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Preparation of acetylstyrene- and benzoylstyrene-tricarbonylchromium, and of 1-acetyl- and 1-benzoyl-2-ferrocenylethylene

Jiling Huang and Yao-Zeng Huang *
The Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Academia Sinica, 345 Lingling Lu, Shanghai 200032 (People's Republic of China)

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Abstract

The title compounds were synthesized by the reaction of a variety of arsonium salts with benzaldehyde tricarbonyl chromium or monoformyl ferrocene in the presence of K_2CO_3 at room temperature under phase transfer conditions, giving good yields.

Introduction

The Wittig and Horner–Emmons reactions have attained great importance as olefination methods [1]. Along this line of investigations Huang has developed an arsonium salt method for the synthesis of polyenal, polyenone, polyenester, and polyenamide and some related natural products by using the weak base K_2CO_3 in mixed solvent at room temperature under solid–liquid phase transfer conditions [2].

Although some work has been done concerning the application of organophosphorane in the synthesis of organometallic compounds [3–5], use of organoarsorane in this field has not yet, to our knowledge, been described.

In this paper we wish to describe the synthesis of organometallic unsaturated ketones by means of our arsonium salt method.

Results and discussion

Recently, some scientists have pointed out that certain organometallic compounds may have potential as synthetic materials. A few papers dealing with nonlinear optical properties of transition-metal-organic compounds have appeared in the literature [6] and it has been found that compounds like arenetricarbonylchromium complexes show larger second harmonic generation efficiencies than ADP (ammonium dihydrogen phosphate) [7,8]. We are therefore interested in synthesizing a series of new organometallic compounds which are of conjugated, charge transfer, and acentric crystal structure [9].

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Table 1

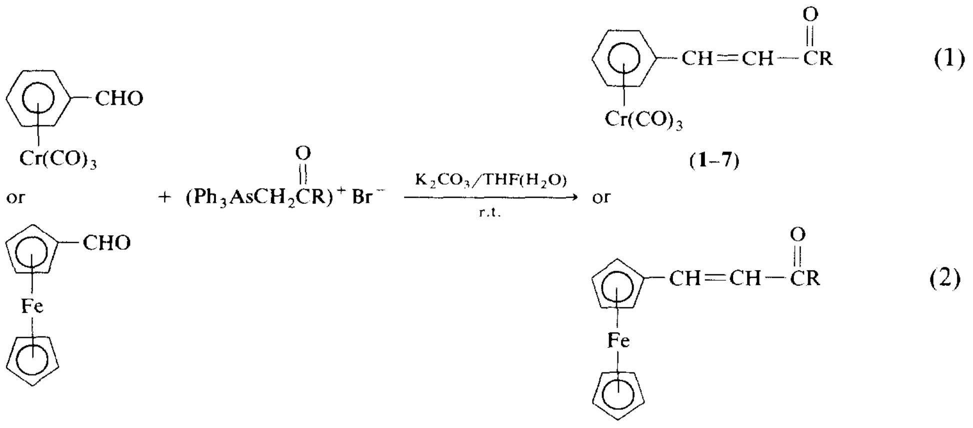
Synthesis of unsaturated ketone chromium compounds (see eq. 1)

Compound	R	Reaction conditions		Yield [a] (%)
		T	t (h)	
1	CH	r.t.	24	90.0
2	C_6H_5	r.t.	24	90.0
	C_6H_5	reflux	2	53.3
3	p-$C_6H_4CH_3$	r.t.	10	93.1
4	p-$C_6H_4OCH_3$	r.t.	6	90.0
5	p-C_6H_4F	r.t.	24	77.7
6	p-$C_6H_4NO_2$	r.t.	24	71.0
7	p-C_6H_4Cl	r.t.	24	65.5

[a] Isolated yield calculated on the basis of benzaldehyde tricarbonyl chromium used.

We have already synthesized a series of unsaturated ketone-organochromium and iron compounds.

