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Nitrene-Transfer Reaction between Azide and Unsaturated Ether in the Presence of Pd(II) Catalyst

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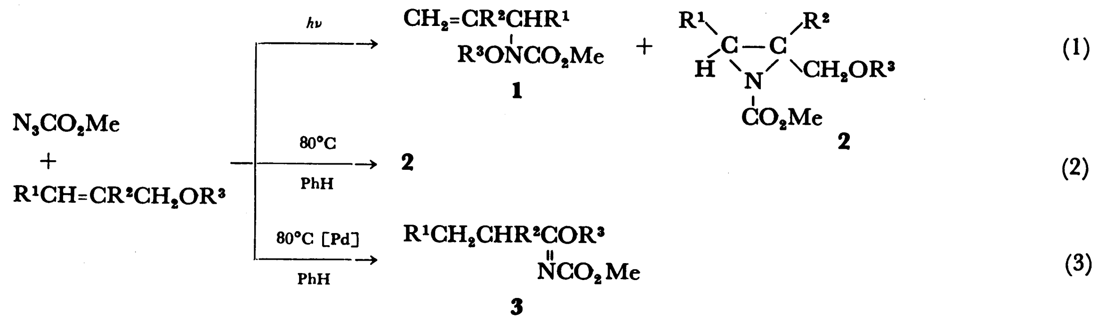
Azidoformate reacted with allylic ethers to give 1-alkoxy-1-(alkoxycarbonylimino)alkane under catalysis by $PdCl_2(PhCN)_2$. The same imines were formed almost quantitatively by noncatalyzed reaction of the azide with the corresponding vinylic ethers. The rate of the catalyzed reaction was found to be first order each in the allylic ether and in the azide. Easiness of the imine formation from the allylic ethers depended on the nature of azide, decreasing in the order of $N_3SO_2Me>N_3CO_2Me>N_3Ph$. Based on these results the most probable mechanism for the catalyzed reaction is proposed.

Photoreaction of azidoformate with allylic ethers has been known to give aziridines (nitrene adducts) **2** and rearranged insertion products **1**, while the thermal reaction at 80 °C in benzene gives only aziridines (30%).1) In the presence of palladium catalysts, however, the thermal reaction has been found to give quite different products, 1-alkoxy-1-(alkoxycarbonylimino)alkanes **3**,2) and dichlorobis(benzonitrile)palladium $PdCl_2(PhCN)_2$ has been reported to be the most effective catalyst for the imine formation.3)



Furthermore, not only allylic but also other unsaturated ethers such as 3-butenyl or 4-pentenyl ethyl ether were found to react similarly giving the corresponding 1-alkoxy-1-(alkoxycarbonylimino)alkanes, **3**, (see Tabe 1).4)

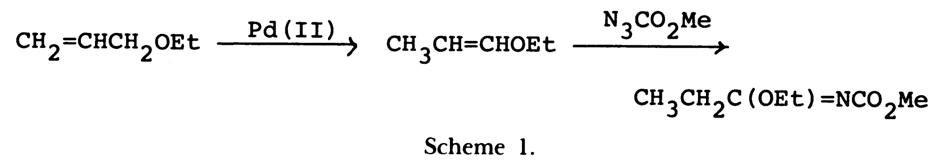
To elucidate the mechanism of the apparently peculiar nitrene-transfer reaction and to survey its scope and limitation, some kinetic and analytical studies were performed. Since vinylic ether reacts with azidoformate smoothly without any catalyst to give the corresponding **3**,5,6) and olefinic compounds have been known to undergo double bond migration under Pd(II)-catalysis,7,8) the most attractive mechanism might involve the Pd(II)-catalyzed isomerization of unsaturated ethers to the corresponding vinylic ether, which then reacts with azide to give **3**, as shown in Scheme 1.

The results shown below, however, suggest that the mechanism has more profound aspects involving ligand exchange in Pd(II) complex and isomerization of the ethers followed by interaction with azide in the Pd(II) coordinate sphere.

Results

Products of Pd(II)-Catalyzed Reaction of Unsaturated Ethers with Azidoformate. The reaction was carried out by heating a degassed solution of unsaturated ethers and azidoformate containing $PdCl_2(PhCN)_2$ (1 mol%) in a sealed tube at 80 °C for 24 h. The products detected in the reaction mixtures were listed in Table 1.

Imines **3** formed in good yields, and the corresponding aziridines were produced in only trivial amounts.



$$CH_2{=}CHCH_2OEt \xrightarrow{Pd(II)} CH_3CH{=}CHOEt \xrightarrow{N_3CO_2Me} CH_3CH_2C(OEt){=}NCO_2Me$$

Scheme 1.

