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

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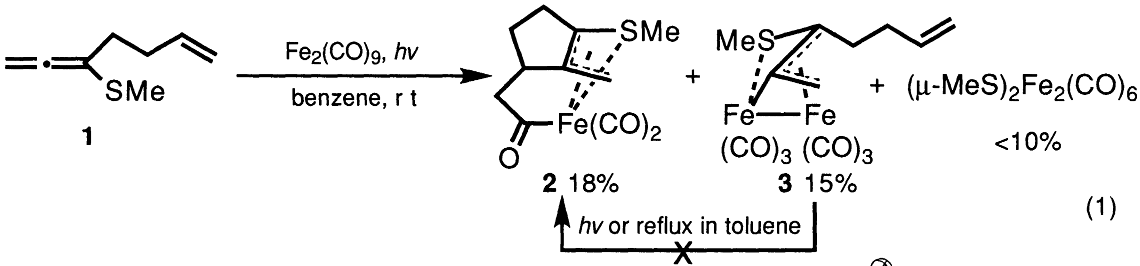
1-(ω–Alkenyl)-1,2-propadienyl sulfide reacts with $Fe(CO)_4(NMe_3)$ under photo irradiation conditions and a cyclized and carbonylated η^3-allyl mononuclear iron complex is isolated. On the other hand, the reaction of 1-(ω–alkynyl)-1,2-propadienyl sulfides and $Fe(CO)_4(NMe_3)$ also proceeds by photo 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 $Fe_2(CO)_9$ provided a cyclized and carbonylated trimethylenemethane comlpex.3a) Photo irradiation of 1,2-propadienyl ketones with $Fe(CO)_5$ 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 $Fe_2(CO)_9$ by photo irradiation (Eq 1). In addition to the formation of η^1,η^3-bridging allyl binuclear iron complex **3**8) and $(\mu\text{-MeS})_2Fe_2(CO)_6$,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 $Fe_2(CO)_9$. Accordingly, the reaction was investigated by using some mononuclear iron carbonyl complexes to



(1)

Table 1. Screening of Iron Carbonyl Complex

Fe complex	Condition	2	3 /%
$Fe_2(CO)_9$	100 W hν, r t	18	15
	80 °C	23	15
	ultrasound	0	42
$Fe(CO)_5$	400 W hν, 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 hν, r t	40	15

BDA = benzylideneacetone

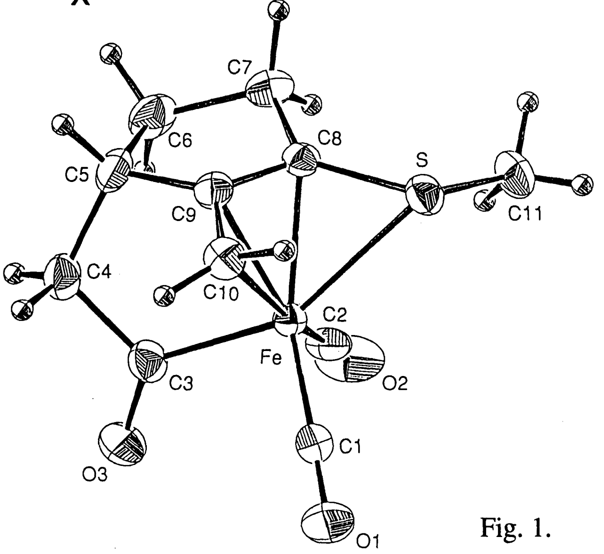
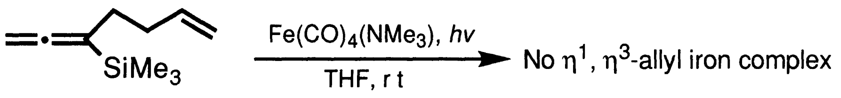


Fig. 1.

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 $Fe(CO)_4(NMe_3)$[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 η^3-allyl iron complex **2** to be isolated.



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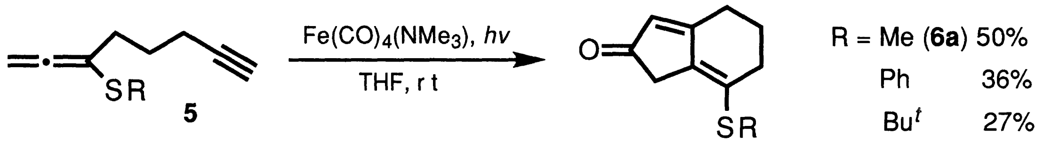
(2)

Methyl 1-(4–pentynyl)-1,2-propadienyl sulfide (**5a**), an acetylenic derivative of **1**, was submitted to the reaction in the presence of $Fe(CO)_4(NMe_3)$ by photo irradiation.[11] In contrast with the reaction of 1,2-propadienyl sulfide **1**, the reaction of **5a** with $Fe(CO)_4(NMe_3)$ afforded no monocyclic π–allyl iron complex but a bicyclic dienone **6a** in moderate yield (Eq 3).

