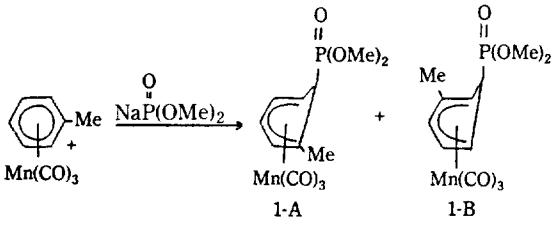
Table 1. Product Distribution of Reaction between Compound 1 and Organolithiums

Organolithium	compound 2	compound 3	Total yield(%)
MeLi	88	≃0	88
PhLi	85	9	94
^{n}BuLi	65	14	79
^{t}BuLi	40	42	82

charge attacks the carbonyl carbon of an aldehyde. To proceed further the reaction, there must be a structural rearrangement to form a bond between the phosphorus and the carobnyl oxygen. For the (exo-phosphate-cyclohexadienyl)Mn $(CO)_3$, due to the steric crowdness it would be very difficult for the phosphorus and the oxygen of the carbonyl group of aldehyde to be on the same plane. The aldehyde would be regenerated and the carbanion would pick up a proton from water molecules to give an endo-isomerized phosphate compound. When the deprotonated species quenched with D_2O, the deuterium was not observed on the alkylated compound. This meant the alkylation would proceed with a different intermediate from the deprotonated species. According to the experimental observations, after removal of phosphate group as lithium dialkylphosphate, alkyl anion would attack the cationic intermediate on the exo fashion to yield alkylated product.

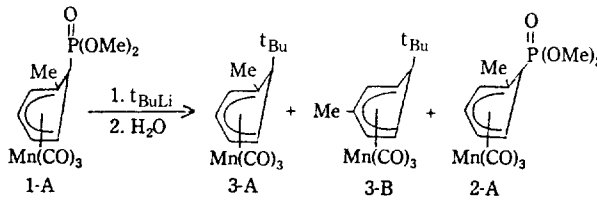
To verify the dependence of base on the above reaction, several other lithium carbanions are used. The results are summarized in Table 1. As the steric hindrance increased, the yield of endo-phosphate compound was decreased. On the other hand, as the basicity increased, the yield of compound 3 increased. It follows the order of the steric crowdness. These results also prove that there are two pathways, each competitive.

While pursuing the mechanism of alkylation, we find an unusual product distribution of the reaction between (exo-dialkylphosphonate-η^5-cyclohexadienyl)$Mn(CO)_3$ and ^{t}BuLi. The phosphonate complexes 1-A and 1-B were synthesized in the ratio 4/3 (eq 2).



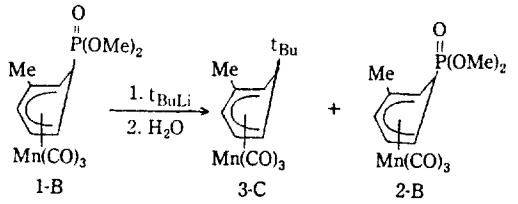
(2)

Chromatography of mixtures of 1-A and 1-B on silica gel using ether as eluant did effect isomer separation. When 1-A was treated with ^{t}BuLi and then with H_2O, two butylated complexes 3-A and 3-B in the ratio 1/3 (yield 68%) were isolated along with a phosphonate complex, 2-A (yield 23%) (eq 3).



(3)

When 1-B was treated with ^{t}BuLi and then with H_2O, only one butylated complex, 3-C (57%) was isolated along with a phosphonate complex, 2-B (10%) (eq 4).



(4)

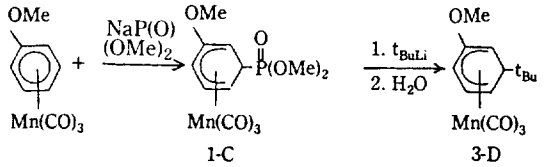
The distribution of products in the above reaction seemed to be very peculiar[3].

Several years ago Hoffmann suggested[11] that activation of coordinated olefins to nucleophilic addition is not primarily due to overall charge (though this is clearly a contributing factor), but rather to activation related to partial displacement of the metal ligand system towards one terminal in the transition state. There would be a change from π to σ-bonding during the addition process. If we adopt Hoffman's suggestion, we could envisage intermediates which would have localized π and σ-bonds in the transition state.

