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Transition metal heterocyclic chemistry

IX *. An α-selenoketoketene. Trapping subsequent to oxidative release from tricarbonyliron complexes to form vinyl selenides

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Abstract

Treatment of α-selenoketocyclohexylene-$Fe_2(CO)_6$ (**1**) and the related α-selenoketoketene complex (**2**) with trimethylamine oxide leads to the formation of a transient α-selenoketoketene, a previously unknown species. The transient species may be trapped by alcohols to produce esters of bis(2-carboxy-1-cyclohexenyl)diselenide, examples of vinylselenides. Reductive elimination of selenium from these esters using Raney Nickel leads to the formation of the cyclohexane carboxylate esters.

Introduction

The use of transition metal complexes to effect stoichiometric and catalytic transformations in organic chemistry is now a mature practice [2,3]. There is considerably less information concerning such use in the area of heterocyclic chemistry [4]. Our studies of the reactions of selena- and thia-diazoles with metal complexes have resulted in a range of complexes containing new hetero-organic fragments complexed to transition metal centers. Among the complexes isolated are those derived from α-thio(seleno)keto-carbenes [5,6,7], -ketenes [7], -imines [8], and α-diazothioketones [9]. These complexes are crystalline materials in which the hetero-organic fragment bridges a $Fe_2(CO)_6$ moiety, and all have been characterized, inter alia, by single crystal X-ray structural analysis. There are no literature references to these various hetero-organic species, therefore we have studied the potential of these complexes to generate the decomplexed ligand as synthons, anticipating that such studies will broaden the range of such species available for further synthetic transformations.

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[*] For part VIII see ref. 1.

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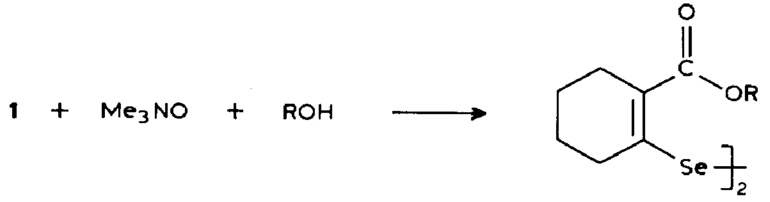
Subsequent to the initial report by Shvo [10] on the use of trimethylamine oxide as a mild oxidizing agent for the removal of dienes from their Fe(CO)$_3$ complexes, this technique has become a widely accepted synthetic procedure. In this article we report the use of Me$_3$NO to release an α-selenoketo-carbene or -ketene from their respective Fe$_2$(CO)$_6$ complexes, **1** and **2**, in the presence of alcohols.

Results and discussion

Under mild conditions, the reaction between trimethylamine oxide and α-selenoketocyclohexylene-Fe$_2$(CO)$_6$ (**1**) in the presence of ROH as solvent (R = Me, Et, i-Pr) leads to moderate to good yields of the corresponding diselenide esters **3**.



(1)

(**3a** : R = Me ;
3b : R = Et ;
3c : R = i-Pr)

Improved yields may be obtained by starting with the preformed α-selenoketoketene complex (**2**).

These results indicate that Scheme 1 represents a reasonable mechanism for the chemistry observed in these reactions and represent the first examples of an α-selenoketoketene.

It is apparent that regardless of whether the starting complex is a carbene (**1**) or ketene complex (**2**), the organic fragment liberated is the ketene species. Clearly in the case of the carbene complex, release of the ligand fragment is associated with a carbonylation. This phenomenon has been observed in other oxidative removal reactions from metal carbonyl complexes [11,12]. The higher yields of the products derived from the ketene complex is thus expected since it implies a single reaction process rather than two.

The above reaction sequence provides a novel route to vinylselenides which are potentially useful synthons. As a simple demonstration of the reactivity of such species we treated one of the diselenides (**3a**) with Raney Nickel in an ethanol/benzene solvent. This reaction produced the facile reductive elimination of selenium resulting in the formation of methyl cyclohexane-carboxylate.

Since the starting complexes are formed from selenadiazoles, which themselves are synthesized from related ketones [13*], the overall process operative in this new chemistry is the transformation of ketones to related carboxylic esters, as shown in Scheme 2. This is not claimed as an optimum pathway to the formation of alkane

