

**REACTIONS OF ALLYLIC COMPOUNDS SUCH AS ALLYL ALCOHOLS,
ALLYL ETHERS, AND ALLYLAMINES USING
trans-Mo(N₂)₂(Ph₂PCH₂CH₂PPh₂)₂**

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Summary

Double-bond migration of allylic alcohols and allylic alkyl ethers was catalytically effected with *trans*-Mo(N₂)₂(dpe)₂ (dpe = Ph₂PCH₂CH₂PPh₂). Decarbonylation occurred simultaneously in the case of allyl alcohol. Diallyl ether and allyl phenol ether gave the fragmentation products presumably through initial oxidative addition of the allyl–O bond. Allylamine was converted to *N*-propylideneallylamine and NH₃. *N,N*-Dimethylallylamine was isomerized to *N-trans*-propenyldimethylamine, which was further transformed into 4-dimethylamino-1,3-hexadiene and dimethylamine on addition of oxygen. The catalytic allylation of methyl acetoacetate with allylic ethers and amines was achieved by use of *trans*-Mo(N₂)₂(dpe)₂.

Introduction

The dinitrogenmolybdenum complex, *trans*-Mo(N₂)₂(dpe)₂ (dpe = Ph₂-PCH₂CH₂PPh₂), I, catalyzes the double-bond migration of α -olefins [1], which is presumed to occur by way of oxidative addition of an allylic C–H bond affording a π -allyl hydride type intermediate [2]. It is also known that I reacts with allyl acetate to give propylene and an acetate complex, arising from cleavage of the allyl–O bond, followed by hydrogen transfer from dpe to the allyl moiety [3]. The ready availability of allylmolybdenum complexes turned our attention towards the reaction of I with a variety of allylic compounds. We now wish to report double-bond migration of allylic alcohols, allylic ethers, and allylamines, C–O bond cleavage of allylic ethers, and allylation of methyl acetoacetate, effected with I. Very recently, Trost and Lautens have reported stoichiometric and catalytic allylic substitution reactions involving molybdenum complexes [4].

Results and discussion

Reactions of allylic alcohols and ethers

When a mixture of 1-butene-3-ol (5 mmol) and I (0.1 mmol) in benzene (4 ml) was refluxed under N_2 for 1 h, methyl ethyl ketone was obtained in 100% yield. In view of the observation that $Mo(\pi\text{-allyl})H(dpe)_2$ is formed by the reaction of I and propylene [2], the isomerization probably proceeded by a mechanism involving a π -allyl hydride species and an enol intermediate, as is the case for the rearrangement of allylic alcohols by $Fe(CO)_5$ [5]. As shown in Table 1, $MoH_4(dpe)_2$ was also effective as catalyst. In this case the hydride ligands are thought to be transferred to the unsaturated substrates to afford a Mo^0 species [1b], similar to that from I. In fact, the formation of 2-butanol was confirmed.

When allyl alcohol was employed, the isomerization was accompanied by decarbonylation of allyl alcohol or the resulting propionaldehyde giving ethylene, ethane, and *cis*- $Mo(CO)_2(dpe)_2$ [6]. Since the carbonyl complex is inactive in the double-bond migration, the yield of propionaldehyde was relatively low.

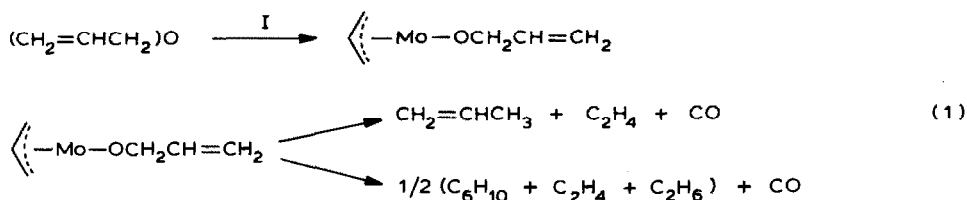
The activity of I for the double-bond migration of allylic ethers was not so high (Table 1). *Cis-trans* mixtures of the corresponding vinyl ethers were obtained. The sensitivity of the double-bond migration to variations in substituents on the allyl residue has been studied. Although methyl crotyl ether was isomerized, methyl methallyl ether remained unchanged. Many catalytic systems consisting of Group VIII metals for the isomerization of allylic alcohols [7] and allylic ethers [8] have been described.