For complex 1-A, there would be two ways which produce compound 3-A and 3-B. However, due to steric hindrance of the methyl group, the compound 3-B would be dominant as experimentally observed. For complex 1-B, there would be two ways, one produces compound 3-C and the other couldn't form the quaternary carbon center due to steric congestion as experimentally unobserved.

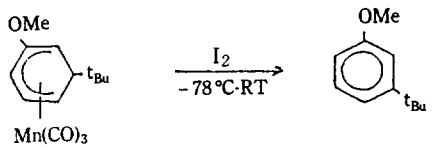
In view of the marked product distribution which have been observed, to the best of our knowledge such product distribution has not been described for other arene or cyclohexadienyl complexes of transition metals.

While pursuing the application of phosphonate-cyclohexadienyl compounds, we found facile meta-tert-butylation of anisole via (dimethylphosphonate-η^5-cyclohexadienyl) manganese tricarbonyl. (6-Dimethylphosphonate-η^5-2-methoxycyclohexadienyl) manganese tricarbonyl compound 1-C, was synthesized. When compound 1-C was treated with ^{t}BuLi followed by quenching with water, (exo-t-butyl-η^5-2-methoxycyclohexadienyl) manganese tricarbonyl, compound 3-D, was obtained with a yield of 73% (eq 5).



(5)

Decomplexation of compound 3-D by using Me_3NO gave fair yield of meta-t-butyl-anisole and cyclohexadiene compounds. The ^1H NMR spectrum, showing unresolved multiplicity of the diene proton resonances, indicated the presence of two diastereoisomers. However, it was not possible on this basis to determine unambiguously which isomer was major. The reaction time did not change the distribution of products and this meant two competitive reactions were going on at the same time. However, when compound 3-D in THF was treated with I_2 at -78 °C, then allowed to warm to room temperature and stirred for 16 hrs, only meta-t-butyl-anisole was isolated with a yield of 77% (eq 6).



(6)

3-D

Uncomplexed arenes have been alkylated with alkyllithium compounds but under much more forcing conditions[12]. For example, a 15% yield of tert-butylbenzene was obtained by heating 1:1 mixture of benzene and ^{t}BuLi in decalin at 165° for 20 hr.

When (ethylbenzene) chromium tricarbonyl was treated with ^{t}BuLi followed by decomplexation of the arenes by oxidation, meta- (32%) and para-ethyl-tert-butylbenzene (9%) was obtained[13]. When (benzene) chromium tricarbonyl was treated with ^{t}BuLi followed by reaction with iodine, tert-butylbenzene was detected by GLC with a yield of 68%[14].

The (arene) manganese tricarbonyl cations are much more reactive than the corresponding (arene) chromium tricarbonyl. However, the reaction of (arene) $Mn(CO)_3^+$ with PhLi or MeLi gave only very low yields of (cyclohexadienyl) $Mn(CO)_3$[15] or led to extensive decomposition with no dectable formation of alkylated manganese compounds[16]. However, the above results show that the reaction between (phosphonate-η^5-cyclohexadienyl) $Mn(CO)_3^+$ and ^{t}BuLi would be useful to introduce the tert-butyl group.

Future work will be directed at exploring the range of substituted anisole and related complexes available using phosphate nucleophiles and the types of nucleophiles which would react with the phosphonate-substituted complexes.

Experimental Section

All manipulations were carried out under an inert atmosphere, using Schlenk techniques. Tetrahydrofuran was dried with sodium/benzophenone and distilled before use. $HP(O)(OR)_2$ (R = Me, Et, and Ph) (Aldrich) were used without further purification. All ^{1}H(200 MHz), ^{2}H(50.7 MHz), and ^{13}C(50 MHz) were obtained on a Bruker wp 200 spectrometer. ^{1}H, ^{2}H, and ^{13}C spectra were referenced to tetramethylsilane. Infrared spectra were recorded on Analect Instrument FX-6160 FTIR spectrophotometer. Microanalyses were performed by KAIST.