The general formulation is as follows:



(8-14)

($R = CH_3$, aryl)

Table 2

Synthesis of unsaturated ketone organoiron compounds (see eq. 2)

Compound	R	Reaction conditions		Yield [a] (%)
		T	t (h)	
8	CH_3	r.t.	24	78.7
9	C_6H_5	r.t.	24	76.0
10	p-$C_6H_4CH_3$	r.t.	10	81.5
11	p-$C_6H_4OCH_3$	r.t.	16	75.6
12	p-C_6H_4F	r.t.	24	76.3
13	p-$C_6H_4NO_2$	r.t.	24	41.7
14	p-C_6H_4Cl	r.t.	24	65.9

[a] Isolated yield calculated on the basis of formyl ferrocene used.

The reaction involves a variety of arsonium salts which react with benzaldehyde tricarbonyl chromium or formyl ferrocene in the presence of K_2CO_3 under phase transfer condition to give the expected compounds. The results in Table 1 and 2. show that the yields are high and the reaction conditions are mild.

As expected, all products are eno-ketones which are dark red or purple solid and easily recrystallized from CH_2Cl_2–hexane. According to ^1H NMR the alkenyl bonds were all of *E*-configuration when acetone-d_6 was used as solvent, in contrast to the case of $CDCl_3$ which could not give a satisfactory spectrum. When arsonium salts with an electron-donating group on the benzene moiety were used, the time for the reaction to complete was apparently shorter implying that the electron-donating groups promote the reaction. If the reaction took place under reflux of THF, the reaction mixture was sticky and the yield dropped to 53%.

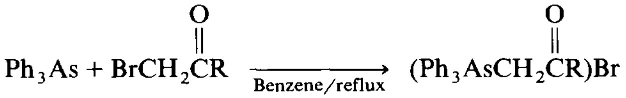
Experimental

General

IR spectra were obtained on a Shimadzu IR-440 or Perkin–Elmer 983 spectrophotometer. Mass spectra were measured on a Finnigan 4021 spectrometer. Melting points were uncorrected. Proton NMR spectra were recorded on a Varian FX-90Q or XL-200 spectrometer. The solvent used was $(CD_3)_2CO$ (unless noted otherwise) with Me_4Si as internal standard. The chemical shift are given in δ (ppm) downfield from Me_4Si, and the coupling constants are in Hz.

All solvents were purified and distilled before use. For column chromatography, aluminium oxide (neutral; 200–300 mesh) was used.

Benzaldehyde tricarbonylchromium was synthesized according to the literature [5] and was recrystallized from ether–hexane. ^1H NMR ($CDCl_3$): δ 5.2–5.4 (m, 2H); 5.4–5.8 (m, 1H); 5.8–6.0 (m, 2H); 9.4 (s, 1H). Formyl ferrocene was produced according to ref. 10. Arsonium salts were prepared by the reaction of Ph_3As and the corresponding bromoacetone or bromoacetophenone under reflux of benzene.



$$Ph_3As + BrCH_2\overset{\overset{O}{\|}}{C}R \xrightarrow[\text{Benzene/reflux}]{} (Ph_3AsCH_2\overset{\overset{O}{\|}}{C}R)Br$$

The bromoketones not commercially available were obtained by bromination of the appropriate ketone in ether according to the literature [11–14].

Typical experiment with compound 2 ($R = C_6H_5$) *

A mixture of benzaldehydetricarbonylchromium (450 mg, 1.8 mmol), acetylphenyltriphenylarsonium bromide (950 mg, 2.2 mmol), potassium carbonate (305 mg, 2.2 mmol) in 20 ml of THF and a trace of H_2O were stirred in a reaction flask under nitrogen at room temperature for 24 h (monitored by TLC). After filtering the solvent was removed under reduced pressure. The residue was dissolved in a small amount of CH_2Cl_2 and subjected to column chromatography (neutral alumina, 200–300 Mesh, 20 by 1.5 cm). The column was first eluted with 100–150 ml of hexane. A red band near the top of the column was removed by elution with

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* All reactions were run under nitrogen.

