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Iron Carbonyl-catalyzed Reactions of Allyl Ethers and Amines Involving Claisen-type Rearrangement

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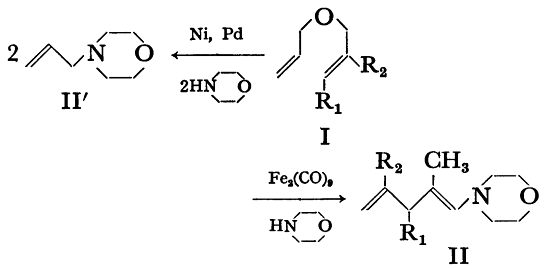
Synopsis. The iron carbonyl-catalyzed reaction of diallyl ether with morpholine gives 1,4-dienylamine. Diallylamine isomerizes to 4-aza-6-methyl-1,4-nonadiene.

Allylic compounds such as allyl alcohol or diallyl ether undergo a variety of reactions under the influence of transition metal complexes. Palladium-,[1] nickel-,[2] rhodium-,[3] and ion carbonyl-[4] catalyzed reactions have already been reported. These reactions attracted our attention from a view-point of synthetic application. Iron carbonyl reacts with cyclic compounds, which have a nitrogen or oxygen atom at the allylic position, resulting in interesting intermediates.[5,6] These reports prompted us to investigated the iron carbonyl-catalyzed reactions of some allylic compounds.

Results and Discussion

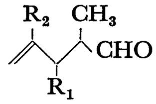
In the presence of $Fe_2(CO)_9$ diallyl ether (I) reacted with morpholine to give 1,4-dienylamine (II) in moderate yield, while nickel[2] and palladium[7]-catalyzed reactions give allyl amine (II'). A considerable amount of diallyl ether was recovered unchanged in each case.



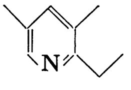
(1)

a: $R_1=R_2=H$, 40%.
b: $R_1=CH_3$, $R_2=H$, 27%.
c: $R_1=H$, $R_2=CH_3$, 17%.

The structure of II is indicated by spectroscopic data. This reaction can be explained reasonably by the isomerization of the double bond, followed by Claisen rearrangement and condensation of the substituted 4-pentanal (III) with morpholine. In fact, the diallyl ether isomerized to III in a very low yield without morpholine. Morpholine was superior to piperidine and benzylamine with regard to the yield of II.



III



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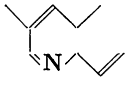
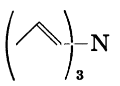


V



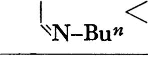
VI

These facts show that the $Fe_2(CO)_9$–morpholine system plays a significant role in the isomerization of the double bond. Under these conditions, however, no reaction was observed with dimethallyl ether and allyl phenyl ether.

The reaction of the allylamines is interesting to note. The reaction of diallylamine catalyzed by $Fe(CO)_5$ or $Fe_2(CO)_9$ in a sealed tube at 160 °C gave 2,3,5-trisubstituted pyridine (IV). However, at *ca.* 112 °C (reflux) linear amine (V) was formed in moderate yield (see Table 1). Falbe *et al.*[8] have reported that the reaction of allylamine $C_3H_5NH_2$ catalyzed by $Fe(CO)_5$ at 250 °C at a high pressure of carbon monoxide forms IV through the formation of V in a 30% yield. The reaction of diallylamine takes place under more mild conditions than those of the latter. Therefore, it seems probable that the first step of the Falbe reaction is the formation of diallylamine, since the primary amine is converted to the secondary or tertiary amine under the influence of transition metal catalysts.[9]

This reaction is also explainable in terms of Claisen-"type" rearrangement. Triallylamine seems to be a key intermediate of this reaction. To gain insight into the reaction, triallylamine was allowed to react in the presence of $Fe_2(CO)_9$. In this case, however, rapid isomerization of the double bond occurred and VI was formed in high yield (>80%), *i.e.*, this isomerization is so fast that Claisen-"type" rearrangement does not take

Table 1. Reaction of allylamines

Run No.	Allylamine (mmol)		Catalyst (mmol)		Reaction Temp. (C)	Reaction Time (h)	Product yield % (mmol)
1	$(C_3H_5)_2NH$,	8.1	$Fe(CO)_5$,	0.5	160	20	V, 42 (1.7)
2	$(C_3H_5)_2NH$,	16.2	$Fe_2(CO)_9$,	0.1	112	10	V, 52 (4.2)
3	$(C_3H_5)_3N$,	6	$Fe_2(CO)_9$,	0.03	120	7	VI>80
4	$(C_3H_5)_3N$,	6	$Pd(NO_3)_2$, $n\text{-}Bu_3P$	0.15 0.4	110	20	VI, 14
5	$(C_3H_5)_3N$, Morpholine,	6 1 ml	$Fe_2(CO)_9$,	0.1	120	20	, 32
6	$(C_3H_5)_2N\text{-}Bu^n$,	6	$Fe_2(CO)_9$,	0.1	160	20	 <10

place. The use of morpholine as the solvent in this reaction resulted in the formation of *N*-(1-propenyl)morpholine (II′). The isomerization of the double bonds of triallylamine by $Fe_2(CO)_9$ proceeded more smoothly than the *t*-BuOK-catalyzed isomerization. Gas chromatographic analysis of the products of the latter reaction showed the presence of many isomers and the yields were in general low.

Experimental

Reactions. All the reactions were carried out in a sealed glass tube (8 mm in diameter).

Diallyl Ether with Morpholine: Iron enneacarbonyl (0.06 mmol) was placed in the tube. The tube was fitted with a three-way stopcock, through which the reagents were introduced by a syringe. Diallyl ether (0.5 ml, *ca.* 4 mmol) and morpholine (1 ml) were added in an atmosphere of argon. The tube was sealed with a flame and heated at 120 °C for 20 h.

Allylamines: All the reactions except run 2 (Table 1) were carried out in a manner similar to that described above. The reaction conditions are summarized in Table 1.

Analysis and Identification. Gas chromatographic analysis was performed on a column of Silicon DC 550 on Celite, 3 m in height, at 100—200 °C, using tetralin or *p*-xylene as an internal standard. The products were identified by analyzing the mass, IR and NMR spectra of the samples collected by gas chromatography.

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