Table 1. Pd(II)-Catalyzed Reaction of Methyl Azidoformate with Unsaturated Ethers

Run	Ether	Product	Yield/%
1	$CH_2=CHCH_2OEt$	$CH_3CH_2C(OEt)=NCO_2Me$	67
2	$CH_2=CHCH_2CH_2OEt$	$CH_3CH_2CH_2C(OEt)=NCO_2Me$	72
3	$CH_2=CH(CH_2)_3OEt$	$CH_3(CH_2)_3C(OEt)=NCO_2Me$	72
4	$CH_2=CMeCH_2OEt$	$Me_2CHC(OEt)=NCO_2Me$	95
5	$CH_2=CHCHMeOEt$	$Me_2CHC(OEt)=NCO_2Me$	44[a]
6	$CH_3CH=CHOEt$	$CH_3CH_2C(OEt)=NCO_2Me$	100[b]

a) $CH_3CH_2C(OEt)=NCO_2Me$ also formed, 8%. b) Without the catalyst.

The essentially same results were obtained when benzene was used as a solvent.

It is interesting that 1-methyl-2-propenyl ether reacted under these conditions to give the imine **3** identical to that obtained from 2-methyl-2-propenyl ether, indicating that the methyl group as well as the hydrogen atom on the allylic α-position of the substrate migrated to the adjacent carbon atom, and the C=N bond formed always at the α-position (Runs 4 and 5).

3-Butenyl and 4-pentenyl ethers (Runs 2 and 3) also afforded good yields of the corresponding imines **3**, in which C=N bonds were introduced again at the α-position of the ethers.

Pd(II)-Catalyzed Isomerization of Unsaturated Ether. Golborn et al. showed that allylic alkenyl phenyl ethers were able to isomerize to vinylic alkenyl phenyl ethers by the aid of $PdCl_2(PhCN)_2$, and the capability of the isomerization depended on the structure of the allylic alkenyl group.[8] But isomerization of alkenyl alkyl ether has not been studied. After 3-butenyl or 4-pentenyl ethyl ether was kept at 80 °C in the presence of 1 mol% of $PdCl_2(PhCN)_2$, the GLC analysis of the mixture showed that the double bond migration occurred considerably. It is noteworthy that the mixture contained allylic ether as shown in the following scheme, but not vinylic ether.

$$CH_2{=}CHCH_2CH_2OEt \xrightarrow[80^\circ C,\ 1\,h]{PdCl_2(PhCN)_2} CH_3CH{=}CHCH_2OEt\ 30\% \tag{4}$$

$$CH_2{=}CHCH_2CH_2CH_2OEt \xrightarrow[80^\circ C,\ 12\,h]{PdCl_2(PhCN)_2} CH_3CH_2CH{=}CHCH_2OEt\ 10\% + CH_3CH{=}CHCH_2CH_2OEt\ 36\% \tag{5}$$

This implies difficulty of isomerization of allylic to vinylic ethers in the presence of $PdCl_2(PhCN)_2$. In fact 2-methyl-2-propenyl ethyl ether which afforded **3** in 95% yield through the Pd(II)-catalyzed reaction with azidoformate (80 °C, 20 h) isomerized quite sluggishly in the presence of the Pd(II)-catalyst alone: after 72h at 80 °C only several % of 2-methyl-1-propenyl ethyl ether was detected.

$$CH_2{=}CMeCH_2OEt \xrightarrow[80^\circ C,\ 72\,h]{PdCl_2(PhCN)_2} Me_2C{=}CHOEt\ \ 5\text{—}6\% \tag{6}$$

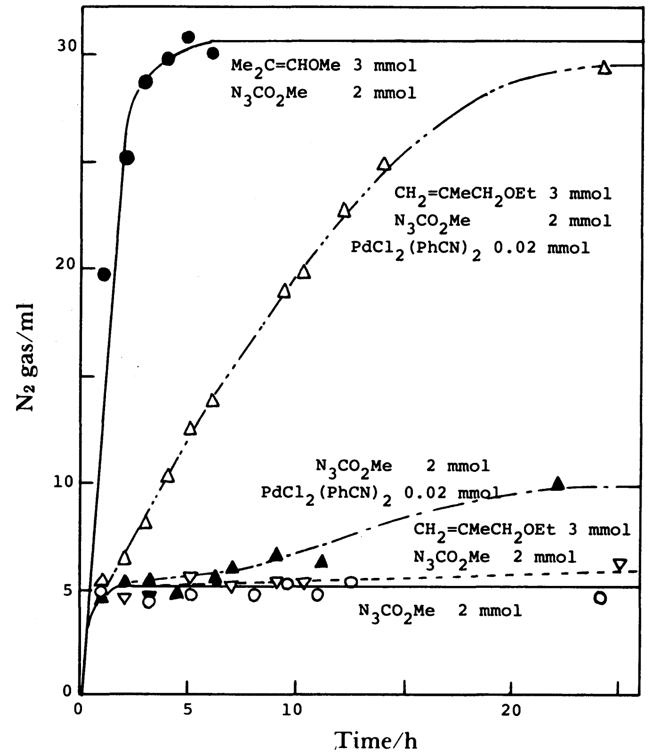


Fig. 1. Evolution of nitrogen.
Solvent=PhH 1 ml, Temp=80 °C.