No double-bond migration occurred when diallyl ether and allyl phenyl ether were employed. Treatment of diallyl ether with I in benzene at reflux for 40 min resulted in the formation of ethylene (15%), ethane (26%), propylene (28%), hexadienes (9%) and *cis*- $Mo(CO)_2(dpe)_2$ (28%, isolated yield), (the yields are based on I). The formation of the products may be accounted for by assuming oxidative addition of the ether to Mo^0 , involving cleavage of the allyl-O bond followed by hydrogen transfer and decarbonylation. Hexadienes, as minor products, are probably due to a coupling reaction between two allyl groups. The amount of ethylene was

TABLE 1
ISOMERIZATION OF ALLYLIC ALCOHOLS AND ETHERS ^a

Substrate	S/Mo Mol ratio	Time (h)	Product	
			Yield(%)	<i>cis/trans</i> ratio
$CH_2=CHCH(OH)CH_3$	50	1	$CH_3COC_2H_5$ (100)	
$CH_2=CHCH(OH)CH_3$	100	1	$CH_3COC_2H_5$ (69)	
$CH_2=CHCH(OH)CH_3^b$	20	1	$CH_3COC_2H_5$ (95)	
$CH_2=CHCH_2OH$	20	1	C_2H_5CHO (20)	
$CH_2=CHCH_2OH^b$	20	1	C_2H_5CHO (27)	
$CH_2=CHCH_2OCH_3$	10	4	$CH_3CH=CHOCH_3$ (44)	48/52
$CH_2=CHCH_2OC_2H_5$	10	4	$CH_3CH=CHOC_2H_5$ (74)	53/47
$CH_3CH=CHCH_2OCH_3$	10	4	$C_2H_5CH=CHOCH_3$ (44)	35/65
$CH_2=C(CH_3)CH_2OCH_3$	10	4	no reaction	

^a 0.1 mmol *trans*- $Mo(N_2)_2(dpe)_2$ in 4 ml benzene, refluxed under N_2 . ^b 0.1 mmol $MoH_4(dpe)_2$.



smaller than that predicted by eq. 1. This may be due to hydrogen transfer from dpe to ethylene, as was observed in the reaction of 1-hexene with I [Ib]. The ethane/ethylene ratio changed with time from 1.1 (reaction time $t = 20$ min) to 1.7 ($t = 40$ min), supporting the hydrogen transfer.

Allyl phenyl ether reacted with I to give equimolar amounts of propylene and phenol and a complex which has proven difficult to characterize. We have previously reported that the reaction of phenyl acetate with I gives methane and phenol [3]. In either case the source of hydrogen transferred seems to be dpe. Cleavage of the C-O bond of allylic ethers by Ni [9a,b] and Rh [9c] complexes has been reported.

Reactions of allylic amines

Relatively little is known about the double-bond migration of allylic amines. Base-catalyzed double-bond migration of allylic amines has been used to prepare enamines [10], which are very active species and widely used in organic synthesis.

Treatment of *N,N*-dimethylallylamine with I in toluene at reflux for 2 h gave *N-trans*-propenyldimethylamine in 100% yield (stereoselectivity 100%). Pertinent data are shown in Table 2. Upon irradiation with UV light, $\text{MoH}_4(\text{dpe})_2$ exhibited a fairly good activity for the isomerization. Without UV irradiation, it proved to be practically inactive. Photoinduced elimination of H_2 from $\text{MoH}_4(\text{dpe})_2$ may lead to a coordinatively unsaturated active species [11]. Although *N,N*-diethylallylamine was similarly converted to the corresponding *trans*-propenylamine, the presence of methyl substituent(s) in the allyl group prevented the isomerization; $\text{CH}_3\text{CH}=\text{CHCH}_2\text{N}(\text{CH}_3)_2$, $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2$, and $(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{N}(\text{C}_2\text{H}_5)_2$ were recovered unchanged.

