

Conversion of 2,5-Dihydrothiophene 1,1-Dioxides into Highly Functionalized (η^4 -Buta-1,3-diene)tricarbonyliron(0) Complexes

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Treatment of functionalized 2,5-dihydrothiophene 1,1-dioxides with nonacarbonyldi-iron in refluxing toluene affords functionalized (η^4 -buta-1,3-diene)tricarbonyliron(0) complexes.

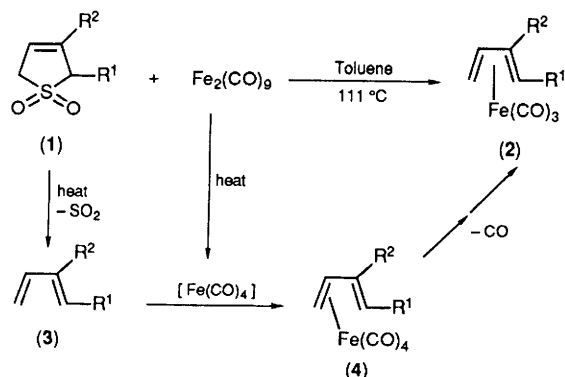
The chemistry of (η^4 -1,3-diene)tricarbonyliron(0) complexes is a subject of continuing interest. The general applications of the complexes are to (i) Friedel–Crafts reactions with electrophiles;¹ (ii) electrophilic reactions with reactive carbon nucleophiles;² (iii) hydride abstraction, followed by reaction with a number of different nucleophiles.³ Their synthetic utility would be further enhanced if highly functionalized (η^4 -1,3-diene)tricarbonyliron(0) complexes could be easily prepared. Further manipulation of molecules would then be possible after the initial reactions. In general, these complexes are obtained by refluxing free dienes with nonacarbonyldi-iron or photolysing free dienes with pentacarbonyliron in the appropriate solvent. Recently, reaction of secondary or tertiary cyclohex-2-enols with pentacarbonyliron in refluxing *n*-butyl ether gave directly the related (η^4 -cyclohexa-1,3-diene)tricarbonyliron(0) complexes in good yields.⁴ However, complexes bearing an electron-withdrawing group such as nitrile, phenylthio, or phenylsulphone at position 2 remain unexplored. The parent 2-substituted dienes are extremely reactive compounds which polymerize even at low temperature (*ca.* -15°C). Furthermore, complexes of type (2) ($\text{R}^2 = \text{CN}, \text{SPh}, \text{SO}_2\text{Ph}$) are not accessible by electrophilic function-

alization of (η^4 -buta-1,3-diene)tricarbonyliron(0) complex (2) ($\text{R}^1, \text{R}^2 = \text{H}$).[†] 2,5-Dihydrothiophene 1,1-dioxides are known to convert into 1,3-dienes after thermal extrusion of sulphur dioxide.⁶ Moreover, the introduction of functional groups into 2,5-dihydrothiophene 1,1-dioxides is apparently easier than to the parent dienes or (η^4 -buta-1,3-diene)tricarbonyliron(0) complex (2) ($\text{R}^1, \text{R}^2 = \text{H}$). Alkylation of 2,5-dihydrothiophene 1,1-dioxides at C-2 is easily performed by treatment with base, followed by alkylating reagents at -105°C .⁷ Such functionalization at position 3 is well documented by Chou.⁸ We now report a general preparation of highly functionalized (η^4 -buta-1,3-diene)tricarbonyliron(0) complexes (2a–i) by the reaction of nonacarbonyldi-iron with various functionalized 2,5-dihydrothiophene 1,1-dioxides. The reaction was performed in the expectation that reactive $\text{Fe}(\text{CO})_4$, generated *in situ* from $\text{Fe}_2(\text{CO})_9$ upon heating, would complex with the free diene before polymerization occurred (Scheme 1). It

Table 1. Reactions of functionalized 2,5-dihydrothiophene 1,1-dioxides with $\text{Fe}_2(\text{CO})_9$.

Entry	Reactant (1)	Product (2)	% Yield ^a
1	a; $\text{R}^1 = \text{H}, \text{R}^2 = \text{SO}_2\text{Ph}$	(2a) ^b	61
2	b; $\text{R}^1 = \text{H}, \text{R}^2 = \text{SOPh}$	(2b) ^b	52
3	c; $\text{R}^1 = \text{H}, \text{R}^2 = \text{CO}_2\text{Me}$	(2c)	45
4	d; $\text{R}^1 = \text{H}, \text{R}^2 = \text{Cl}$	(2d)	32
5	e; $\text{R}^1 = \text{H}, \text{R}^2 = \text{CN}$	(2e) ^b	43
6	f; $\text{R}^1 = \text{SiMe}_3, \text{R}^2 = \text{H}$	(2f)	41
7	g; $\text{R}^1 = \text{CN}, \text{R}^2 = \text{Me}$	(2g) ^b	44
8	h; $\text{R}^1 = \text{COMe}, \text{R}^2 = \text{CO}_2\text{Me}$	(2h) ^{b,c}	64
9	i; $\text{R}^1 = \text{Me}, \text{R}^2 = \text{CO}_2\text{Me}$	(2i) ^b	57

^a All products were purified by flash column chromatography on silica gel, followed by distillation under reduced pressure. ^b All new compounds have been fully characterized by ^1H and ^{13}C NMR, IR, MS, and high resolution mass spectra. ^c Isolated as a mixture of *exo* and *endo* isomers.