A. Synthesis of [exo-$(RO)_2P(O)$-η^5-C_6H_6]$Mn(CO)_3$ (R = Me, Et, Ph), 1. A typical procedure. Sodium dialkylphosphite solution was prepared by the addition of dialkylphosphite (3.1 mmole) to a suspension of sodium hydride (4.2 mmole) in THF (30 m*l*) under an inert atmosphere at room temperature. After the completion of the reaction, the resulting sodium dialkylphosphate solution was added to a slurry of $[(C_6H_6)Mn(CO)_3]PF_6$ (1.4 mmole) in THF (30 m*l*) via a gas-tight syringe under nitrogen at room temperature. After 30 min, water was added to destroy excess sodium dialkyl-phosphate and the neutral compound was extracted with diethyl ether. The ether extract was dried over anhydrous $MgSO_4$ and the solvent was evaporated. The residue was recrystallized from hexane to give yellow crystalline solids. The analytical data for 1 (R = Me and Et)) were published[10]. 1(R = Ph): IR(ν(CO)) 2019, 1945 cm^{-1}; ^{1}H NMR($CDCl_3$) δ 3.08(t), 3.62(m), 5.02(t), 6.00(t), 7.0-7.2(Ph) ppm. Anal. Found: C, 56.0; H, 3.58. $C_{21}H_{16}MnPO_6$ Calcd.: C, 56.0; H, 3.40%.

B. Reaction of [exo-$(MeO)_2P(O)$-η^5-C_6H_6]$Mn(CO)_3$ with organolithium Compounds. To a solution of 1(R = Me) in THF was added about 2 mole excess of organolithium compound under an inert atmosphere at room temperature. Then water was added to destroy the excess of organolithium compound and the neutral compound was extracted with diethyl ether. The ether extract was dried over anhydrous $MgSO_4$ and the solvent was evaporated. The residue was chromatographed on silica gel. Elution with hexanes gave the alkylated product[3], and elution with ethyl ether, after elution with chloroform, gave endo-isomerized product, compound 2(R = Me). 2(R = Me): IR(ν(CO)) 2007, 1928 cm^{-1}; ^{1}H NMR($CDCl_3$): δ 2.58(d, J = 17.7 Hz), 2.83(t, J = 10.4 Hz), 3.84(d, OMe, J = 10.7 Hz), 4.96(q), 5.82(t, J = 5 Hz) ppm. M.P. 72.0-72.4 °C. 2(R = Et): ^{13}C NMR($CDCl_3$) δ 16.69 (Me), 47.06(OCH_2), 62.39(ring carbon), 80.25(ring carbon), 97.95(ring carbon), 220.25(CO) ppm. 3(R′ = ^{n}Bu): ^{1}H NMR ($CDCl_3$) δ 0.66-1.49(m, ^{n}Bu), 2.44(m), 3.21(t, J = 5.9 Hz), 4.76 (t, J = 5.8 Hz), 5.76(t, J = 5.4 Hz) ppm. M/S, m/e 55.91, 133, 190, 217, 246, 274. 3(R′ = ^{t}Bu): ^{1}H NMR($CDCl_3$) δ 0.60(s), 2.44(t), 3.24(t), 4.90(t), 5.68(t), Anal. Found: C, 56.5; H, 5.40. $C_{13}H_{15}MnO_3$ Calcd.: C, 56.9; H, 5.51%. 3(R′ = Ph): IR((CO)) 2020, 1940 cm^{-1}; ^{1}H NMR(d_6-acetone) δ 3.66(t, J = 6.1 Hz), 3.86(t, J = 6.0 Hz), 5.18(t, J = 5.9 Hz), 5.98(t, J = 5.3 Hz) ppm. M.P. 120 °C. Anal. Found: C, 61.4; H, 3.87. $C_{15}H_{11}MnO_3$. Calcd: C, 61.2; H, 3.77%.

C. Reaction of compound 1(R = Et) with ^{n}BuLi and D_2O. The same procedure as employed with B was used yielding 2(R = Et) and 3(R′ = ^{n}Bu). 2H{^{1}H} of compound 2(R = Et)(C_6D_6) δ 2.43 ppm.