Et_2O–CH_2Cl_2. A red solid (550 mg, 90%) was obtained after removal of the solvent from the red solution. M.p. 144–146 °C. IR (KCl, cm^{-1}): 1970s, 1908s, 1889s, 1670m, 1612m, 1020m. ^1H NMR: δ 8–8.2 (m, 2H); 7.81 (d, 1H, $J = 16$); 7.38 (d, 1H, $J = 16$); 7.15–7.7 (m, 3H); 6.1–6.3 (m, 2H); 5.6–5.85 (m, 3H). MS (*m/e*): 344 (M^+, 30%), 345 ($M^+ + 1$,11%), 260 ($M^+ - 3CO$, 100%), 52 (Cr, 88%). Anal. Found: C, 62.42; H, 3.36. $C_{18}H_{12}CrO_4$ calcd.: C, 62.69; H, 3.48%.

Compound **1** ($R = CH_3$): red solid, yield 91%. M.p. 97–99 °C. IR (KCl, cm^{-1}): 1960s, 1905s, 1880s, 1665m, 1620m, 965m. ^1H NMR: δ 7.04 (d, 1H, $J = 15.7$); 6.50 (d, $J = 15.7$); 5.4–6.2 (m, 5H); 2.35 (s, 3H). MS (*m/e*): 282 (M^+, 21%), 198 ($M^+ - 3CO$, 63%), 52 (Cr, 100%). Anal. Found: C, 55.04; H, 3.23. $C_{13}H_{10}CrO_4$ calcd.: C, 55.32; H, 3.59%.

Compound **3** ($R = p$-$C_6H_4CH_3$): red solid, yield 93.1%. M.p. 148–150 °C. IR (KCl, cm^{-1}): 1975s, 1895s, 1665m, 1610m. ^1H NMR: δ 7.95 (m, 2H); 7.65 (d, 1H, $J = 16.2$); 7.34 (d, 1H, $J = 16.2$); 7.32 (m, 2H); 6.17 (m, 2H); 5.70 (m, 3H); 2.40 (s, 3H). MS (*m/e*): 358 (M^+, 14%), 274 ($M^+ - 3CO$, 100%), 52 (Cr, 42%) Anal. Found: C, 63.46; H, 3.62. $C_{19}H_{14}CrO_4$ calcd.: C, 63.68; H, 3.91%.

Compound **4** ($R = p$-$C_6H_4OCH_3$): red solid, yield 90.1% M.p. 140–142 °C. IR (KCl, cm^{-1}): 1975s, 1960s, 1880s, 1675m, 1595m. ^1H NMR: δ 8.10 (m, 2H); 7.78 (d, 1H, $J = 16$); 7.25 (d, 1H, $J = 16$); 7.03 (m, 2H); 6.10 (m, 2H); 5.70 (m, 3H); 3.9 (s, 3H). MS (*m/e*): 374 (M^+, 28%), 290 ($M^+ - 3CO$, 100%), 52 (Cr, 21%). Anal. Found: C, 60.61; H, 3.60. $C_{19}H_{14}CrO_5$ calcd.: C, 60.96; H, 3.74%.

Compound **5** ($R = p$-C_6H_4F): red solid, yield 77.7%. M.p. 136–137 °C. IR (KCl, cm^{-1}): 1975s, 1920s, 1900s, 1670m, 1615m. ^1H NMR: δ 8.22 (m, 2H); 7.84 (d, 1H, $J = 16$); 7.40 (d, 1H, $J = 16$); 7.31 (m, 2H); 6.24 (m, 2H); 5.78 (m, 3H). MS (*m/e*): 362 (M^+, 19%), 278 ($M^+ - 3CO$, 69%), 52 (Cr, 100%). Anal. Found: C, 59.40; H, 2.69. $C_{18}H_{11}CrFO_4$ calcd.: C, 59.66; H, 3.01%.

Compound **6** ($R = p$-$C_6H_4NO_2$): dark red solid, yield 71%. M.p. 178–180 °C. IR (KCl, cm^{-1}): 1960s, 1890s, 1660m, 1600m. ^1H NMR: δ 8.33 (s, 4H); 7.84 (d, 1H, $J = 16$); 7.43 (d, 1H, $J = 16$); 6.25 (m, 2H); 5.76 (m, 3H). MS (*m/e*): 389 (M^+, 26%), 305 ($M^+ - 3CO$, 44.7%), 52 (Cr, 100%). Anal. Found: C, 55.60; H, 2.83. $C_{18}H_{11}CrNO_6$ calcd.: C, 55.52; H, 2.83%.