More conveniently, a Mo catalyst is prepared in situ from $\text{Mo}(\text{acetylacetonate})_3$, with dpe and triethylaluminum (mol ratio, 1:2:10). Satisfactory yields were obtained as compared to I. In a nitrogen atmosphere, this Ziegler-type mixture is well

TABLE 2
REACTIONS OF ALLYLIC AMINES^a

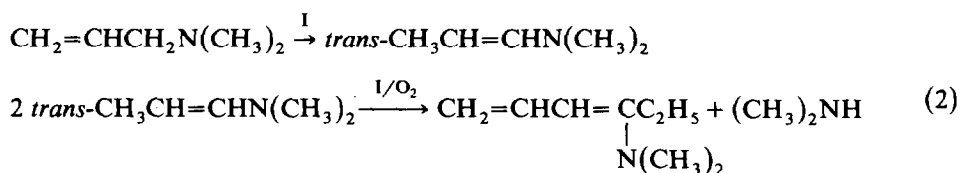
Allylic amines	Mo complex	Temp. (°C)	Time (h)	Product yield(%)
$\text{CH}_2=\text{CHCH}_2\text{N}(\text{CH}_3)_2$	I	rfx	2	<i>trans</i> - $\text{CH}_3\text{CH}=\text{CHN}(\text{CH}_3)_2$ (100)
$\text{CH}_2=\text{CHCH}_2\text{N}(\text{CH}_3)_2$	II	100	4	<i>trans</i> - $\text{CH}_3\text{CH}=\text{CHN}(\text{CH}_3)_2$ (80)
$\text{CH}_2=\text{CHCH}_2\text{N}(\text{C}_2\text{H}_5)_2$	I	rfx	2	<i>trans</i> - $\text{CH}_3\text{CH}=\text{CHN}(\text{C}_2\text{H}_5)_2$ (100)
$\text{CH}_2=\text{CHCH}_2\text{N}(\text{C}_2\text{H}_5)_2$	II	100	4	<i>trans</i> - $\text{CH}_3\text{CH}=\text{CHN}(\text{C}_2\text{H}_5)_2$ (50)
$\text{CH}_2=\text{CHCH}_2\text{N}(\text{C}_2\text{H}_5)_2$	III	100	5	<i>trans</i> - $\text{CH}_3\text{CH}=\text{CHN}(\text{C}_2\text{H}_5)_2$ (100)
$\text{CH}_2=\text{CHCH}_2\text{NH}_2$	I	100	1.5	$\text{C}_2\text{H}_5\text{CH}=\text{NCH}_2\text{CH}=\text{CH}_2$ (72)

^a 0.1 mmol Mo complex, 10 mmol allylic amine in 10 ml toluene, rfx; refluxed, I; *trans*- $\text{Mo}(\text{N}_2)_2(\text{dpe})_2$, II; $\text{MoH}_4(\text{dpe})_2$ on UV irradiation, III; $\text{Mo}(\text{acetylacetonate})_3/\text{dpe}/\text{Al}(\text{C}_2\text{H}_5)_3$ (mol ratio, 1/2/10).

known to give I [12]. When PPh_3 was employed in place of dpe , no isomerization was observed. Exclusive formation of *trans* enamines was also reported in the Co complex-catalyzed isomerization of allylic amines [13].

Of great interest is the fact that introduction of oxygen into the reaction mixture containing the isomerization product, *N-trans*-propenyldimethylamine, and I at ambient temperature or 40°C resulted in the formation of 4-dimethylamino-1,3-hexadiene and dimethylamine. Figure 1 shows the effect of the O_2/Mo ratio on the enamine conversion at 40°C 20 h after the addition of O_2 . A O_2/Mo ratio of ca. 1.5 gave the best result for the reaction; 4-dimethylamino-1,3-hexadiene (54% based on the starting amine) and dimethylamine were obtained. Five isomers of dimethylaminohexadienes and three isomers of dimethylaminononatrienes were also confirmed as the by-products. Without addition of oxygen, the yields of the coupling products and dimethylamine were negligibly small. When oxygen ($\text{O}_2/\text{Mo} = 1.5$) was initially added, no reaction of *N,N*-dimethylallylamine occurred.

This coupling reaction is reminiscent of the 1:1 reaction of enamines with allylic amines [14a] or π -allyl-Pd complexes [14b]. When the double-bond migration of *N,N*-dimethylallylamine was interrupted at the stage of ca. 50% conversion and followed by addition of oxygen, however, only the enamine was consumed with the formation of half as much dimethylaminohexadienes and dimethylamine as the consumed enamine. Therefore, it is reasonable to assume that dimethylaminohexadienes were formed by the reaction of two molecules of *N-trans*-propenyldimethylamine (eq.2). To the best of our knowledge, there is no example known of such dimerization accompanied by elimination of amines. Further work is necessary to clarify the mechanism of this reaction and the role of oxygen.