Scheme 1. Proposed reaction pathway for the formation of (η^4 -buta-1,3-diene)tricarbonyliron(0) complexes (2).

[†] A new route to the stable (2-acylbuta-1,3-diene)tricarbonyliron(0) complexes has been reported,⁵ based on the palladium catalysed coupling between acid chlorides and 2-stannylated buta-1,3-diene complexes.

was presumed that diene (**3**) and $\text{Fe}(\text{CO})_4$ would be formed initially, followed by complexation of (**3**) with $\text{Fe}(\text{CO})_4$ to form (**4**). The postulated intermediate (**4**) could lose one molecule of CO, followed by co-ordination of the pendant double bond with the $\text{Fe}(\text{CO})_3$ moiety to give complex (**2**).

In a typical experiment, treatment of 2,5-dihydro-3-(phenylsulphonyl)thiophene 1,1-dioxide (**1a**) with $\text{Fe}_2(\text{CO})_9$ (4.0 mol equiv., toluene, 5 h, 111 °C, under nitrogen) affords the corresponding $[\eta^4\text{-2-(phenylsulphonyl)buta-1,3-diene}]$ -tricarbonyliron(0) complex (**2a**) in 61% yield after flash column chromatography and short-path distillation. The spectroscopic data of complex (**2a**) is consistent with those found for the $(\eta^4\text{-isoprene})$ tricarbonyliron(0) complex (**2**) ($\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Me}$).[‡] However, the reaction does not proceed smoothly with $\text{Fe}(\text{CO})_5$ or at low temperature (for instance, refluxing in ethyl ether, benzene, or dioxane). Results of the reaction $\text{Fe}_2(\text{CO})_9$ with a variety of functionalized 2,5-dihydrothiophene 1,1-dioxides are summarized in Table 1. In general, 4 mol equiv. of $\text{Fe}_2(\text{CO})_9$ are needed for completion. In the case of 2,5-dihydro-3-(phenylthio)thiophene 1,1-dioxide (**1b**), 8 mol equiv. were added with a longer reaction time (8 h). Only one stereoisomer (*exo*) is obtained in the case of complexes (**2f**, **g**, and **i**). Complex (**2h**) is isolated as a mixture of *exo* and *endo* isomers (*exolendo* = 2/1). The moderate

yields (32–64%) in most examples may be explained by a certain amount of polymerization of the free diene before complexation occurred.

In conclusion, we have shown that highly functionalized $(\eta^4\text{-buta-1,3-diene})$ tricarbonyliron(0) complexes are easily available by the reaction of functionalized 2,5-dihydrothiophene 1,1-dioxides with $\text{Fe}_2(\text{CO})_9$. This one pot reaction avoids the isolation of unstable dienes.

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[‡] Spectroscopic data for (**2a**): m.p. 124–125 °C; ¹H NMR (CDCl_3) δ 8.03 (2H, dd, *J* 6.4, 1.3 Hz, aromatic H), 7.62 (3H, m, aromatic H), 6.08 (1H, dd, *J* 9.0, 7.3 Hz, 3-H), 2.33 (1H, dd *J* 3.4, 1.4 Hz, *exo*-1-H), 1.95 (1H, dd, *J* 7.3, 2.2 Hz, *exo*-4-H), 0.29 (1H, dd, *J* 9.7, 2.2 Hz, *endo*-4-H), 0.15 (1H, dd, *J* 3.4, 0.8 Hz, *endo*-1-H); ¹³C NMR (CDCl_3) δ 208.1, 140.8, 133.5, 129.4, 127.8, 106.4, 89.2, 40.0, 36.3; IR (CDCl_3 , solution) 3056w, 2986w, 2929w, 2068sh, 1997sh, 1446m, 1319sh, 1267m, 1141sh cm^{-1} ; mass (EI) *m/z* 334 (*M*⁺, 1%), 306 (*M* – CO, 12), 278 (*M* – 2 CO, 52), 250 (*M* – 3 CO, 100), 199 (38), 186 (92), 160 (18), 133 (38); high resolution MS calc. for $\text{C}_{13}\text{H}_{10}\text{FeO}_5\text{S}$ 333.9598. Found 333.9587.