

Novel Nucleophilic Additions to  
[ $\eta^4$ -2-(Phenylsulfonyl)-1,3-butadiene]tricarbonyliron(0) Complex

Shang-Shing P. Chou,\* Chien-Hung Hsu

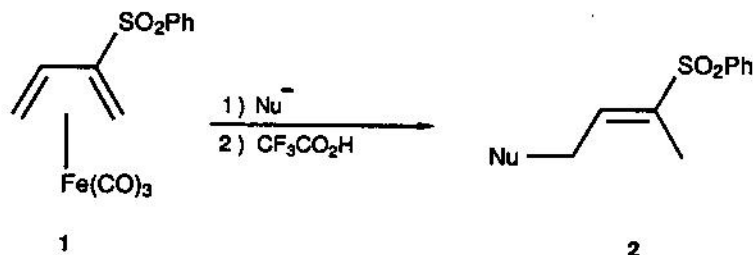
Department of Chemistry, Fu Jen Catholic University, Taipei, Taiwan 242

Ming-Chang P. Yeh\*

Department of Chemistry, National Normal University, Taipei, Taiwan 117  
Republic of China

Abstract: Reactions of the title compound (1) with various nucleophiles give the addition products (2) regio- and stereospecifically in good yield.

2-Sulfonyl 1,3-dienes can be used as Diels-Alder dienes and dienophiles,<sup>1</sup> as well as Michael acceptors.<sup>2</sup> Several methods for their preparation have been reported,<sup>3</sup> but our method using 2,5-dihydrothiophene 1,1-dioxides (3-sulfolenes) as precursors to 1,3-dienes has certain advantages.<sup>4</sup> We have recently reported the conversion of 3-sulfolenes into highly functionalized ( $\eta^4$ -1,3-butadiene)tricarbonyliron(0) complexes.<sup>5</sup> Although diene tricarbonyliron(0) complexes are known to react with nucleophiles kinetically (-78 °C) at the unsubstituted internal position, and thermodynamically (25 °C) at the terminal position,<sup>6</sup> very little information is available for diene tricarbonyliron(0) complexes carrying electron-withdrawing groups. We now report the first example of such a diene complex (1)<sup>5</sup> bearing a sulfonyl group at C-2, which can undergo the nucleophilic addition reaction to give products (2).



The results of the reaction are shown in Table I. Several important features are noteworthy. (i) Both kinetic (condition A) and thermodynamic (condition B) conditions yielded the same products (2), in contrast to the

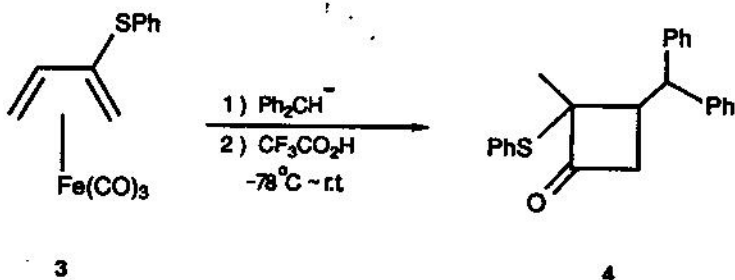
literature reports for the parent butadiene and for dienes bearing electron-donating groups where the regiochemistry varied with the reaction temperature.<sup>6</sup> (ii) Weak nucleophiles such as malonate anion (entry 4) and malononitrile anion (entry 5) added efficiently to the diene complex (1). These are the only examples reported for ( $\eta^4$ -1,3-diene)tricarbonyliron(0) complexes; without the phenylsulfonyl group on the diene, these weak nucleophiles do not give any of the addition product.<sup>6</sup> Apparently, the above two features (reactivity and regioselectivity) are due to the electronic and steric effects of the phenylsulfonyl group in (1). It should also be pointed out that products (2) result from attack of nucleophiles at C-4 of (1) whereas without the tricarbonyliron moiety the nucleophiles add to the C-1 position.<sup>2</sup> In this way, we can control the nucleophilic addition to 2-(phenylsulfonyl)-1,3-butadiene at either C-1 or C-4 position. (iii) Only the *E* isomer of the product (2) was obtained. The stereochemistry was determined by NOE measurements. (iv) Without hexamethylphosphoric triamide (HMPA), the yield of the addition reaction was much lower (entries 1 and 4, condition C). (v) The quenching condition was very important. The best result was obtained with trifluoroacetic acid. In the reaction with the malonate anion (entry 4), if methyl iodide was used to quench the reaction, only the unreacted starting material (1) was obtained together with methylated diethyl malonate, indicating that the addition of the malonate anion to (1) was reversible and a proton source was needed to drive the equilibrium to product (2d).