Kinetic Observation. Rates of nitrogen evolution were followed under various conditions using 2-methyl-2-propenyl ethyl ether which was the best substrate for the Pd(II)-catalyzed reaction with azidoformate. Figure 1 shows amount of gas evolved vs. reaction time. As seen in Fig 1, spontaneous decomposition of azidoformate did not occur in any appreciable extent. The presence of the allylic ether did not promote the decomposition of the azide, although a binary system of the azide and the vinylic ether evolved nitrogen and the reaction was almost completed after several hours at 80 °C. Addition of 1 mol% of $PdCl_2(PhCN)_2$ in an azide solution at 80 °C slightly accelerated the decomposition of the azide, the yield of evolved nitrogen was only 25% based on the azide after 24 h. These facts suggest that some interaction arises between the azide and Pd(II), but the presence of allylic ether much accelerated the Pd(II)-catalyzed decomposition of the azide.

Table 2. The Reaction of Vinylic Ether with Methyl Azidoformate

Vinylic ether	Product	Yield/%
$CH_3CH=CHOEt$	$CH_3CH_2C(OEt)=NCO_2Me$	98
$CH_3CH_2CH=CHOMe$	$CH_3CH_2CH_2C(OMe)=NCO_2Me$	95
$Me_2C=CHOMe$	$Me_2CHC(OMe)=NCO_2Me$	98
$Me_2C=CHOEt$	$Me_2CHC(OEt)=NCO_2Me$	98
$CH_3CH=CMeOMe$	$Me_2CHC(OMe)=NCO_2Me$	72
	$CH_3CH_2C(OMe)=NCO_2Me$	5

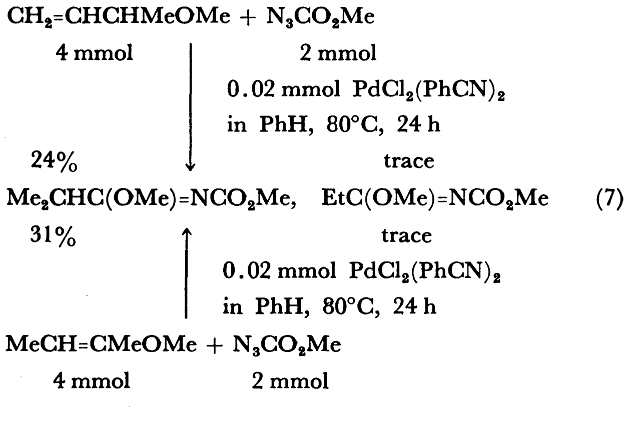
Table 3. Pd(II)-Catalyzed Reaction of Allylic Ethers with Azides

Azide	Allylic ether	Pd(II)-catalyzed aziridine/%	Pd(II)-catalyzed imine/%	Uncatalyzed aziridine/%
$N_3SO_2CH_3$	$CH_2=CHCH_2OMe$	0	100	33
	$CH_2=CHCH_2OEt$	0	100	51
	$CH_2=CMeCH_2OMe$	0	100	36
	$CH_2=CMeCH_2OEt$	0	100	45
$N_3CO_2CH_3$	$CH_2=CHCH_2OMe$	8	53	46
	$CH_2=CHCH_2OEt$	Trace	67	42
	$CH_2=CMeCH_2Me$	Trace	95	45
	$CH_2=CMeCH_2OEt$	Trace	95	16
N_3Ph	$CH_2=CHCH_2OMe$	67	5	62
	$CH_2=CHCH_2OEt$	55	6	68
	$CH_2=CMeCH_2OMe$	15	61	26
	$CH_2=CMeCH_2OEt$	15	74	26

The profile of amount of nitrogen evolved vs. reaction time for the system of azide–ether–Pd(II) showed a sigmoid curve, suggesting the consecutive nature of the reaction. Accurate kinetic treatment of the catalyzed reaction was difficult probably due to that the concentration of the species of the real catalysts could not be controlled easily. Semiquantitative survey using a benzene solution of azidoformate and 2-methyl-2-propenyl ethyl ether (molar ratio of 1: 2—8) containing 1 mol% of $PdCl_2(PhCN)_2$ and using a solution of the azide and 1 mol% of the catalyst in a large excess of the ether showed the first-order dependence of the catalyzed reaction rate on both the azide and the allylic ether. These observations show that the mechanism of the catalyzed reaction is not so simple as shown in Scheme 1, which involves a very slow isomerization of allylic ether followed by a relatively rapid bimolecular reaction.

Comparison with the Reation of Vinylic Ethers. In order to check the similarity in products between the Pd(II)-catalyzed reaction of an allylic ether and the reaction of the corresponding vinylic ether, various vinylic ethers were allowed to react with azidoformate, and the products were compared with those obtained from the corresponding allylic ether. The results were summarized in Table 2.

