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Preparation of tricarbonyl(benzene)chromium and ferrocene containing unsaturated amides and nitriles

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Abstract

A series of tricarbonyl(benzene) chromium-containing and ferrocene-containing α,β-unsaturated amides and nitriles has been prepared via a variety of arsonium salts with tricarbonyl(benzaldehyde)-chromium or monoformyl-ferrocene with high E stereoselectivity in moderate to good yields.

Introduction

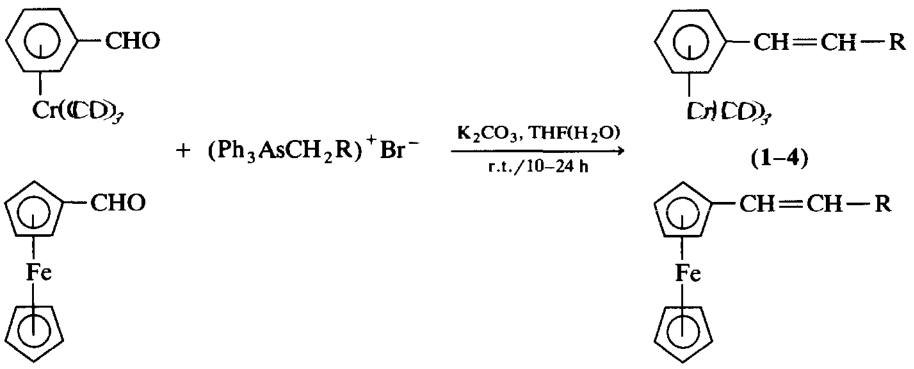
In recent years there has been considerable interest in materials with nonlinear optical properties. Some papers [1,2] concerning the organometallic complexes with nonlinear optical properties have appeared in the literature showing that arenetricarbonylchromium compounds [3] and ferrocene compounds [4] possess larger second harmonic generation efficiencies than ADP. This result demonstrated that organotransition metal compounds can play an important role in the development of nonlinear optical properties of materials. Therefore it is interesting to synthesize some novel organometallic compounds and study their properties.

In a previous publication, we reported the synthesis of organometallic compounds containing ketones [5]. In this paper we would like to report the successful application of arsonium salts in the preparation of organometallic compounds containing unsaturated amides and nitriles.

Results and discussion

To introduce a double bond in the molecule, the arsorane reagent has become a useful method other than Wittig and Horner–Emmons reagents [6]. Huang et al. found [7] that arsonium ylides, formed in situ by the reaction of arsonium bromide and potassium carbonate, reacts with aldehydes under solid–liquid phase transfer conditions to give the desired products. Because of the simple procedure and mild conditions, it has been successfully applied to polyenal, polyenone and polyenamide and some related natural products [8,9]. In continuous studies on arsonium reagents, coupled with our research interest, we found that arsonium salts were also suitable for synthesizing organometallic compounds containing unsaturated amides and nitriles.

The outline of our method is as follows:



(1–4)

(5–8)

R = $CONR^1R^1$ or CN

In the presence of K_2CO_3 under phase transfer conditions, tricarbonyl(benzaldehyde)chromium or formylferrocene reacted with corresponding arsonium salts to give the desired compounds.

The arsonium salts were easily prepared by the reaction of Ph_3As with 2-bromoacetyl pyrrolidine, 2-bromoacetyl piperidine, 2-bromoacetyl diisobutyl amine or bromoacetonitrile under reflux with high yields.

The results are summarized in Table 1. All products are orange-red solids in *E* configuration and easily recrystallized from CH_2Cl_2/hexane.

Experimental

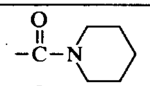
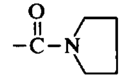
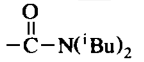
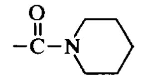
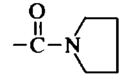
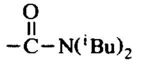
General

IR Spectra were run as KBr pellets using a Perkin-Elmer 983 Spectrophotometer. Proton NMR spectra were recorded on a JEOL FX-90Q or a Varian XL-200 spectrometer. The solvent used was $(CD_3)_2CO$ (unless noted otherwise) with Me_4Si *as internal standard. The chemical shifts are given in δ (ppm) downfield* from Me_4Si and the coupling constants are in Hz. Melting points were uncorrected.