The reaction of allylamine in the presence of I gave *N*-propylideneallylamine and

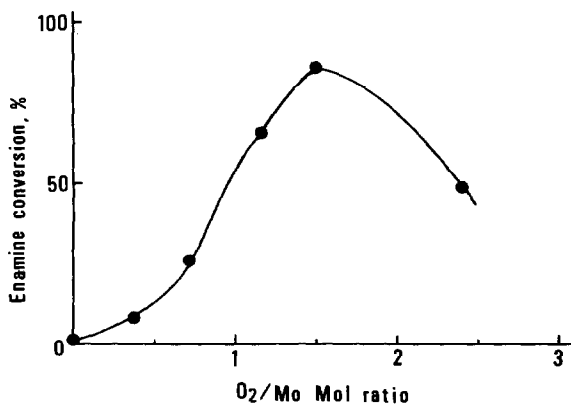
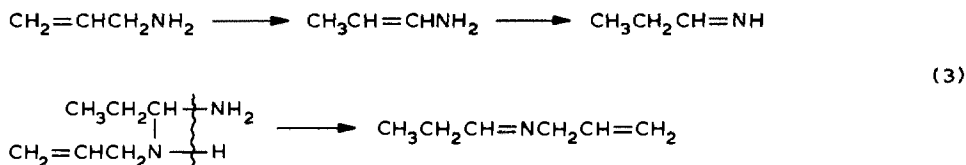


Fig. 1. Effect of O_2/Mo mol ratio on the conversion of *N-trans*-propenyldimethylamine.

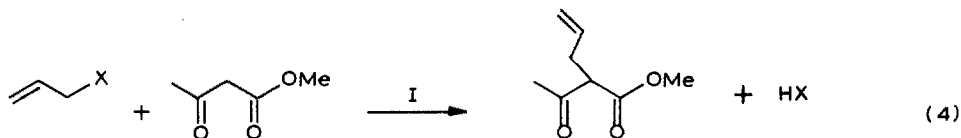
ammonia. This reaction occurred in the strict absence of oxygen and can be illustrated by addition of allylamine to the intermediate imine derived from double-bond migration of allylamine, followed by elimination of ammonia, as shown in eq. 3. No reaction took place when primary alkylamines were allowed to react with I. This is in contrast with the action of Pd black, which catalyzed the exchange reaction of alkylamines as well as allylamine [15].



Allylation of methyl acetoacetate with allylic ethers and amines

Allylation of amines, alcohols, phenols, carboxylic acids, and active methylene compounds and their salts can be catalytically effected with Pd complexes [16]. This reaction is postulated to proceed via π -allylpalladium intermediates, formed by oxidative cleavage of the allyl-O or allyl-N bond. Facile cleavage of the C-O bonds of allyl acetate and allyl ethers by I prompted us to investigate the allylation of active hydrogen compounds with allylic compounds in the presence of I.

Reaction of methyl acetoacetate, allyl phenyl ether and I at 150°C gave methyl 2-acetyl-4-pentenoate and phenol in good yields (eq. 4, X = PhO). To determine the effectiveness as an allylating agent, several compounds were examined (Table 3). No



allyl transfer occurred when allyl methyl ether or allyl acetate was employed.

TABLE 3
ALLYLATION OF METHYL ACETOACETATE (MAA)^a

Allylic compounds	(mmol)	MAA (mmol)	Product yield (%)
CH ₂ =CHCH ₂ OC ₆ H ₅	5	25	84
CH ₂ =CHCH ₂ OC ₆ H ₅	10	5	5 ^b
CH ₂ =CHCH ₂ N(CH ₃) ₂	5	25	CH ₂ =CHCH ₂ CH(COCH ₃)CO ₂ CH ₃
CH ₂ =CHCH ₂ N(CH ₃) ₂	10	10	
CH ₂ =CHCH ₂ N(C ₂ H ₅) ₂	5	25	53
CH ₂ =CHCH ₂ N(C ₂ H ₅) ₂	10	10	2
CH ₃ CH=CHCH ₂ N(CH ₃) ₂ ^c	5	25	CH ₃ CH=CHCH ₂ CH(COCH ₃)CO ₂ CH ₃
CH ₃ CH=CHCH ₂ N(CH ₃) ₂ ^c	10	10	
CH ₂ =C(CH ₃)CH ₂ N(C ₂ H ₅) ₂ ^c	5	25	CH ₂ =C(CH ₃)CH ₂ CH(COCH ₃)CO ₂ CH ₃
CH ₂ =C(CH ₃)CH ₂ N(C ₂ H ₅) ₂ ^c	10	10	
(CH ₃) ₂ C=CHCH ₂ N(C ₂ H ₅) ₂ ^c	5	25	(CH ₃) ₂ C=CHCH ₂ CH(COCH ₃)CO ₂ CH ₃

^a 0.1 mmol *trans*-Mo(N₂)₂(dpe)₂, heated under reflux (bath temp. 120–150°C) under N₂ for 4 h.