All vinylic ethers bearing no substituent on its α-position reacted with azidoformate to give the corresponding imines **3** almost quantitatively. As shown in Table 1, the Pd(II)-catalyzed reaction of 1-methyl-2-propenyl ethyl ether gave the methyl-migrated product and the demethylated imine in 44% and 8%, respectively. It is noteworthy that the α-substituted vinylic ether, 1-methyl-1-propyl methyl ether reacted with the azide without the catalyst gave the methyl migrated and the demethylated imines in 72 and 5%, respectively. Under the same conditions (in the presence of 1 mol% of the catalyst, in benzene at 80 °C for 24 h) both 1-methyl-2-propenyl methyl ether and 1-methyl-1-propyl methyl ether gave the same products in similar yields.



Such similarity strongly supports the occurrence of the isomerization of allylic to vinylic substrates in the Pd(II)-catalyzed reaction of allylic ether.

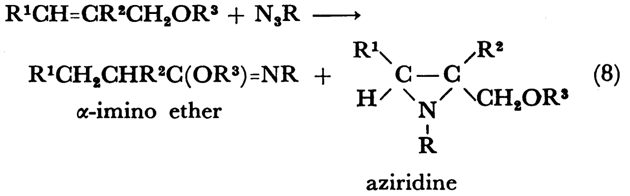
Reaction of Other Azides. Table 3 shows the products of the reaction of methanesulfonyl and

Table 4. Reaction of Methyl Azidoformate with Allylic Sulfides in the Presence of $PdCl_2(PhCN)_2$

Sulfide	Product	Yield/%
$CH_2=CMeCH_2SMe$	$CH_2=CMeCH_2N(SMe)CO_2Me$	70
$CH_3CH=CHCH_2SMe$	$CH_2=CHCHMeN(SMe)CO_2Me$	65[a]
$Me_2C=CHCH_2SMe$	$CH_2=CHCMe_2N(SMe)CO_2Me$	60
$CH_2=CHCHMeSMe$	$CH_3CH=CHCH_2N(SMe)CO_2Me$	56
$PhCH=CHCH_2SMe$	$CH_2=CHCHPhN(SMe)CO_2Me$	54

a) Cf. 26% (in photoreaction) and 27% (without the catalyst).

phenyl azides with allylic ethers in the presence of $PdCl_2(PhCN)_2$ catalyst, containing also the results on azidoformate for comparison. Without the catalyst, only aziridines (nitrene adduct to the double bond of the allylic ether) were produced in rather low yield. The presence of $PdCl_2(PhCN)_2$, however, lead the reaction to production of the corresponding α-imino ethers. And tendency toward α-imino ether formation decreases in the following order: $N_3SO_2Me>N_3CO_2Me>N_3Ph$.


$$R^1CH=CR^2CH_2OR^3 + N_3R \longrightarrow R^1CH_2CHR^2C(OR^3)=NR + \text{aziridine} \quad (8)$$

Thus the catalyzed reaction of sulfonyl azide gave the α-imino ethers almost quantitatively. Phenyl azide gave the α-imino ethers as well as aziridines, and the distribution of the products seriously depended on the allylic structure.

On the other hand, these all azides gave the α-imino ethers almost quantitatively through the noncatalyzed reaction with vinylic ethers. These facts again imply that imine production from allylic ethers may be related to the Pd(II)-assisted isomerization of allylic to vinylic ether.

Reaction of Allylic Sulfides. The reaction of allylic sulfides, sulfur analogues of allylic ethers, with azidoformate did not give the imino compounds corresponding to **3**, but the [1·5] rearranged C–S nitrene insertion products even in the presence of $PdCl_2(PhCN)_2$ as shown in Table 4. Photo- and thermal reactions of allylic sulfides have been known to react with azidoformate to give the [1·5] rearranged C–S nitrene insertion products which is considered to form via the ylide formation between nitrene and the sulfur atom, and enamines which have been considered to be derived from adducts between the azide and the sulfides, in total yield of about 30%.[1] Comparing these facts with the present results, the presence of $PdCl_2(PhCN)_2$ is thought to enhance the formation of the nitrene-ylide.

Discussion

The results which allow us to discuss the mechanism of the Pd(II)-catalyzed reaction of azides with unsaturated ethers are summarized as follows.

(1) In the presence of $PdCl_2(PhCN)_2$ alone, isomerization of allylic to vinylic ether is extremely slow, although the more remotely functionated substrates isomerize to allylic ether (Eqs. 4 and 5).

(2) The catalyzed reaction is first order in the allylic ether as well as in the azide. Since the reaction of azidoformate with allylic ether without the Pd(II) catalyst does not give imine, the Pd(II)-catalyzed imine-formation is not, at least, zeroth-order in Pd(II). The overall kinetic observation shows that the transition state of the rate determining step should be composed of three species, Pd(II), allylic ether, and azide.

