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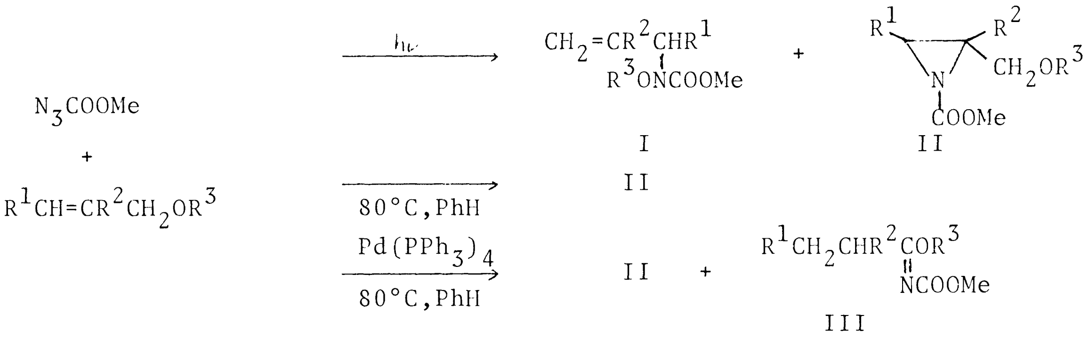
THE REACTION OF AZIDOFORMATES WITH ALLYL ETHERS IN THE PRESENCE OF TRANSITION METAL COMPLEXES

Toshihiko MIGITA, Mitsuo CHIBA, Masanori KOSUGI, and Setsuko NAKAIDO
Department of Chemistry, Faculty of Technology, Gunma University,
Kiryu, Gunma 376

Palladium complex catalyzed reaction of azidoformates with allyl ethers afforded N-carboalkoxyimines III as major products, contrasting with the corresponding photo-induced and thermal reactions. Formation of III is thought to involve α-C-H insertion of carboalkoxy nitrene as a primary step.

Photoreactions of azidoformate with allylic ethers are known to give aziridines (nitrene adduct) II and rearranged insertion product I, 1) while thermal reactions at 80°C in benzene give only aziridines (80%). Here we wish to communicate that thermal reactions at 80°C in benzene, however, gave quite peculiar products, N-carboalkoxyimine III, when the reactions were carried out in the presence of a catalytic amount of transition metal complex.



When a solution of allyl methyl ether (2.5 mmol) and methyl azidoformate (2 mmol) in benzene (1.5 cm^3) containing 0.02 mmol of tetrakis(triphenylphosphine)-palladium was heated at 80°C for 24 h, two products were detected by vpc analysis. Each product was collected and determined by vpc method. The minor product was identified to be aziridine derivative II (R^1=H, R^2=H, and R^3=CH_3), and the major was assigned as N-carbomethoxyimine III (R^1=H, R^2=H, and R^3=CH_3) on the basis of elemental and spectral analyses. The ir bands at 1720 and 1670 cm^{-1} show the existence of C=O and C=N groups in III, and the nmr signals of III indicate the presence of one ethyl and two methyl groups: δ: 1.16 (t, J=7.9 Hz, 3H), 2.37 (q, J=7.9 Hz, 2H), 3.68 (s, 3H), and 3.71 (s, 3H). Other allylic ethers also reacted similarly, as shown in the following Table.

Similar results were observed in the reactions of ethyl azidoformate. Instead of $Pd(PPh_3)_4$, the presence of $RhCl(PPh_3)_3$ or $Pd(OAc)_2$ also induced the formation of imines, but $Cu(acac)_2$ did not.

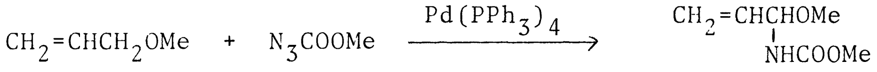
TABLE. Reaction of Methyl Azidoformate with Allylic Ethers in the Presence of $Pd(PPh_3)_4$

Allyl Ethers ($R^1CH=CR^2CH_2OR^3$)			Product Yields*	
R^1	R^2	R^3	II	III
H	H	CH_3	6%	37%
CH_3	H	CH_3	trace	37
H	CH_3	CH_3	11	10
H	H	C_2H_5	10	28

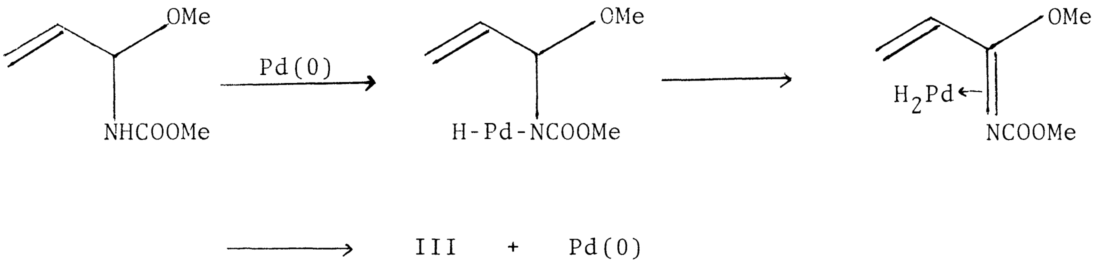
* Determined by vpc analysis.

When the palladium complex was added to a solution of allyl ethers and methyl azidoformate at room temperature, gas evolution was observed at the beginning and ceased soon. And the formation of the products was detected only when the mixture was heated up to 80°C. Furthermore, the characteristic ir band of the azide group at 2180 cm^{-1}, which can be recognized distinctly to a benzene solution of the azidoformate, was almost completely diminished by the addition of an equimolar amount of $Pd(PPh_3)_4$ to the solution.

From these facts, the actual species attacking allyl ether is thought to be a nitrene-palladium complex. Since the product III was found not to be formed by treating II with $Pd(PPh_3)_4$ or $Pd(OAc)_2$, at 80°C for 24 h. in a benzene solution, we feel that the primary process is nitrene transfer between the nitrene-palladium complex and the allyl ethers, giving α-C-H insertion products,[2)] which may be converted into III in the coordination sphere of the transition metal complex. Similar amine-imine transformation has been shown to be catalyzed by palladium black.[3)]



$$CH_2=CHCH_2OMe + N_3COOMe \xrightarrow{Pd(PPh_3)_4} CH_2=CH\underset{NHCOOMe}{\underset{|}{C}}HOMe$$



References

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