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Synthesis and Characterization of Ferrocene Bonding Agents

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New bonding agents, viz., 1,1′-(1,1′-ferrocenediyldiethylidene)bis(thiocarbonohydrazide) (DAFT), 1,1′-diacetylferrocene disemicarbazone (DAFS), 1,1′-diacetylferrocene benzoylhydrazone (FDBAH), and 1,1′-diacetylferrocene *p*-nitrobenzoylhydrazone (FDNBAH), have been synthesized and characterized by IR, ^{1}H NMR, ^{13}C NMR, and UV spectroscopic techniques.

Introduction

Currently used composite solid propellants generally contain hydroxy-terminated polybutadiene (HTPB) and ammonium perchlorate (AP) as the fuel–oxidant system; the bonding between them is poor but is improved by using bonding agents (BA) to afford better mechanical properties. Recently, we have been studying ferrocene-based compounds (*1*, *2*) which not only act as bonding agents but also may act as burning rate modifiers, antioxidants, etc. We have synthesized four new ferrocene compounds (Table I). The ^{1}H NMR and broad-band and off-resonance ^{13}C NMR spectra of all the compounds agree well with the proposed structures (Figure 1).

Experimental Section

Acetylation of ferrocene gave 1,1′-diacetylferrocene (DAF) (*3*) which was subsequently converted to DAFT, DAFS, FDBAH, and FDNBAH in the following manner.

Thiocarbonohydrazide (TCH) was prepared as described by Audrieth et al. (*4*); TCH (2.65 g, 0.025 mol) was dissolved in acetic acid (100 mL, 0.5 N) at 80 °C to which a solution of DAF (2.7 g, 0.011 mol) in ethanol (100 mL) was slowly added over a period of 2 h with stirring. The DAFT thus obtained was filtered under hot conditions and washed with water and later with ethanol and dried under vacuum (yield, 3.79 g (85%); mp 200 °C); IR (KBr, cm^{-1}): 3240, 3120 (ν_{N-H}); 1600 ($\nu_{C=N}$); 1500 ($\nu_{C=S}$) IR data for the other three compounds agree well with their structures.

Semicarbazide hydrochloride (SCH) (1.12 g, 0.01 mol) and crystallized sodium acetate (3.0 g) were dissolved in 10–15 mL of water and the solution was heated on a water bath. To this solution, a solution of DAF (1.35 g, 0.005 mol) in ethanol (100 mL) was added dropwise with stirring. The stirring was continued for a further 30 min after the addition. The separated DAFS was filtered while hot and washed with 1:1 aqueous ethanol and then with water and dried under vacuum (yield, 1.73 g (90%)). This compound did not show any definite melting point but decomposed above 250 °C).

Benzoic acid hydrazide (BAH) was prepared by condensing hydrazine hydrate (5 mL) with ethyl benzoate (4.5 g, 0.03 mol) in ethanol (15 mL) at 80 °C. The BAH that separated as white rectangular plates was filtered and dried (yield, 3.55 g (87%); mp 113 °C (lit.^{5} 114 °C)). BAH (4.08 g, 0.03 mol) was dissolved in ethanol (25 mL) and to this solution DAF (4.05 g, 0.016 mol) was added in one lot. The mixture was refluxed for 6 h in the presence of 4 drops of acetic acid. The FDBAH that separated as orange-red crystals during the course of the reaction was filtered, washed with hot ethanol, and dried (yield, 6.1 g (80%); mp 199 °C).