(3) Products of the catalyzed reaction of any kind of allylic ethers are the same as those of the reaction of the corresponding vinylic ethers, showing an important role of the Pd(II)-catalyed isomerization of allylic to vinylic ether.

(4) Easiness of formation of the imino products by the catalyzed reaction depends on the nature of the azide: the more electron-withdrawing group the azide has, the better yield of the imine is observed.

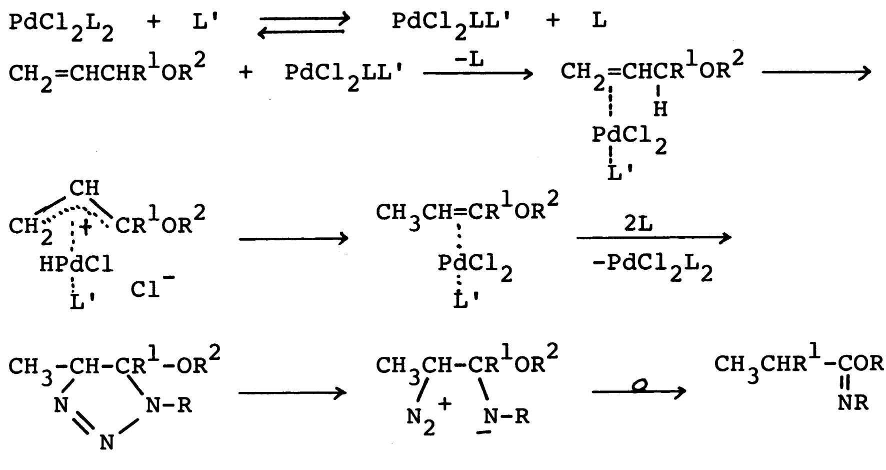
Based on these features, the mechanism shown in Scheme 2 is proposed to be most probable for the Pd(II)-catalyzed reaction of azides with allylic ethers. The mechanism involves the Pd(II)-catalyzed isomerization of allylic to vinylic ether as the rate-determining step. But the real catalyst is thought to be $PdCl_2(PhCN)(N_3R)$ which may be formed by the ligand exchange between $PdCl_2(PhCN)_2$ and the azide. Unfortunately preparative or spectroscopic evidences for the ligand exchange could not be obtained, perhaps due to that the complex thus formed is rather labile and the azide ligand is apt to decompose as seen in the gradual evolution of nitrogen from the system of the azide–$PdCl_2(PhCN)_2$(Fig. 1). Since the Pd(II)-catalyzed isomerization is essentially the hydride transfer between Pd(II) and the ether, the rate would be influenced by the nature of the ligand coordinated to Pd(II). The more electron demanding the ligand is, the faster the hydride abstraction from the allyic ether would be. The tendency is thought to be reflected on the yields of the imino-ethers from the reaction of a series of azides: the electron-withdrawing group on azide promotes the formation of the imino ether (Table 3).

Table 3 also clearly shows that 2-methyl-2-propenyl ether is a better substrate for the imino-ether formation than 2-propenyl ether. This result is quite interesting and probably due to the steric or electronic effects on the reaction in the Pd(II) coordinate sphere, although the real reason is not yet clear.

The vinylic ether thus formed reacts with the azide to give the imino-ether, via 1,3-dipolar addition followed by heterolysis of the triazoline as proposed by Huisgen et al. for the thermal reaction of enol ether with aryl azide.[5] Since appreciable amounts of vinylic ethers were not detected in the reaction mixtures during and after the reaction carried out in the large excess of allylic ethers, the interaction between the vinylic ether and the azide is considered to take place in the Pd(II) coordinate sphere, that is, the coordinated azide molecule is brought into the interaction with vinylic ether derived in the Pd(II) coordinate sphere.

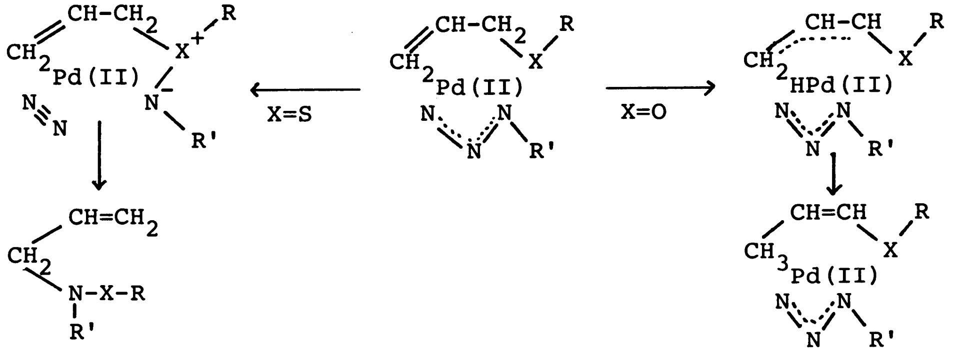
On the heterolysis of the triazoline and evolution of nitrogen, a hydrogen atom or a methyl group located on the α-position of the ether can be migrated to the electron deficient β-carbon via 1,2-shift. Thus the α-methylated allylic or vinylic ethers afford the rearranged imino products (Tables 1 and 2). These ethers also gave the demethylated imino products as shown in Tables 1 and 2. Although their yields are quite low, the results may be interesting, suggesting new aspects of decomposition of the triazolines. Because the carbonium ion formed after nitrogen evolution is hardly thought to degradate with a C–C bond rupture. To elucidate its mechanism, however, further surveys are required.

