

Conversion of 1-(ω -Alkynyl)-1,2-propadienyl Sulfides to Bicyclic Dienones
by the Use of Iron Carbonyl Complex

Koichi NARASAKA and Takanori SHIBATA
Department of Chemistry, Graduate School of Science,
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

1-(ω -Alkenyl)-1,2-propadienyl sulfide reacts with $\text{Fe}(\text{CO})_4(\text{NMe}_3)$ under photo irradiation conditions and a cyclized and carbonylated η^3 -allyl mononuclear iron complex is isolated. On the other hand, the reaction of 1-(ω -alkynyl)-1,2-propadienyl sulfides and $\text{Fe}(\text{CO})_4(\text{NMe}_3)$ also proceeds by photo irradiation to give various bicyclic dienones through the η^3 -allyl iron complex.

The reactions of allenes and various metal carbonyl complexes were widely investigated,¹⁾ and with iron carbonyl complex, a unique binuclear complex was afforded in which one iron atom is π -bonded to the allyl group and another atom is σ -bonded to the center carbon of allyl ligand and two iron atoms are linked by a metal-metal bond (η^1, η^3 -bridging allyl complex).²⁾ In recent years, attention has been drawn to the iron carbonyl complexation with allenes possessing electron withdrawing groups:³⁾ Thermal reaction of allene carboxylate with $\text{Fe}_2(\text{CO})_9$ provided a cyclized and carbonylated trimethylenemethane complex.^{3a)} Photo irradiation of 1,2-propadienyl ketones with $\text{Fe}(\text{CO})_5$ gave lactones by carbonylation and successive demetallation.^{3d)}

We have reported 1,2-propadienyl and vinyl sulfides exhibit good reactivity in the reactions such as the [2+2] cycloaddition reaction with electron deficient olefins,⁴⁾ the aldol type addition reaction with aldehydes,⁵⁾ and the ene reaction with Schiff's bases.⁶⁾ Since the introduction of alkylthio group increases the electron density of olefins,⁷⁾ 1,2-propadienyl sulfides are expected to make complexes readily with metal carbonyl compounds. When such an iron complex is generated from 1,2-propadienyl sulfide having terminal olefinic moiety, successive intramolecular cyclization reaction would occur to give a cyclic η^3 -allyl iron complex.

1-(3-Butenyl)-1,2-propadienyl methyl sulfide (**1**), prepared by alkylation of 1-methylthio-1,2-propadienyl lithium with 4-bromo-1-butene, reacted with $\text{Fe}_2(\text{CO})_9$ by photo irradiation (Eq 1). In addition to the formation of η^1, η^3 -bridging allyl binuclear iron complex **3**⁸⁾ and $(\mu\text{-MeS})_2\text{Fe}_2(\text{CO})_6$,⁹⁾ the cyclic η^3 -allyl mononuclear iron complex **2** was obtained in 18% yield whose structure was established by X-ray crystallography as shown in Fig. 1.¹⁰⁾ By photo irradiation or heating in refluxing toluene, the complex **3** could not be converted to the cyclized complex **2**. This observation implies there are two different pathways for the formation of complex **2** and **3**, respectively, and the binuclear complex **3** is never an intermediate in the transformation of 1,2-propadienyl sulfide **1** to the cyclized product **2**.

Since the binuclear complex could not be converted to the mononuclear iron complex **2**, **2** was thought to be formed by the reaction of the propadienyl sulfide **1** with mononuclear iron carbonyl species generated from $\text{Fe}_2(\text{CO})_9$. Accordingly, the reaction was investigated by using some mononuclear iron carbonyl complexes to