D. Preparation of compound 1-A and 1-B. A little excess of $NaP(O)(OMe)_2$ was added to a slurry of $[(C_6H_5CH_3)Mn(CO)_3]PF_6$ in THF via a gas-tight syringe under nitrogen at room temperature. After 30 min, water was added to destroy the excess of $NaP(O)(OMe)_2$ and the neutral compound was extracted with ethyl ether. After evaporation of the solvent, the residue was chromatographed on silica gel. Elution with ethylether gave the compound 1-A as the major component and with acetone gave the compound 1-B as the major. The separation was continued until pure compound 1-A and 1-B were obtained in the ratio 4/3. 1-A: ^{1}H NMR ($CDCl_3$): δ 5.83(t, H(3), $J_{3,2}$ 5 Hz), 4.93(t, H(4), $J_{4,5}$ 5Hz), 4.75 (d, H(2), $J_{2,3}$ = 5 Hz), 3.27(dd, H(6), $J_{5,6}$ 5Hz, $J_{6,p}$ 13 Hz), 3.66 (d, OMe, $J_{p,OMe}$ 10.6 Hz), 1.71(s, CH_3) ppm. IR((CO)): 2011, 1916 cm^{-1}. Anal. Found: C, 42.1; H, 4.14. $C_{12}H_{14}MnO_6P$ Calcd.: C, 42.2; H, 4.43%. 1-B: ^{1}H NMR($CDCl_3$): δ 5.92(d, H(3), $J_{3,4}$ 5Hz), 4.97(t, H(4)), 3.3(m, H(6)), 2.9(m, H(1,5)), 3.65(d, J(P, OMe) 10.2 Hz), 1.90(s, CH_3).

E. Reaction between compound 1-A and ^{t}BuLi. The same procedure as employed with D was used yielding compound 3-A and 3-B in the ratio of 1/3 (yield 68%) and an isomerized product 2-A (yield 23%). 3-A: ^{1}H NMR($CDCl_3$) δ 5.48(t, H(3), $J_{3,4}$ 5 Hz), 4.8(m, H(4)), 4.65(d, H(2), $J_{2,3}$ 5 Hz), 3.0(m, H(5)), 2.27(H(6)), 1.74(s, CH_3), 0.64(s, ^{t}Bu) ppm. 3-B: ^{1}H NMR($CDCl_3$) δ 4.88(d, H(2,4), $J_{4,5}$ 7 Hz), 3.09(t, H(1.5), $J_{5,6}$ 7Hz), 2.37(t, H(6)), 2.39(s, CH_3), 0.55(s, ^{t}Bu) ppm.

F. Reaction between compound 1-B and ^{t}BuLi. The same procedure as employed with D was used yielding compound 3-C (yield 57%) and 2-B(10%). 3-C: ^{1}H NMR($CDCl_3$) δ 5.52(d, H(3), $J_{3,4}$ 5 Hz), 4.82(t, H(4)), 3.23(t, H(5)), 3.14(d, H(1), $J_{1,6}$ 5 Hz), 2.42(t, H(6)), 1.85(s, CH_3), 0.54(s, ^{t}Bu) ppm. IR(ν(CO)) 2015, 1934 cm^{-1}. Anal. Found: C, 57.9; H, 5.96. $C_{14}H_{17}MnO_3$ Calcd.; C, 58.1; H, 6.27%.

G. Preparation of compound 1-C. The same procedure as employed with A was used yielding compound 1-C. 1-C: IR(ν(CO)) 2017, 1921 cm^{-1}, ^1H NMR($CDCl_3$) δ 2.90(dd, 1H), 3.50(m, 2H), 3.65(d, -OMe, J(p, OMe) 10 Hz), 4.06(s, -OMe), 4.99(t, 1H), 5.90(d, 1H).

H. Reaction between compound 1-C and ^{t}BuLi. The same procedure as employed with was used yielding compound 3-D (73%). 3-D: IR(ν(CO)) 2013, 1921 cm^{-1}, ^1H NMR ($CDCl_3$) δ 0.58(δ, ^{t}Bu), 2.48(t, 1H), 3.00(d, 1H), 3.20(m, 1H), 3.47(s, OMe), 4.90(t, 1H), 5.53(d, 1H).

I. Demetallation of compound 3-D. I-a). A little excess of Me_3NO was added to compound 3-D(0.85 mmole) in benzene (30 m*l*). The reaction mixture was refluxed for 4 hrs. After cooled to room temperature, any solids were filtered off. After removal of the solvent, NMR spectrum was taken.

I-b). A solution of iodine (7-10 mg-atoms) in THF (10 m*l*) was added rapidly via syringing to the solution of compound 3-D at -78 °C. The resulting mixture was warmed to room temperature and stirred for 16 hrs. After evaporation of the solvent, extracted with ethylether. After chromatographed on silica gel, the meta-tert-butyl-anisole was obtained in 77%. The ^1H NMR spectrum of the meta-tert-butyl-anisole was δ1.27(s, ^{t}Bu), 3.70(s. OMe), 6.5-7.1 (Ph).