^b Diallylated compound was obtained (2%). ^c Reaction time, 8 h.

Moreover, allyl methyl ether was not isomerized at all in the presence of methyl acetoacetate. Interestingly, allyl and substituted-allylamines were found to be effective for the allylation of methyl acetoacetate. Methyl substituent(s) in the allyl residue had a small retarding effect on the reactivity of allylic amines. Addition of a large excess of methyl acetoacetate to allylic compounds was favorable for obtaining the products in fairly good yields. When twice as much allyl phenyl ether as methyl acetoacetate was allowed to react, a small amount of diallyl derivative was observed. Acetic acid was unreactive to allyl phenyl ether in the presence of I. A combination of $\text{Mo}(\text{acetylacetonate})_3$, dpe and triethylaluminum did not show any activity for the reaction of methyl acetoacetate with *N,N*-diethylallylamine.

Experimental

$\text{Mo}(\text{acetylacetonate})_3$ [18], *trans*- $\text{Mo}(\text{N}_2)_2(\text{dpe})_2$, I [12], and $\text{MoH}_4(\text{dpe})_2$ [19] were prepared by the methods described in the literature. Allylic alkyl ethers [20], *N,N*-diethylallylamine [21], *N,N*-dimethylcrotylamine [22], *N,N*-diethylmethallylamine [21], and *N,N*-diethylprenylamine [23] were prepared by the methods in the literature. Other organic reagents were purchased, dried and purified by distillation.

All the reactions were carried out under a nitrogen atmosphere. IR, ^1H NMR, ^{13}C NMR, and mass spectra were recorded with a Hitachi 215 spectrometer, a Hitachi R-40 instrument, a JEOL PS-100 instrument, and a Hitachi M-52 spectrometer, respectively. UV irradiation was conducted with a Ushio HB-501A mercury lamp.

Reaction of 1-butene-3-ol

A solution of 1-butene-3-ol (5 mmol) and I (0.1 mmol) in benzene (4 ml) was refluxed for 1 h. The mixture turned reddish brown; analysis by GLC on a PEG 20M/Chromosorb W column indicated that methyl ethyl ketone was obtained in 100% yield. Addition of hexane deposited the starting material, I, quantitatively, which was confirmed by IR.

Reaction of allyl alcohol

A solution of allyl alcohol (2 mmol) and I (0.1 mmol) in benzene (4 ml) was refluxed for 1 h. The mixture turned yellow-brown. GLC analysis of the gas phase on a Porapak Q column showed formation of C_2H_4 (43%) and C_2H_6 (20%). Addition of hexane deposited yellow microcrystals of *cis*- $\text{Mo}(\text{CO})_2(\text{dpe})_2$ (41 mg, 44%), which was confirmed by IR.

Other reactions of allylic alcohols were carried out in a similar manner.

Reaction of methyl allyl ether

A solution of methyl allyl ether (1 mmol) and I (0.1 mmol) in benzene (4 ml) was refluxed for 4 h to give 2-propenyl methyl ether (*cis/trans* = 48/52) in 44% yield. The ratio of the products was determined by GLC on a squalane/Diasolid E column. $\delta(\text{C}_6\text{D}_6)$: 1.5(d, *cis*, $\text{CH}_3\text{-C=}$), 1.7 (d, *trans*, $\text{CH}_3\text{-C=}$), 3.1(s, *cis* and *trans*, $\text{CH}_3\text{-O}$), 4.5 (m, *cis* and *trans*, $=\text{CH-C}$), 5.8 (d, *cis*, $=\text{CH-O}$), and 6.2 ppm (d, $J = 13.5$ Hz, *trans*, $=\text{CH-O}$).

Other reactions of allylic alkyl ethers were carried out in a similar manner.