Table I. Spectral Data of DAFT, DAFS, FDBAH, and FDNBAH

		^{13}C NMR	
compd	^{1}H NMR δ	broad band δ	off-reson split pattern
DAFT	2.09 (s, 6 H)	14.79	q (CH_3)
	4.33 (s, 4 H)	68.21	d (C_3,4)
	4.84 (s, 4 H)	70.70	d (C_2,5)
	4.91 (s, 4 H)	94.08	s (C_1)
	9.46 (s, 2 H)	149.90	s (C_6)
	9.93 (s, 2 H)	177.47	s (C_9)
DAFS	1.97 (s, 6 H)	13.26	q (CH_3)
	4.27 (s, 4 H)	66.81	d (C_3,4)
	4.68 (s, 4 H)	69.41	d (C_2,5)
	6.33 (s, 4 H)	84.70	s (c_1)
		145.07	s (C_6)
	9.01 (s, 2 H)	156.67	s(C_9)
FDBAH	2.22 (s, 6 H)	15.65	q (CH_3)
	4.45 (s, 4 H)	68.33	d ($C_{3,4}$)
	4.75 (s, 4 H)	71.15	d ($C_{2,5}$)
		84.15	d (C_1)
	7.45–7.89	127.73	d ($C_{12,13,14}$)
	(m, 10 H, J = 8 Hz)	131.20	d ($C_{11,15}$)
	10.54 (s, 2 H)[a]	134.12	s (C_{10})
		159.16	s (C_6)
		162.96	s (C_9)
FDNBAH	2.30 (s, 6 H)	14.89	q (CH_3)
	4.49 (s, 4 H)	68.11	d ($C_{3,4}$)
	4.78 (s, 4 H)	70.82	d ($C_{2.5}$)
	7.99–8.33	83.61	s (C_1)
	(AB quartet,	122.63	d ($C_{11,15}$)
	8 H, J = 8 Hz)	129.03	d ($C_{12,14}$)
	10.8 (s, 2 H)[a]	139.87	s (C_{10})
		148.54	s (C_{13})
		161.24	s (C_6)
		177.55	s (C_9)

[a] Disappeared on D_2O treatment.

p-Nitrobenzoic acid hydrazide (NBAH) was prepared by condensing hydrazine hydrate (5 mL) with ethyl *p*-nitrobenzoate (3.9 g, 0.02 mol) in ethanol at 80 °C. NBAH that separated as yellow flakes was filtered, washed with hot ethanol, and dried (yield, 3.2 g (88%); mp 213 °C (lit.^{5} 213 °C)). NBAH (3.62 g, 0.02 mol) was dissolved in ethanol (25 mL) and to this solution DAF (2.7 g, 0.011 mol) was added in one lot. The mixture was refluxed for 6 h in the presence of a few drops of acetic acid. FDNBAH that separated as red crystals was filtered, washed with hot ethanol, and dried (yield 5.722 g, (96%), mp 238 °C).

IR spectra were recorded as KBr pellets on a Perkin-Elmer-597 spectrophotometer. ^{1}H NMR spectra were recorded on a Burker WH 270 FT spectrometer at room temperature in DMSO-d_6 containing Me_4Si as an internal standard. ^{13}C NMR spectra were recorded on JEOL FX 90Q spectrometer at ambient temperature in DMSO-d_6 which also provided the required deuterium lock. The solutions (ca. 10% w/v) contained Me_4Si (1%) as internal standard. Instrumental parameters were as follows: frequency of irradiation 22.5 MHz; spectral width 5000 Hz, pulse width 12 μs; pulse decay 1 s; number of scans 300 and number of data points 8K; UV spectra were recorded in DMF on a UV Hitachi U-3400 spectrometer. UV absorption

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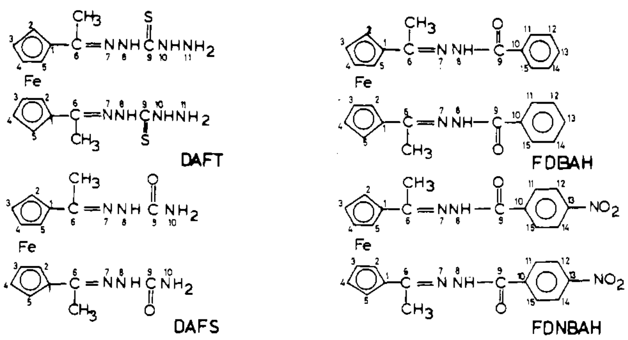

Figure 1.

spectrum of the four compounds showed absorptions in the region 451–456 nm assignable to n–π* transition.