Table I. Reactions of Diene Tricarbonyliron(0) Complex (1) with Nucleophiles to give Product (2)

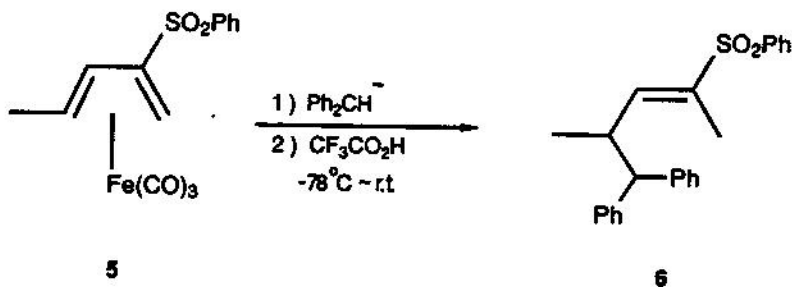
entry	Nucleophile ( $\text{Nu}^-$ )	Product (2)	% Yield <sup>a</sup> (Condition) <sup>b</sup>
1	$\text{Ph}_2\text{CH}^-$	(2a)	76 (A); 76 (B); 16 (C)
2	$\text{Ph} \overline{\text{C}}\text{HS}(\text{CH}_2)_3\text{S}$	(2b)	68 (A); 67 (B)
3	$(\text{CH}_3)_2\text{C}^- \text{CN}$	(2c)	68 (A); 66 (B)
4	$\overline{\text{C}}\text{H}(\text{CO}_2\text{Et})_2^-$	(2d)	86 (A); 79 (B); 0 (C)
5	$\overline{\text{C}}\text{H}(\text{CN})_2^-$	(2e)	88 (A); 87 (B)

(a) All products were purified by flash column chromatography on silica gel, and were fully characterized spectrally and analytically. (b) Condition A: at  $-78^\circ\text{C}$  for 2 h before quench. Condition B: warmed to room temperature, stirred for 2 h before quench at  $-78^\circ\text{C}$ . Condition C: no HMPA was added.

To show that the phenylsulfonyl group in the diene iron complex (1) was dominant in determining the regioselectivity of the addition reaction, the corresponding phenylthio-substituted diene iron complex (3) was subjected to the reaction with diphenylmethanide at  $-78^{\circ}\text{C}$ . A cyclobutane compound (4) was obtained in 37% yield. Here the nucleophilic attack occurred at the C-3 position, in accordance with the literature precedents for electron-donating substituents.<sup>6</sup>



It should also be noted that when the diene complex (5) was reacted with diphenylmethanide, compound (6) was the only product obtained (46% yield), indicating that the methyl group at C-4 of compound (5) has resulted in greater steric hindrance than hydrogen at the same position in compound (1) has, but the electronic and steric effects of the sulfonyl group still control the regiochemistry of the addition reaction.



In summary, we have observed novel reactivity and complete regio- and stereospecificity of the nucleophilic addition reaction of diene tricarbonyliron(0) complex (1), which is the first of its kind bearing an electron-withdrawing group on the diene. We are now investigating the effect of other electron-withdrawing groups as well as different metals and ligands.

A general procedure is as follows. To a solution of (1) (1 mmol) in THF (4 mL) and HMPA (1 mL) at  $-78^{\circ}\text{C}$  was added the nucleophile (1.3 mmol). The reaction mixture was quenched with trifluoroacetic acid, followed by extraction with diethyl ether. The crude product was purified by flash column chromatography on silica gel using a mixture of hexane and ethyl acetate as the eluent.

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