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Reinvestigation of the Pd-catalyzed Reaction of Azidoformate with Allylic Ethers

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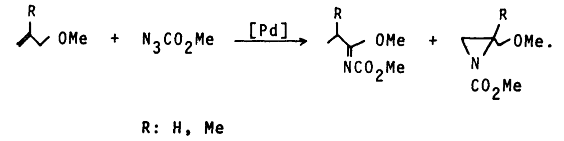
Synopsis. The most effective catalyst for leading reaction between azidoformate and allylic ethers to formation of 1-alkoxy-1-(alkoxycarbonylimino)alkane is $PdCl_2(PhCN)_2$; $Pd(PPh_3)_4$ can hardly show catalytic activity when pure reactants are employed.

Our previous report[1)] showed that allylic ethers react with azidoformate in the presence of tetrakis(triphenylphosphine)palladium, $Pd(PPh_3)_4$, to give *N*-alkoxycarbonyl imines besides aziridines:



During a further investigation on the scope and limitation or mechanism of the reaction, some problems were found with respect to the reproducibility of the yield of the imine. Careful surveys to establish reaction conditions revealed that impurities in the reactants, *e.g.*, chloroformate in azidoformate and allyl chloride in allyl ether, affected seriously the yield of the imine, and that dichlorobis(benzonitrile)palladium, $PdCl_2(PhCN)_2$, was a much more effective catalyst than $Pd(PPh_3)_4$ if well refined reactants were used.

Table 1 shows the effect of chloroformate added to a mixture of well refined azidoformate and allylic ethers free of the corresponding allylic chlorides, on the yield of the imines from the reaction carried out at 80 °C for 20 h in the presence of $Pd(PPh_3)_4$. When pure reactants were employed, $Pd(PPh_3)_4$ could hardly promote the formation of imines, and considerable amounts of azidoformate were recovered. However, the presence of a slight amount (1 mol%) of chloroformate enhanced the yield of imine.

This fact suggests that the species effective as a catalyst is not of Pd(0) but of Pd(II), since chloroformate may oxidatively add to Pd(0). Then, catalytic efficiencies of several Pd(II) complexes were examined for the reaction of azidoformate with 2-methyl-2-propenyl ether, which was found to be a better substrate for imine formation than allyl ether. Among the complexes examined, $PdCl_2(PhCN)_2$ was particularly effective, while $Pd(acac)_2$ and $Pd(OAc)_2$ were poor catalysts as shown in Table 2.

The substrate allylic ethers also should be well refined; particularly they should be free of allylic chlorides from which the ethers have been prepared. Table 3 shows that the presence of a small amount of allyl chloride remarkably retards the formation of imine, even with $PdCl_2(PhCN)_2$ used as a catalyst, the reason for the retardation being not yet made clear.

In conclusion, the reaction between allylic ether and azidoformate is led to form *N*-alkoxycarbonyl imines by the presence of catalytic amounts of $PdCl_2(PhCN)_2$ but hardly by $Pd(PPh_3)_4$. The previous observation[1)] on the catalytic effect of $Pd(PPh_3)_4$ must have resulted from the presence of small amounts of impurities in the reactants, perhaps chloroformate from which the azidoformate was prepared.

TABLE 1. THE EFFECT OF CHLOROFORMATE ON THE REACTION OF AZIDOFORMATE WITH ALLYLIC ETHERS IN THE PRESENCE OF $Pd(PPh_3)_4$[a)]

Substrate	$ClCO_2CH_3$ (mmol)	Yields of products/%[b)]	
		Imine	Aziridine
CH_2=$CHCH_2OCH_3$	0	0	24
	0.02	28	—
	0.04	40	18
	0.04[c)]	37	4
CH_2=$C(CH_3)CH_2OCH_3$	0.04	63	28

a) $N_3CO_2CH_3$ (2 mmol), $Pd(PPh_3)_4$ (0.02 mmol) in allylic ether (2 ml), 80 °C, and 20 h. b) Based on $N_3CO_2CH_3$, by GLPC. c) $N_3CO_2CH_3$ (2 mmol), allyl ether (25 mmol), and $Pd(PPh_3)_4$ (0.02 mmol) in benzene (1 ml).

TABLE 2. THE REACTION OF AZIDOFORMATE WITH 2-METHYL-2-PROPENYL ETHER IN THE PRESENCE OF SOME Pd-COMPLEXES[a)]

Pd-complex	Yields of products/%[b)]	
	Imine	Aziridine
$Pd(PPh_3)_4$	5	24
$Pd(acac)_2$	7	18
$Pd(OAc)_2$	12	22
$PdCl_2(PhCN)_2$	95	Trace

a) $N_3CO_2CH_3$ (2 mmol), 2-methyl-2-propenyl ether (1 ml), Pd-complex (0.02 mmol), 80°C, and 20 h. b) Base on $N_3CO_2CH_3$, by GLPC.

TABLE 3. EFFECT OF ALLYL CHLORIDE ON THE REACTION OF AZIDOFORMATE WITH ALLYLIC ETHERS CATALYZED BY $PdCl_2(PhCN)_2$

Substrate	Allyl chloride (mmol)	Yields of products/%	
		Imine	Aziridine
CH_2=$CHCH_2OCH_3$	0	53	8
	1	9	10
	2	0	10
CH_2=$C(CH_3)OCH_3$	0	95	Trace
	1	6	6

a) $N_3CO_2CH_3$ (2 mmol), $PdCl_2(PhCN)_2$ (0.02 mmol) in allylic ether (1 ml), 80 °C, and 20 h. b) Based on $N_3CO_2CH_3$, by GLPC.

Experimental

Materials. Methyl azidoformate was prepared by the known method[2] from sodium azide and methyl chloroformate and purified by repeating distillation under reduced pressure, bp 33—34 °C (8×10^3 Pa). Allylic ethers were prepared by the usual method,[3] and the products were collected by distilling the reaction mixtures. The distillates were washed several times with saturated brine in order to remove allylic chloride or alcohols, and dried over $MgSO_4$, then distilled under atmospheric pressure. Allyl methyl ether: bp 42.5—43 °C, 2-methyl-2-propenyl methyl ether: bp 66—67 °C. The purities of these reactants were checked by GLPC. The catalysts $Pd(PPh_3)_4$,[4] $PdCl_2(PhCN)_2$,[5] and Pd $(acac)_2$[6] were prepared by the methods described in the literature.

Reaction Procedure. A solution of methyl azidoformate (2 mmol) and a catalyst (0.02 mmol) in an allylic ether (1 ml) was prepared in a tube and degassed. Then the tube was sealed and immersed in a bath kept at 80 °C. After about 20 h, the products were collected from the reaction mixture by GLPC, and their structures were determined by elemental and NMR and IR spectroscopic analyses. The yields of the products were determined by GLPC.

Products. Analytical data for two aziridines[7] and 1-methoxy-1-(methoxycarbonylimino)propane[1] have been described elsewhere. 1-Methoxy-1-(methoxycarbonylimino)-2-methylpropane: ^{1}H NMR (CCl_4) $\delta=1.17$ (6H, d, $-CH_3$), 2.76 (1H, m, CH), 3.62 (3H, s, OCH_3), and 3.63 (3H, s, CO_2CH_3); IR 1670 (C=N), 1725 (C=O), and 1100 (C–O–C) cm^{-1}. Found: C, 52.55; H, 8.22: N, 8.70%. Calcd for $C_7H_{13}O_3N$: C, 52.81; H, 8.23; N, 8.80%.

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