Elemental analyses were submitted for review.

Registry No. DAFT, 113219-05-9; DAFS, 113219-06-0; FDBAH, 113219-07-1; FDNBAH, 113219-08-2; BAH, 613-94-5; NBAH, 636-97-5; DAF, 1273-94-5; TCH, 2231-57-4; SCH, 563-41-7; ethyl benzoate, 93-89-0; ethyl *p*-nitrobenzoate, 99-77-4.

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Preparation of Sterically Hindered Phosphoramidates

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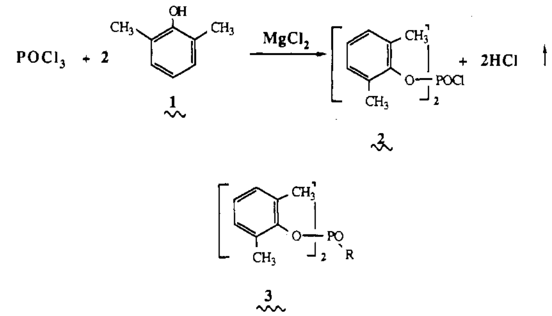
Treatment of phosphorus oxychloride with two equivalents of 2,6-dimethylphenol in the presence of magnesium chloride produced the sterically hindered bis(2,6-dimethylphenyl) chlorophosphate in excellent yield. The diaryl phosphorochloridate reacted with a variety of primary and secondary amines to produce phosphoramidates in good to excellent yield.

We recently required a synthesis of a diaryl chlorophosphate that gave product of high purity and high overall yield without an elaborate purification scheme. We found that treatment of phosphorus oxychloride with two equivalents of the sterically hindered phenol, 2,6-dimethylphenol (**1**), in the presence of a catalytic amount of magnesium chloride produced bis(2,6-dimethylphenyl) chlorophosphate (**2**) in excellent yield (Scheme I). The crude reaction mixture contains esentially pure **2** and can easily be purified by simple distillation, bp 165 °C/1 mm in 90–95% isolated yield. Pure **2** is quite stable providing the necessary precautions are taken to prevent its exposure to excessive moisture.

The hydrolysis product of **2**, bis(2,6-dimethylphenyl) hydrogen phosphate (**3a**) (*1*, *2*) and the adduct from **2** with benzylamine (**3b**) (*1*) have been described previously; however in neither case was **2** actually isolated. In spite of the very hindered nature of **2**, it is readily converted to phosphoramidates and bis(phosphoramidates) upon treatment with a variety of primary and secondary amines and diamines in the presence of triethylamine. Presented in Table I is a list of some representative phosphoramidates prepared from **2**. The products were identified by their spectral data (see Table II), and melting points. For all new compounds satisfactory high-resolution mass spectral data as well as correct elemental analyses were obtained.

Scheme I



Experimental Section

Melting points were determined on a Thomas Hoover apparatus and are uncorrected. Infrared spectra were determined with a Beckman Microlab MX-250 spectrophotometer as KBr disks; absorbance positions are reported in reciprocal centimeters (cm^{-1}). Proton magnetic resonance spectra were recorded on Varian EM-390 spectrometer as solutions in chloroform-*d* unless otherwise stated. High-resolution mass spectra were recorded on a MAT instrument. Elemental analyses were determined by the General Electric analytical services group.

Preparation of Bis(2,6-dimethylphenyl) Chlorophosphate. A mixture of 2,6-dimethylphenol (484 g, 4.0 mol) and phosphorus oxychloride (307 g, 2.0 mol) containing anhydrous magnesium chloride (9.5 g, 0.1 mol) was heated to 150 °C over a 4-h period. During the heating period a copious amount of hydrochloric acid gas was evolved and the solution aquired a light brown color. After the gas evolution ceased, the residue was distilled under reduced pressure to provide 598 g, 92% of pure **2**, bp 165 °C/1 mm, which solidified upon standing, mp ca. 50 °C.

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