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References

1. M. F. Semmelhack, *Tetrahedron*, **37**, 3959 (1981).
2. J. P. Collman and L. S. Hegedus, "Principles and Applications of Organotransition Metal Chemistry", University Science Book, Mill Valley, Calif., 1980, p658.
3. P. J. C. Walker and R. J. Mawby, *Inorg. Chim. Acta*, **7**, 621 (1973); P. L. Pauson and J. A. Segal, *J. Chem. Soc., Dalton Trans.*, 1683 (1975); S. G. Davies, M. L. H. Green, and D. M. P. Mingos, *Tetrahedron*, **34**, 3047 (1978); LA. P. Kane-Maguire, E. D. Honig, and D. A. Sweigart, *Chem. Rev.*, **84**, 525 (1984); G. Winkhaus, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 3807 (1961); D. Jones, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4458 (1962); P. J. C. Walker and R. J. Mawby, *J. Chem. Soc.*, Dalton Trans., 622 (1973); Y. K. Chung, P. G. Williard, and D. A. Sweigart, Organometallics, **1**, 1053 (1982); D. J. Evans, L. A. P. Kane-Maguire, and D. A. Sweigart, *J. Organomet. Chem.*, **215**, 127 (1981); A. Mawby, P. J. C. Walker, and R. J. Mawby, *J. Organomet. Chem.*, **55**, C39 (1973).
4. G. Wittig and G. Geissler, *Ann. Chim.*, **44**, 580 (1953).
5. A. W. Johnson, 'Ylid chemistry', Academic Press, New York, 1966, Ch. 4.
6. G. Drefahl, H.H. Horhold, and K. Kunhe, *Chem. Ber.*, **98**, 1826 (1965).
7. P. L. Pauson and W. E. Waters, *J. Chem. Soc.*, 2990 (1963).
8. P. Hackett, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc.*, Dalton Trans., 1247 (1982).
9. L. Horner, H. Hoffmann, and H. G. Wippel, *Chem. Ber.*, **91**, 61 (1958); W. S. Wadsworth and W. D. Emmons, *J. Am. Chem. Soc.*, **83**, 1733 (1961); W. S. Wadsworth, Jr., 'Synthetic Applications of Phosphoryl-Stabilized Anions', Organic Reactions, v25, Wiley, 1977, Ch. 2.
10. H. K. Bae, I. N. Jung, and Y. K. Chung, *J. Organomet. Chem.*, **317**, C1 (1986).
11. O. Einstein and R. Hoffmann, *J. Am. Chem. Soc.*, **102**, 6148 (1980).
12. M. S. Carpenter, W. M. Easter, and T. F. Wood, *J. Org. Chem.*, **16**, 586 (1951).
13. J. A. Dixon and D. H. Fishman, *J. Am. Chem. Soc.*, **85**, 1356 (1963).
14. M. F. Semmelhack, H. T. Hall, Jr., R. Farina, M. Yoshifuji, G. Clark, T. Bargar, K. Hirotsu, and J. Clardy, *J. Am. Chem. Soc.*, **101**, 3535 (1979).
15. P. L. Pauson and Segal, *J. Chem. Soc., Dalton Trans*, 1683 (1975).
16. A. J. Pearson and I. C. Richards, *J. Organomet. Chem.*, **258**, C41 (1983).

Clean Reduction of α,β-Unsaturated Carboxylic Acid Derivatives to the Saturated Derivatives by Potassium Triphenylborohydride in the Presence of Phenol

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α,β-Unsaturated carboxylic acid derivatives such as esters, amides, and nitriles are readily reduced to the corresponding saturated derivatives by potassium triphenylborohydride, KPh_3BH, in the presence of phenol, a quenching agent, in excellent yields.

Introduction

Aside from the catalytic hydrogenation,[1] there have been reported several reducing systems which could be effectively used for the reduction of α,β-unsaturated acid derivatives to the corresponding saturated ones. These are Mg/MeOH[1], Lis-Bu_3BH (L-Selectride)/t-BuOH[2], copper(I) hydride complex[3], DIBAH with MeCu[4] and silicone hydrides with Pd[5] or