The Pd(II)-catalyzed reaction of allylic sulfides did not lead to formation of the imino products but [1·5] rearranged insertion products. This may be due to the greater nucleophilic reactivity of a sulfur atom compared with an oxygen atom. Much higher yields of the rearranged products in the catalyzed reaction compared with those in the ordinary thermal reaction (Table 4) and accelerated nitrogen evolution in the presence of $PdCl_2(PhCN)_2$ suggest that the production

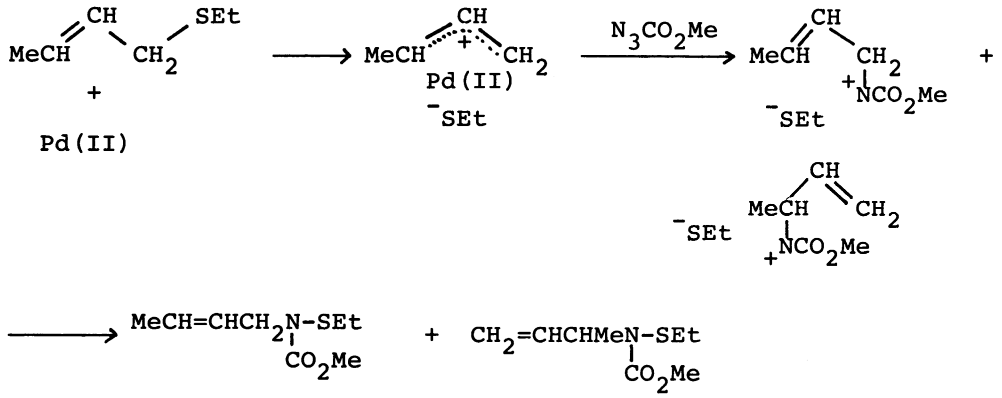


L= PhCN, L'= N_3R, R^1= H or Me

Scheme 2.



Scheme 3.



Scheme 4.

of the insertion products are also controlled by the Pd(II) coordinate sphere.

The coordinated azide molecule has an enhanced electrophilicity and easily interacts with a nucleophilic sulfur atom of the sulfide, to produce the nitrene-ylide, which undergoes [1·5] rearrangement through the cyclic transition state as well documented.[1] In the case of sulfides, therefore, the ylide formation seems much faster than the hydride transfer between Pd(II) and the substrate sulfide. Summarized scheme involving allylic sulfide and ether are shown in Scheme 3.

The route shown in Scheme 4 in which a π-allyl complex is formed from allylic sulfide and Pd(II) and reacts with nitrene from the azide to give the insertion product is unlikely. If this were the true mechanism, unsymetrically substituted π-allyl complexes should give both rearranged and unrearranged insertion products, and the products through the attack of nitrene on the less sterically hindered site of the π-allyl complex would be the major. The results (Table 4) is not the case, showing the formation of the C–N bond exclusively at a γ-carbon atom of allylic sulfide, even though the site is more hindered.

Experimental

Materials. Methyl azidoformate (bp 36—37 °C/58 mmHg (1 mmHg=133.322 Pa)),[9] phenylazide (bp 41 °C/5 mmHg),[10] methanesulfonyl azide (bp 44—45 °C/1 mmHg)[11] were prepared by the known methods. 2-Methyl-2-propenyl alkyl ethers, and 3-butenyl and 4-pentenyl ethyl ethers were prepared by Williamson method[12] from the corresponding chloride, and 1-methyl-2-propenyl methyl ether (bp 55.5 °C)[13] was synthesized by the reaction of acrylaldehyde with methylmagnesium iodide. 1-Methyl- and 1-ethyl-2-methylpropene[14] were prepared from the corresponding acetals of 2-methylpropanal by the *p*-toluenesulfonic acid catalyzed elimination of alcohols. Dichlorobis(benzonitrile)palladium(II)[15] was obtained by treatment of palladium(II) chloride with benzonitrile.

Products of the Reactions. The reaction was carried out according to the procedure already described.[2] The structural determination of aziridines derived from allylic ethers[1] or [1·5] rearranged insertion products from allylic sulfides[1] has been described elsewhere. Analytical data of some unknown α-imino ethers are presented in Table 5.