All solvents were purified and distilled before use. Alumina (neutral 200–300 mesh) was used for column chromatography.

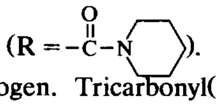
Tricarbonyl(benzaldehyde)chromium and formyl ferrocene were obtained according to the literature [10,11]. Arsonium salts were synthesized by the reaction of Ph_3As and 2-bromoacetyl amide or bromo-acetonitrile according to references [8,12,13].

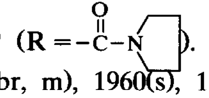
Table 1

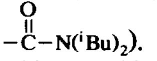
Compound	R	Condition time (h) [a]	Yield (%) [b]
1		10	87
2		24	87
3	 $-\overset{\overset{O}{\|}}{C}-N(^iBu)_2$	24	51
4	-CN	24	69
5		20	71
6		24	73
7	 $-\overset{\overset{O}{\|}}{C}-N(^iBu)_2$	24	34
8	-CN	24	67

[a] All reactions were carried out at room temperature. [b] Isolated yield.

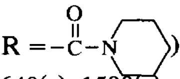
Typical experiment

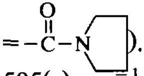
Compound 1 (R = ). All reactions were carried out under an atmosphere of nitrogen. Tricarbonyl(benzaldehyde)chromium (450 mg, 1.8 mmol), acetylpiperidine triphenylarsonium bromide (1.1 g, 2.16 mmol), potassium carbonate (300 mg, 2.16 mmol), and 20 ml THF (trace H_2O) were mixed and stirred at room temperature for 10 h (monitored by TLC). The reaction mixture was filtered. After removal of the solvent the crude product was chromatographed using alumina and eluting with hexane and methylene chloride. A red solid 550 mg (yield = 87%) was obtained after removal of the solvent; m.p. 156–158 °C. IR (KCl): 3420(br. m), 1960(s), 1890(s), 1600 (m) cm^{-1}. ^1H NMR: 7.24 (d, 1H, $J = 16$), 7.12 (d, 1H, $J = 16$), 6.06 (m, 2H), 5.65 (m, 3H), 3.60 (br, m, 4H), 1.58 (br, m, 6H). MS(m/e): 351 (M^+, 15%), 267 ($M^+ - 3CO$, 100%), 52 (Cr, 40%). Anal. $C_{17}H_{17}O_4NCr$ calc.: C, 58.12; H, 4.85. Found: C, 57.75; H, 5.16%.

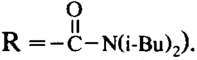
Compound 2 (R = ). Yield = 87%. Orange solid, m.p. 164–166 °C. IR(KCl): 3400(br, m), 1960(s), 1890(s), 1650(m), 1610(m) cm^{-1}. MS(m/e): 337 (M^+, 11%), 253 ($M^+ - 3CO$, 93%), 52 (Cr, 100%). ^1H NMR: 7.24 (d, 1H, $J = 15$), 6.96 (d, 1H, $J = 15$), 6.06 (m, 2H), 5.74 (m, 3H), 3.56 (br, m, 4H), 1.94 (br, m, 4H). Anal. $C_{16}H_{15}O_4NCr$ calc.: C, 56.97; H, 4.45. Found: C, 56.51; H, 4.48%.

