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A NEW REACTION OF AZIDOFORMATE WITH UNSATURATED ETHERS CATALYZED BY DICHLORO-BIS(BENZONITRILE)PALLADIUM

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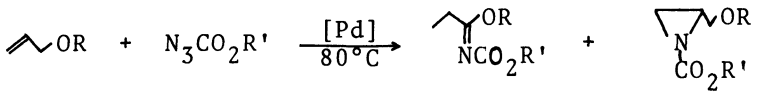
In the presence of dichloro-bis(benzonitrile)palladium, azidoformate reacts with various unsaturated ethers to give 1-alkoxy-1-carboalkoxyiminoalkanes. Reaction with 1-methyl-2-propenyl ether was accompaied by methyl migration, giving 1-alkoxy-1-carboalkoxyimino-2-methylpropane.

Previously[1] allylic ethers have been reported to react with azidoformate in the presence of tetrakis(triphenylphosphine)palladium to give N-carboalkoxyimines besides aziridines, contrasting with the thermal and photo-initiated reactions.[2]



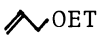
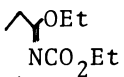
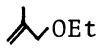
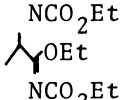
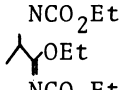
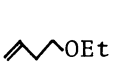
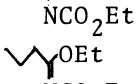
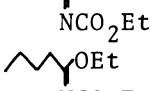
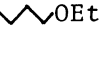
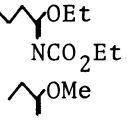
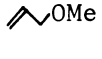
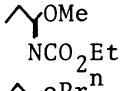
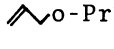
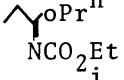
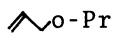
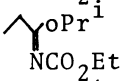
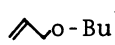
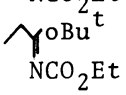
This paper deals with the results of further studies which reveal that the reaction leading to the imines takes place not only with allylic ethers but acyclic unsaturated ethers commonly, and is catalyzed much effectively by dichloro-bis-(benzonitrile)palladium(II), $PdCl_2(PhCN)_2$. These are a quite new nitrene-transfer reaction between azide and unsaturated ethers.

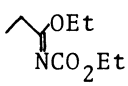
The reaction was carried out by heating a degassed mixture of a substrate ether (1 ml) and azidoformate (2 mmol) containing $PdCl_2(PhCN)_2$ (0.02 mmol) in a sealed tube at 80°C for 24 h. The products were isolated by glc and their structures were determined by elemental and ^1H NMR spectroscopic analyses. The results were listed in Table. Under these conditions, imines formed in good yields, and the corresponding aziridines were produced in only trivial amounts.

It is interesting that 1-methyl-2-propenyl ether (Run 3) reacts under these conditions to give the imine 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 was trensferred to the adjacent unsaturated carbon, and the C=N bond formed at the α-position.

3-Butenyl and 4-pentenyl ethers (Run 4 and 5) also afforded good yields of the corresponding imines, in which C=N bonds were introduced at the α-position of the ethers. The structure of the alkyl part of the ether gives a little influence on the yield of the imine, which appeared to be enhanced by length but retarded by

Table Reaction of Unsaturated Ethers with N_3CO_2Et Catalyzed by $PdCl_2(PhCN)_2$

Run	Unsaturated Ether	Product	Yield %
1			67
2			95
3			44[a]
4			72
5			72
6			56
7			80
8			70
9			48
10			100[b]

a)  also formed (8 %)

b) without the catalyst N_3CO_2Et (2 mmol) in $CH_3CH{=}CHOEt$ (1 ml), 80°C, 24 h.

bulkiness of the alkyl group (Run 1, 6, 7, 8 and 9).

Vinylic ether such as 1-propenyl ether (Run 10) reacts with azidoformate to give quantitatively the N-carboalkoxyimine identical to that from allyl ether, even without the palladium catalyst, perhaps involving 1,3-dipolar addition of the azide to the vinylic ether. This fact might imply that the catalyzed reactions of non-vinylic ethers were initiated by catalyzed rearrangement of non-vinylic to vinylic ether, followed by the noncatalytic addition of the azide. However, this is unlikely since such rearrangement cannot be observed on heating the non-vinylic ethers in the presence of $PdCl_2(PhCN)_2$.[3]

Mechanistic surveys on these reactions particularly on a role of the catalyst are in progress.

References

1) T. Migita, M. Chiba, M. Kosugi, and S. Nakaido, Chem. Lett., 1978, 1403.
2) W. Ando, H. Fujii, I. Nakamura, N. Ogino, and T. Migita, Int. J. Sulfur Chem., 8, 13 (1973).
3) Allyl phenyl ether has been known to rearrange to 1-propenyl phenyl ether. P. Golborn, and F. Scheinmann, J. Chem. Soc. Perkin I, 1973, 2870.

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