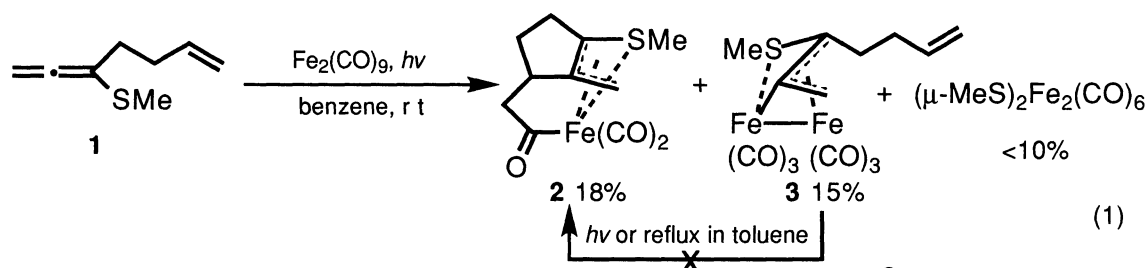
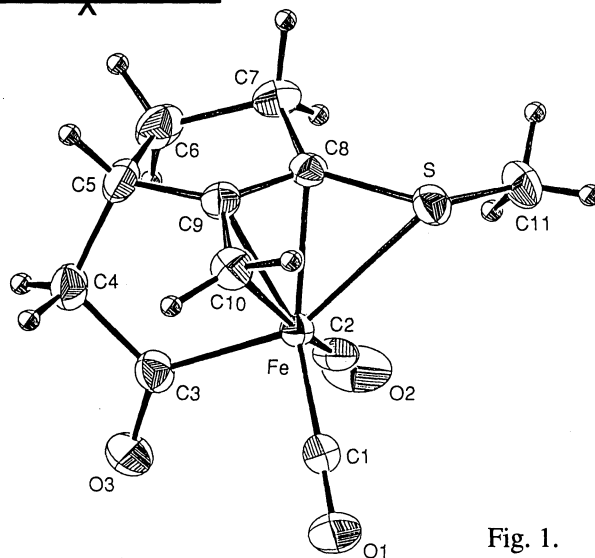


Table 1. Screening of Iron Carbonyl Complex

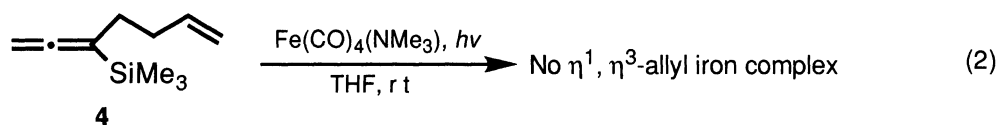
Fe complex	Condition	2	3 /%
Fe ₂ (CO) ₉	100 W <i>hν</i> , r t	18	15
	80 °C	23	15
	ultrasound	0	42
Fe(CO) ₅	400 W <i>hν</i> , r t	21	10
	150 °C	10	0
Fe(CO) ₃ (BDA) ¹²⁾	80 °C	<10	<10
Fe(CO) ₄ (acetone) ¹³⁾	r t	0	0
Fe(CO) ₄ (NMe ₃)	100 W <i>hν</i> , r t	40	15

BDA = benzylideneacetone



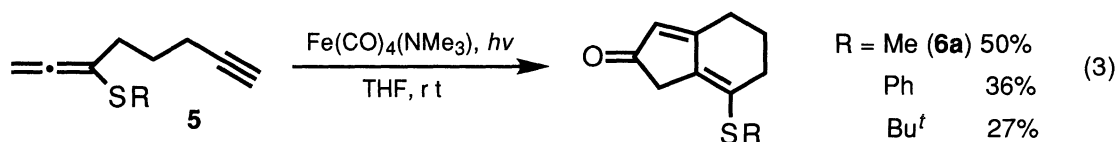
improve the yield of **2**. As shown in Table 1, the cyclized product **2** was provided in the best yield of 40% by photo irradiation at room temperature with Fe(CO)₄(NMe₃)¹¹⁾ which was prepared *in situ* from Fe(CO)₅ and trimethylamine *N*-oxide in THF, along with the formation of the binuclear complex **3** in 15% yield.

The reaction of 1,2-propadienyl silane **4**, a silicon analogue of **1**, was also examined but afforded no cyclic iron complex (Eq 2). Accordingly, alkylthio substituent plays a pivotal role in stabilizing monocyclic η³-allyl iron complex **2** to be isolated.