Compound **7** ($R = p$-C_6H_4Cl): red solid, yield 65.6%. M.p. 159–161 °C. IR (KCl, cm^{-1}): 1980s, 1960s, 1880s, 1665m, 1595m. ^1H NMR: δ 8.10 (m, 2H); 7.82 (d, 1H, $J = 16$); 7.56 (m, 2H); 7.41 (d, 1H, $J = 16$); 6.20 (m, 2H), 5.73 (m, 3H). MS (*m/e*): 378 (M^+, 6%), 294 ($M^+ - 3CO$, 25%), 52 (Cr, 100%). Anal. Found: C, 57.66; H, 2.66; Cl, 9.15. $C_{18}H_{11}ClCrO_4$ calcd.: C, 57.07; H, 2.90; Cl, 9.38%.

Compound **8** ($R = CH_3$): red solid, yield 78.7%. M.p. 81–82 °C. IR (KCl, cm^{-1}): 1660s, 1640s, 1620s. ^1H NMR: δ 7.46 (d, 1H, $J = 16$); 6.33 (d, 1H, $J = 16$); 4.64 (m, 2H); 4.47 (m, 2H); 4.19 (s, 5H); 2.20 (s, 3H). MS (*m/e*): 254 (M^+, 100%), 189 ($M^+ - Cp$, 77%). Anal. Found: C, 66.29; H, 5.43. $C_{14}H_{14}FeO$ calcd.: C, 66.14; H, 5.51%.

Compound **9** ($R = C_6H_5$): red solid, yield 76%. M.p. 130–131 °C. IR (KCl, cm^{-1}): 1660s, 1600s, 1590s, 1580s. ^1H NMR: δ 8.0 (m, 2H); 7.7 (d, 1H, $J = 15$); 7.5 (m, 3H); 7.32 (d, 1H, $J = 15$); 4.64 (m, 2H); 4.48 (m, 2H); 4.19 (s, 5H). MS (*m/e*): 316 (M^+, 56%), 251 ($M^+ - Cp$, 100%). Anal. Found: C, 72.09; H, 5.51. $C_{19}H_{16}FeO$ calcd.: C, 72.15; H, 5.10%.

Compound **10** ($R = p$-$C_6H_4CH_3$): red solid, yield 81.5%. M.p. 128–130 °C. IR (KCl, cm^{-1}): 1650s, 1610m, 1590s. ^1H NMR: δ 7.95 (m, 2H); 7.70 (d, 1H, $J = 16$);

7.36 (m, 2H); 7.34 (d, 1H, $J = 16$); 4.76 (m, 2H); 4.50 (m, 2H); 4.15 (s, 5H); 2.40 (s, 3H). MS (m/e): 330 (M^+, 99%), 265 ($M^+ -$ Cp, 100%). Anal. Found: C, 72.47; H, 5.60. $C_{20}H_{18}FeO$ calcd.: C, 72.77; H, 5.46%.

Compound **11** (R $= p$-$C_6H_4OCH_3$): red solid yield 75.6%. M.p. 137–138° C. IR (KCl, cm^{-1}): 1650s, 1610s, 1590s. ^1H NMR: δ 8.1 (m, 2H); 7.74 (d, 1H, $J = 15$); 7.23 (d, 1H, $J = 15$); 7.10 (m, 2H); 4.8 (m, 2H), 4.56 (m, 2H), 4.12 (s, 5H); 3.85 (s, 3H). MS (m/e): 346 (M^+, 100%), 281 ($M^+ -$ Cp, 71%). Anal. Found: C, 68.95; H, 5.14. $C_{20}H_{18}FeO_2$ calcd.: C, 69.36; H, 5.20%.