Kinetic Measurement. i) Three stock solutions were prepared by dissolving a weighed amount of azidoformate (20 mmol) in 5 ml of benzene, PdCl$_2$(PhCN)$_2$ (0.2 mmol) in 25 ml of benzene, and acetophenone (the internal standard, 1 mmol) in 5 ml of benzene. To a 10 ml volumetric flask, 1 ml, 5 ml, and 0.5 ml of the stock solution of the azide, Pd(II), and the internal standard, respectively, were taken, and a weighed amount of 2-methyl-2-propenyl ethyl ether (8, 16, or 32 mmol) was added, and the solution was diluted to 10 ml. One ml of the solution was put into a reaction tube and degassed. The tube was sealed and immersed in a thermostatt kept at 80 °C. After an appropriate reaction time, the mixture was analyzed for the imine product by GLC. The amounts of the imine formed were accomodated approximately to the second-order rate law (first-order each in azide and in ether), and the apparent second-order rate constants obtained for the solution containing the ether at the concentration of 0.8, 1.6, and 3.2 mol·l^{-1} were almost constant, being 1.4, 1.5, and 1.4X10^{-6} s^{-1}·mol^{-1}·l, respectively.

ii) An amount (0.2 mmol) of PdCl$_2$(PhCN)$_2$ was dissolved in 25 ml of 2-methyl-2-propenyl ethyl ether. To a 10 ml volumetric flask, 1 ml of the above solution and weighed amounts of azidoformate (2 or 4 mmol) and acetophenone (the internal standard, 0.2 or 0.4 mmol) were taken and diluted by 2-methyl-2-propenyl ethyl ether to 10 ml. One ml of the solution was degassed and kept at 80 °C in a sealed tube. The amounts of the imine formed were determined by GLC. The rate obeyed to the psudo-first-order rate law, giving the rate constants 4.3 and 4.8 s^{-1} for the 0.2 and 0.4 mol dm^{-3} solution of the azide, respectively.

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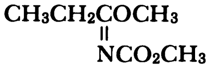
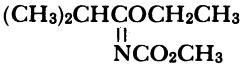
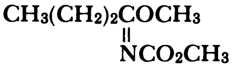
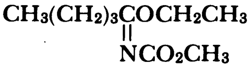
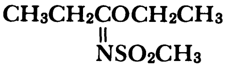
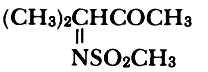
Table 5. Analytical Data for the Imines