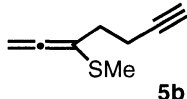
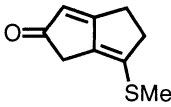
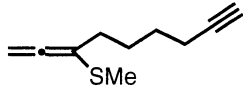
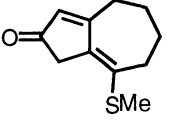
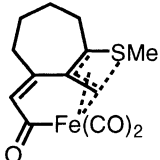
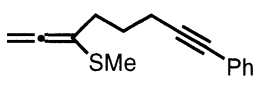
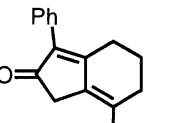
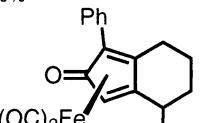
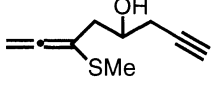
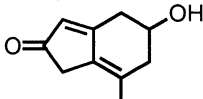
Methyl 1-(4-pentynyl)-1,2-propadienyl sulfide (**5a**), an acetylenic derivative of **1**, was submitted to the reaction in the presence of Fe(CO)₄(NMe₃) by photo irradiation.¹¹⁾ In contrast with the reaction of 1,2-propadienyl sulfide **1**, the reaction of **5a** with Fe(CO)₄(NMe₃) afforded no monocyclic π-allyl iron complex but a bicyclic dienone **6a** in moderate yield (Eq 3).

Iron carbonyl complexes have been known to promote intramolecular alkene-alkyne¹³⁾ and alkyne-alkyne¹⁴⁾ carbonylative coupling reactions. All these reactions proceed under high pressure of carbon monoxide or by heating over 130 °C. On the contrary, the intramolecular coupling reaction¹⁵⁾ between alkyne and allene functionality proceeded at ambient temperature under argon atmosphere.



Various 1-(ω -alkynyl)-1,2-propadienyl sulfides (**5a-5e**) were converted into [n.3.0] bicyclic dienones (n = 3-5) under the same reaction conditions (Table 2).¹¹⁾ In the reaction of **5c**, monocyclic π -allyl iron complex **7c** whose structure was ascertained by X-ray measurement was afforded as a major product. The reductive elimination from **7c** easily occurred by heating **7c** in refluxing benzene to give the bicyclic dienone **6c** in high yield (Entry 2). η^3 -Allyl mononuclear iron complex was a hypothetical intermediate in the intermolecular carbonylative cyclization reaction of allene and acetylene to methylenecyclopentenone.¹⁵⁾ The isolation of **7c** and transformation of **7c** to dienone **6c** definitely show that the η^3 -allyl mononuclear iron complex is really the intermediate, which was stably isolated with aid of the coordination of sulfur to iron atom. 1,2-Propadienyl sulfide **5d** possessing a substituted acetylene on the side chain also reacted under the same conditions,¹⁶⁾ giving bicyclic dienone **6d** in 30% yield. In addition to **6d**, (cyclopentadienone)iron complex **7d** was obtained in 19% yield (Entry 3). Existence of hydroxyl group in the tether of 1,2-propadienyl sulfide gave no effect on this reaction (Entry 4).

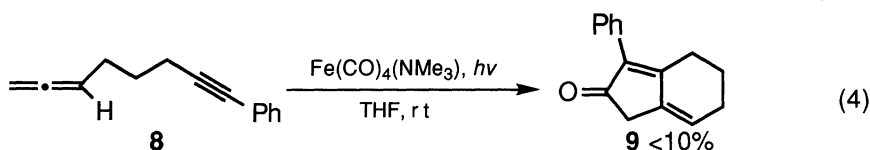
Table 2. Conversion of 1-(ω -Alkynyl)-1,2-propadienyl Sulfides to Dienones

Entry	Allenes	Products
1		 6b 60%
2		 6c 15%  7c 32% ↑ reflux in benzene
3		 6d 30%  7d 19% 80%
4		 6e 45%

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 - 11) General procedures using $\text{Fe}(\text{CO})_4(\text{NMe})_3$; to a Pyrex test tube equipped with argon balloon, trimethylamine N-oxide (225 mg, 3.0 mmol) and THF (4 ml) was charged. Addition of a THF solution (3 ml) of $\text{Fe}(\text{CO})_5$ (293 mg, 1.5 mmol) to the suspension at -30 $^\circ\text{C}$ gave a red solution of $\text{Fe}(\text{CO})_4(\text{NMe})_3$.¹⁷⁾ A THF solution (3 ml) of 1,2-propadienyl sulfide (0.5 mmol) was then added. After external photo irradiation by 100 W high pressure mercury lamp at room temperature, the resulting precipitates were removed by filtration through a small pad of silica gel. Purification of the crude products by preparative thin layer chromatography gave η^3 -allyl iron complex and dienone.
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