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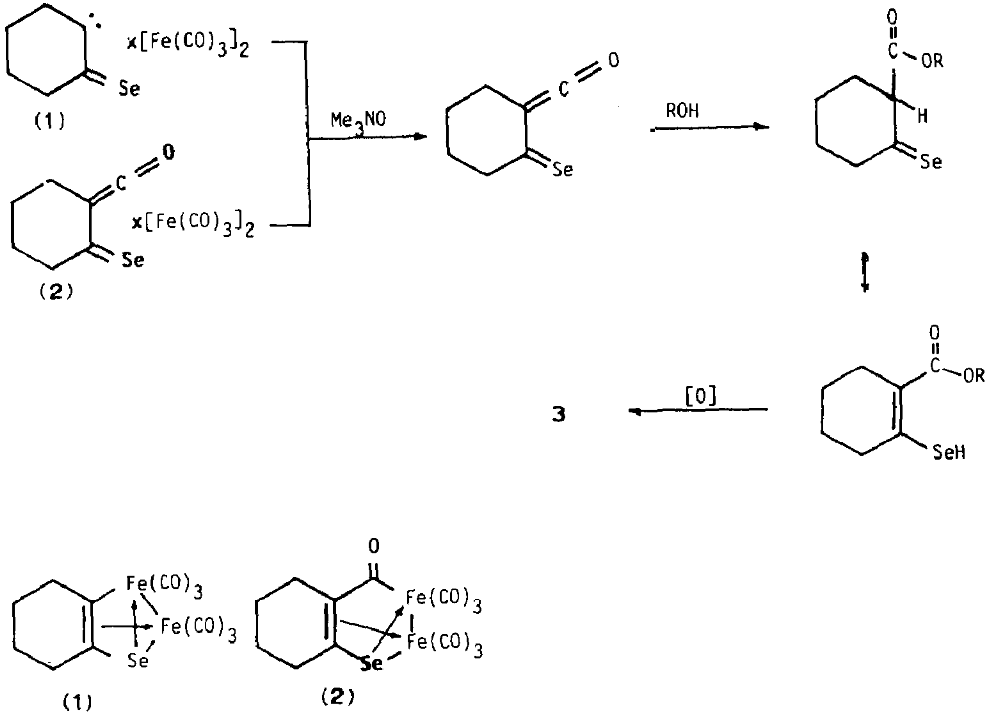
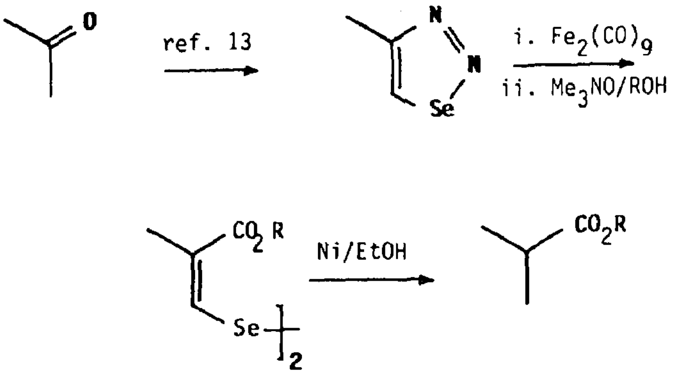
* Reference number with asterisk indicates a note in the list of references.



Scheme 1.



Scheme 2.

carboxylic esters, but is rather a simple illustration of the potential of the trapping of the selenoketoketenes, and in particular the formation of vinylselenides.

Experimental

The $Fe_2(CO)_6$ complexes were synthesized by literature procedures from selenadiazoles and $Fe_2(CO)_9$ [5,6,7]. All solvents used are dry and oxygen free. Analyses were performed by Galbraith Laboratories Inc., Knoxville, TN. A typical reaction procedure is outlined below.

Table 1

Analytical and spectral data for compounds **3a**, **3b**, and **3c**

Compound	M.p.	Yield (%)	ν(CO) [a] (cm^{-1})	^1H NMR [b]	Analysis (Found (calcd.) (%))	
					C	H
3a	162–163	63	1678	CH_3 3.74	44.2	5.26
					(44.1)	(5.08)
3b	140–141	33	1671	CH_3, 1.3(t)	46.5	5.72
				CH_2, 4.23(q)	(46.6)	(5.64)
3c	127–129	20	1668	CH_3, 1.26(d)	48.8	6.30
				CH, 5.1(spt)	(48.8)	(6.14)

[a] CH_2Cl_2 solvent. [b] $CDCl_3$ solvent, values in ppm relative to tetramethylsilane. The protons of the cyclohexenyl ring are multiplets in the region 2.5–1.6 ppm.

Reaction of α-selenoketocyclohexylene-$Fe_2(CO)_6$ (1) with Me_3NO in MeOH

A mixture of 0.50 g (1.14 mmol) of the title complex and 5.0 g (67 mmol) of sublimed trimethylamine oxide in 50 ml of dry methanol was stirred for 4 h after which time a brown precipitate was observed. The mixture was heated to reflux for 2 h, then the solvent was removed under reduced pressure. The residue was extracted with methylene chloride and the resulting solution concentrated to 3 ml and placed upon a neutral alumina column, (1 × 15 cm). Initial elution with hexane developed a slow moving yellow band which upon elution with methylene chloride produced a pale yellow solution. Removal of the solvent resulted in a pale yellow solid, **3a**, which was recrystallized from ethanol (0.16 g 0.36 mmol, 63%). Spectral and analytical data for the various compounds are presented in Table 1. A similar reaction with the selenoketoketene complex (**2**, 0.5 g, 1.07 mmol) resulted in the recovery of 0.20 g (0.46 mmol, 86%) of the same product.

Treatment of 3a with Raney nickel

To a solution of **3a**, (2.6 g, 5.96 mmol) in 60 ml of a 1/2 ethanol/benzene mixture was added 0.25 g of Raney nickel. The solution was heated to reflux for 12 h. Filtration of the solution was followed by distillation of the solvent and the resulting liquid to yield 0.36 g (2.53 mmol, 21%) of methyl cyclohexane carboxylate, b.p. 180 °C (lit. 183 °C [14]).

Acknowledgements

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