 $\mathrm{CH_3CH_2\underset{\underset{NCO_2CH_3}{\|}}{C}OCH_3}$	IR (CCl_4): 1719 (C=O), 1673 (C=N), 1230 (CO_2CH_3) cm^{-1}. ^{1}H NMR (CCl_4): δ=1.15 (3H, t, J=7Hz), 2.36 (2H, q, J=7Hz), 3.70 (3H, s), 3.73 (3H, s). Found: C, 50.30; H, 7.60; N, 9.76%. Calcd for $C_6H_{11}NO_3$: C, 49.65; H, 7.64; N, 9.65%.
 $\mathrm{CH_3CH_2\underset{\underset{NCO_2CH_3}{\|}}{C}OCH_2CH_3}$	IR (CCl_4): 1728 (C=O), 1678 (C=N), 1234 (CO_2CH_3) cm^{-1}. ^{1}H NMR (CCl_4): δ=1.19 (3H, t, J=7Hz), 1.33 (3H, t, J=6Hz), 2.37 (2H, q, J=7Hz), 3.73 (3H, s), 4.17 (2H, q, J=6Hz). Found: C, 52.45; H, 8.10; N, 8.98%. Calcd for $C_7H_{13}NO_3$: C, 52.81; H, 8.23; N, 8.80%.
 $\mathrm{(CH_3)_2CH\underset{\underset{NCO_2CH_3}{\|}}{C}OCH_2CH_3}$	IR (CCl_4): 1720 (C=O), 1668 (C=N), 1240 (CO_2CH_3) cm^{-1}. ^{1}H NMR (CCl_4): δ=1.18 (6H, d, J=7Hz), 1.30 (3H, t, J=6Hz), 2.73 (1H, m), 3.72 (3H, s), 4.18 (2H, q, J=7Hz). Found: C, 56.13; H, 8.61; N, 8.42%. Calcd for $C_8H_{15}NO_3$: C, 55.47; H, 8.73; N, 8.09%.
 $\mathrm{CH_3(CH_2)_2\underset{\underset{NCO_2CH_3}{\|}}{C}OCH_3}$	IR (CCl_4): 1728 (C=O), 1680 (C=N), 1249 (CO_2CH_3) cm^{-1}. ^{1}H NMR (CCl_4): δ=0.89 (3H, t, J=7Hz), 1.16 (2H, m), 2.30 (2H, t, J=7Hz), 3.70 (3H, s), 3.72 (3H, s). Found: C, 52.45; H, 8.02; N, 9.21%. Calcd for $C_7H_{13}NO_3$: C, 52.81; H, 8.23; N, 8.80%.
 $\mathrm{CH_3(CH_2)_3\underset{\underset{NCO_2CH_3}{\|}}{C}OCH_2CH_3}$	IR (CCl_4): 1720 (C=O), 1670 (C=N) cm^{-1}. ^{1}H NMR (CCl_4): δ=0.75—1.90 (10H, m), 2.31 (2H, t, J=7Hz), 3.68 (3H, s), 4.14 (2H, q, J=7Hz). Found: C, 57.53; H, 8.83; N, 7.19%. Calcd for $C_9H_{17}NO_3$: C, 57.73; H, 9.15; N, 7.48.
 $\mathrm{CH_3CH_2\underset{\underset{NSO_2CH_3}{\|}}{C}OCH_3}$	IR (CCl_4): 1670 (C=N) cm^{-1}. ^{1}H NMR (CCl_4): δ=1.16 (3H, t, J=8Hz), 2.75 (2H, q, J=8Hz), 2.93 (3H, s), 4.18 (3H, s).
 $\mathrm{CH_3CH_2\underset{\underset{NSO_2CH_3}{\|}}{C}OCH_2CH_3}$	IR (CCl_4): 1670 (C=O) cm^{-1}. ^{1}H NMR (CCl_4): δ=1.16 (3H, t, J=8HZ), 1.29 (3H, t, J=6Hz), 2.80 (2H, q, J=8Hz), 2.90 (3H, s), 4.20 (2H, q, J=6Hz). Found: C, 40.50; H, 7.28; N, 7.58%. Calcd for $C_6H_{13}NO_3S$: C, 40.21; H, 7.31; N, 7.81%.
 $\mathrm{(CH_3)_2\underset{\underset{NSO_2CH_3}{\|}}{C}HCOCH_3}$	IR (CCl_4): 1670 (C=N) cm^{-1}. ^{1}H NMR (CCl_4): δ=1.25 (6H, d, J=8Hz), 2.98 (3H, s), 3.54 (1H, m), 3.80 (3H, s). Found: C, 40.00; H, 7.03; N, 7.41%. Calcd for $C_6H_{13}NO_3S$: C, 40.21; H, 7.31; N, 7.81%.
 $\mathrm{(CH_3)_2CH\underset{\underset{NSO_2CH_3}{\|}}{C}OCH_2CH_3}$	IR (CCl_4): 1670 (C=N) cm^{-1}. ^{1}H NMR (CCl_4): δ=1.0—1.45 (9H, m), 2.94 (3H, s), 3.50 (1H, m), 4.16 (2H, q, J=7Hz). Found: C, 43.12; H, 7.46; N, 7.36%. Calcd for $C_7H_{15}NO_3S$; C, 43.50; H, 7.82; N, 7.25%.
 $\mathrm{CH_3CH_2\underset{\underset{NPh}{\|}}{C}OCH_3}$	IR (CCl_4): 1670 (C=N) cm^{-1}. ^{1}H NMR (CCl_4): δ=1.16 (3H, t, J=7Hz), 2.37 (2H, q, J=7Hz), 3.71 (3H, s), 7.00 (5H, Ph).
 $\mathrm{CH_3CH_2\underset{\underset{NPh}{\|}}{C}OCH_2CH_3}$	IR (CCl_4): 1670 (C=N) cm^{-1}. ^{1}H NMR (CCl_4): δ=1.16 (3H, t, J=7Hz), 1.29 (3H, t, J=6Hz), 2.20 (2H, q, J=7Hz), 4.16 (2H, q, J=6Hz), 7.00 (5H, Ph). Found: m/z 177.1220. Calcd for $C_{11}H_{15}ON$: M, 177.1154.
 $\mathrm{(CH_3)_2CH\underset{\underset{NPh}{\|}}{C}OCH_3}$	IR (CCl_4): 1670 (C=N) cm^{-1}. ^{1}H NMR (CCl_4): δ=1.07 (6H, d, J=7Hz), 2.65 (1H, m), 3.73 (3H, s), 7.06 (5H, Ph). Found: m/z 177.1129; Calcd for $C_{11}H_{15}NO$: M, 177.1154.
 $\mathrm{(CH_3)_2CH\underset{\underset{NPh}{\|}}{C}OCH_2CH_3}$	IR (CCl_4): 1670 (C=N) cm^{-1}. ^{1}H NMR (CCl_4): δ=1.17 (6H, d, J=Hz), 1.29 (3H, t, J=6Hz), 2.76 (1H, m), 4.14 (2H, q, J=6Hz), 7.06 (5H, Ph). MS (70 eV) m/z (rel intensity) 191 (M^+, 90), 120 (45), 104 (25), 93 (100), 77 (25).

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