Compound 3 (R =  $-\overset{\overset{O}{\|}}{C}-N(^iBu)_2$). Yield = 51%. Red solid, m.p. 134–136 °C. IR(KCl): 2880(m), 1970(s), 1870(s), 1650(m), 1590(m) cm^{-1}. MS(m/e): 395 (M^+, 31%), 311 ($M^+ - 3CO$, 87%), 52 (Cr, 75%). ^1H NMR (in $CDCl_3$): 7.15 (d, 1H, $J = 15.3$), 6.68 (d, 1H, $J = 15.3$), 5.40 (m, 5H), 3.24 (m, 4H), 20.02 (m, 2H), 0.93 (d, 12H). Anal. $C_{20}H_{25}NO_4Cr$ calc.: C, 60.76; H, 6.33. Found: C, 60.21; H, 6.27%.

Compound 4 (R = -CN). Yield = 69%. Red solid, m.p. 110–112 °C. IR(KCl): 2230(m), 1970(s), 1880(s), 1620(m) cm^{-1}. MS(*m/e*): 265 (M^+, 32%), 181 (M^+-3CO, 55%), 52 (Cr, 100%). ^1H NMR: 7.32 (d, 1H, $J = 16$), 6.28 (d, 1H, $J = 16$), 6.05 (m, 2H), 5.78 (m, 3H). Anal. $C_{12}H_7NO_3Cr$ calc.: C, 54.34; H, 2.64. Found: C, 54.26; H, 2.50%.

Compound 5 (R = ). Yield = 74%. Orange-red solid, m.p. 140–143 °C. IR(KCl): 1640(s), 1590(s) cm^{-1}. MS(*m/e*): 323 (M^+, 100%), 258 (M^+-Cp, 48%). ^1H NMR: 7.41 (d, 1H, $J = 15.2$), 6.76 (d, 1H, $J = 15.2$), 4.61 (m, 2H), 4.36 (m, 2H), 4.15 (s, 5H), 3.58 (br, m, 4H), 1.6 (br, m, 6H). Anal. $C_{18}H_{21}NOFe$ calc.: C, 66.87; H, 6.50. Found: C, 66.24; H, 6.52%.

Compound 6 (R = ). Yield = 73%. Orange-red solid, m.p. 140–142 °C. IR(KCl): 1645(s), 1595(s) cm^{-1}. MS(*m/e*): 309 (M^+, 100%), 244 (M^+-Cp, 84%). ^1H NMR: 7.42 (d, 1H, $J = 15.2$), 6.52 (d, 1H, $J = 15.2$), 4.60 (m, 2H), 4.37 (m, 2H), 4.15 (s, 5H), 3.60 (m, 2H), 3.42 (m, 2H), 1.95 (m, 4H). Anal. $C_{17}H_{19}NOFe$ calc.: C, 66.02; H, 6.15. Found: C, 65.65; H, 6.08%.

Compound 7 (R =  $-\overset{\displaystyle O}{\overset{\|}{C}}-N(i\text{-}Bu)_2$). Yield = 34%. Brown solid, m.p. 74–76 °C. IR(KCl): 1640(s), 1585(s) cm^{-1}. MS(*m/e*): 367 (M^+, 95%), 302 (M^+-Cp, 100%). ^1H NMR: 7.37 (d, 1H, $J = 15.2$), 6.72 (d, 1H, $J = 15.2$), 4.61 (m, 2H), 4.37 (m, 2H), 4.14 (s, 5H), 3.30 (M, 4H), 0.90 (m, 14H). Anal. $C_{21}H_{29}NOFe$ calc.: C, 68.66; H, 7.90. Found: C, 68.67; H, 8.02%.

Compound 8 (R = -CN). Yield = 67%. Red solid, m.p. 90–92 °C. IR(KCl): 2210(s), 1610(s) cm^{-1}. MS(*m/e*): 237 (M^+, 100%), 172 (M^+-Cp, 51%). ^1H NMR: 7.40 (d, 1H, $J = 16.2$), 5.76 (d, 1H, $J = 16.2$), 4.65 (m, 2H), 4.49 (m, 2H), 4.22 (s, 5H). Anal. $C_{13}H_{11}NFe$ calc.: C, 65.82; H, 4.64. Found: C, 65.69; H, 4.50%.

Acknowledgement

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