Compound **12** (R $= p$-C_6H_4F): red solid, yield 76.3%. M.p. 146–148° C. IR (KCl, cm^{-1}): 1660s, 1600s, 1580s. ^1H NMR: δ 8.1 (m, 2H); 7.66 (d, 1H, $J = 15$); 7.38 (d, 1H, $J = 15$); 6.23 (m, 2H), 4.78 (m, 2H); 4.50 (m, 2H); 4.19 (s, 5H). MS (m/e): 334 (M^+, 100%), 269 ($M^+ -$ Cp, 100%). Anal. Found: C, 67.76; H, 4.38. $C_{19}H_{15}FFeO$ calcd.: C, 68.26; H, 4.50%.

Compound **13** (R $= p$-$C_6H_4NO_2$): dark purple solid, yield 41.07%. M.p. 194–195° C. IR (KCl, cm^{-1}): 1645m, 1570s. ^1H NMR: δ 8.34 (m, 4H); 7.82 (d, 1H, $J = 15$); 7.43 (d, 1H, $J = 15$); 4.84 (m, 2H); 4.60 (m, 2H); 4.24 (s, 5H). MS (m/e): 361 (M^+, 100%), 296 ($M -$ Cp, 13.3%). Anal. Found: C, 63.17; H, 3.90. $C_{19}H_{15}FeNO_3$ calcd.: C, 63.16; H, 4.15%.

Compound **14** (R $= p$-C_6H_4Cl): red solid, yield 65.93%. M.p. 122–124° C. IR (KCl, cm^{-1}): 1680m, 1660m, 1590s. ^1H NMR: δ 8.02 (m, 2H); 7.72 (d, 1H, $J = 15$); 7.52 (m, 2H); 7.32 (d, 1H, $J = 15$); 4.78 (m, 2H); 4.55 (m, 2H); 4.18 (s, 5H). MS (m/e): 350 (M^+, 100%), 285 ($M^+ -$ Cp, 90%). Anal. Found. C, 65.08; H, 4.29. $C_{19}H_{15}ClFeO$ calcd.: C, 65.05; H, 4.27%.

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References

1 A. Maercker, in A.C. Cope (Ed.), Organic Reaction, Vol. 14, John Wiley & Sons Inc., New York, 1965, p. 270.

2 (a) Y.-Z. Huang, L.-L. Shi, J.-H. Yang, W.-J. Xiao, S.-W. Li and W.-B. Wang, in E. Block (Ed.), Heteroatom Chemistry, VCH Publishers, New York, 1990, p. 189; (b) Y.-Z. Huang and Y.-C. Shen, in F.G.A. Stone and R. West (Eds.), Advances in Organometallic Chemistry, Vol. 20, Academic Press, New York, 1982, p. 115.

3 R. Davis and L.A.P. Kane Maguire, in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Vol. III, Pergamon Press, Oxford, 1982; p. 953.

4 G. Drafahl, H.H. Horhold and K. Kehna, Chem. Ber., 98 (1965) 1862.

5 M.D. Rausch, G.A. Moser, E.J. Zaiko and A.L. Lipmar Jr., J. Organomet. Chem., 23 (1970) 185.

6 D.J. Williams, Angew. Chem., Int. Ed. Engl., 23 (1984) 690.

7 J.A. Bandy and D. Bloor, Nature, 330 (1987) 360.

8 C.C. Frazier, M.A. Harvey and M.P. Cockerham, J. Phys. Chem., 90 (1986) 5730.

9 D.F. Eation, A.G. Anderson W. Tom and Y. Wang, J. Am. Chem. Soc., 109 (1987) 1886.

10 P.J. Graham, R.V. Lindsey, G.W. Parshall, M.L. Peterson and G.M. Whitman J. Am. Chem. Soc., 79 (1957) 3416.

11 Y.-Z. Huang, W.-Y. Ting and H.-S. Cheng, Acta Chim. Sin., 31 (1965) 38.

12 R.W. Bost and C.A. Howe, J. Am. Chem. Soc., 73 (1951) 5864.

13 J.R. Corrigan, M.-J. Sullivan, H.W. Bishop and A.W. Ruddy, J. Am. Chem. Soc., 75 (1953) 6258.

14 R.E. Lutz and R.K. Allison, J. Org. Chem., 12 (1947) 617.