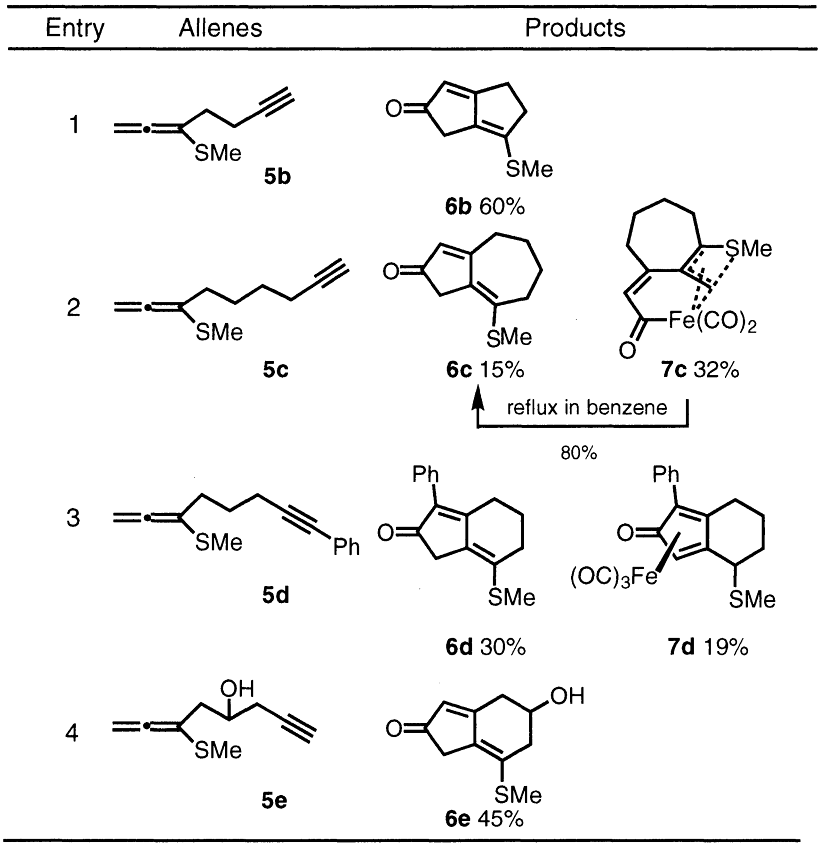
Iron carbonyl complexes have been known to promote intramolecular alkene-alkyne[13] and alkyne-alkyne[14] carbonylative coupling reactions. All these reactions proceed under high pressure of carbon monoxide or by heating over 130 °C. On the contrary, the intramolecular coupling reaction[15] between alkyne and allene functionality proceeded at ambient temperature under argon atmosphere.



(3)

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



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10) Crystallographic data: MF = $C_{11}H_{12}FeO_3S$, MW = 280.12, monoclinic, a = 7.93 (1), b = 11.039(4), c = 13.622(3) (Å), V = 1179(1) (Å^3), β = 98.40(4)°, space group $P2_1/n$, Z = 4, Dc = 1.577 g/cm^3, μ(MoKα) = 14.34 cm^{-1}. Data collection: Crystal size = 0.2 x 0.1 x 0.1 mm, Tc = 24 °C, MoKα radiation (graphite monochrometer), 3071 independent reflections ($2\theta < 55.1°$). The structure was finally refined anisotropically for Fe, S, O, and C and isotropically for H to give an R factor of 0.036 for 1930 reflections with $Fo > 3\sigma$ (Fo).

11) General procedures using $Fe(CO)_4(NMe)_3$; 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 $Fe(CO)_5$ (293 mg, 1.5 mmol) to the suspension at -30 °C gave a red solution of $Fe(CO)_4(NMe)_3$.[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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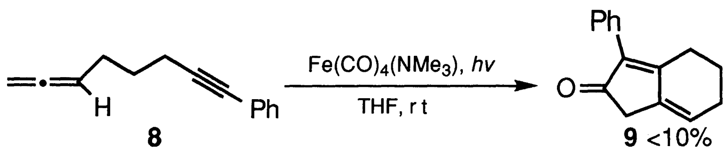
16) The reaction of 1-(ω-alkynyl)-1,2-propadiene **8** was examined under the same conditions (Eq 4), but gave a complex mixture including a small amount of the bicyclic dienone **9**. Therefore introduction of alkylthio group controls the reaction to give the intramolecular alkyne -allene carbonylative coupling products.



(4)

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