Reaction of diallyl ether

A solution of diallyl ether (0.7 mmol) and I (0.07 mmol) in benzene (4 ml) was refluxed for 40 min. GLC of the gas phase on Porapak Q and VZ-7 columns showed formation of C_2H_4 (15%), C_2H_6 (22%) and C_3H_6 (28%). After cooling, GLC analysis of the liquid on a PEG 20M/Chromosorb W column showed formation of hexadienes (combined yield, 9%). Addition of hexane deposited yellow microcrystals of *cis*- $Mo(CO)_2(dpe)_2$ (19 mg, 29%), which was confirmed by IR spectra.

Reaction of allyl phenyl ether

A solution of allyl phenyl ether (1 mmol) and I (0.1 mmol) in toluene (4 ml) was refluxed for 4 h. GLC analysis of the gas phase showed formation of C_3H_6 (47%). After cooling, GLC analysis of the liquid on an inositol/Uniport B column showed formation of phenol (42%). Addition of hexane deposited a brown powder, the purification of which by recrystallization was unsuccessful. Its structure could not be determined.

Reaction of *N,N*-dimethylallylamine

A solution of *N,N*-dimethylallylamine (10 mmol) and I (0.1 mmol) in toluene (4 ml) was refluxed for 2 h. After cooling, GLC analysis of the liquid on an Apiezon grease L-KOH/Chromosorb W column indicated formation of *N-trans*-propenyldimethylamine. $\delta(C_6D_6)$: 1.7(d, $CH_3-C=$), 2.2(s, CH_3-N), 4.2(m, $=CH-C$), and 5.9(d, $J = 15$ Hz, $=CH-N$).

Other reactions of allylic tertiary amines were carried out in a similar manner.

Reaction of allylamine

A solution of allylamine (10 mmol) and I (0.1 mmol) in toluene (4 ml) was heated at 100°C for 1.5 h to give *N*-propylideneallylamine in 72% yield. ^{13}C NMR, δ from TMS (C_6D_6): 10.1 (q, CH_3), 28.9 (t, $=CH-CH_2-C$), 63.4 (t, $=C-CH_2-N$), 114.8 (t, $CH_2=C$), and 133.1 ppm (d, $-CH=C$), m/e : 97(18%), 82(39%), 68(47%), and 41(100%). Ammonia was quantitatively analyzed by using indophenol (75%).

Reaction of *N-trans*-propenyldimethylamine

A toluene (4 ml) solution of *N-trans*-propenyldimethylamine (10 mmol), which was prepared from *N,N*-dimethylallylamine in the presence of I (0.1 mmol), was allowed to react with oxygen (0.15 mmol) at 40°C. Analysis by GLC on an Apiezon grease L-KOH column indicated the formation of dimethylamine (4.3 mmol) and 4-dimethylamino-1,3-hexadiene (2.7 mmol, 54%). The latter was identified by NMR, mass spectrometry, and hydrolysis. $\delta(C_6D_6)$: 0.85 (t, CH_3-C), 1.7 (q, $C-CH_2-C=$), 2.2 (s, CH_3-N), 5.0–6.1 ppm (m, $CH_2=CH-CH=$), m/e : 125(100%), 110(81%), 96(90%), 81(20%), and 42(12%). Its hydrolysis gave the expected product [24], *cis*-4-hexene-3-one. $\delta(C_6D_6)$: 0.90 (t, CH_3-C-C), 1.86 (d, $CH_3-C=$), 2.75 (q, $C-CH_2-C=O$), 5.3 (d, $J = 7$ Hz, $C(=O)-CH=$), and 6.0 ppm (m, $C(=O)-C=CH-C$), m/e : 98 (100%), 69 (76%), 57 (76%), and 41 (93%).

Five isomers of dimethylaminohexadienes (combined yield, 0.2 mmol) and three isomers of dimethylaminononatrienes (0.6 mmol) were found as the by-products.

Reaction of allyl phenyl ether with methyl acetoacetate

A mixture of allyl phenyl ether (5 mmol), methyl acetoacetate (25 mmol), and I

(0.1 mmol) was refluxed at 150°C (bath temperature) for 4 h. GLC analysis on a FFAP column showed the formation of methyl 2-acetyl-4-pentenolate in 84% yield based on allyl phenyl ether. The sample was identified by comparison with the authentic sample prepared by the known method [25]. Phenol was confirmed as the by-product.

Other reactions of allylic compounds with methyl acetoacetate were carried out in a similar manner.

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