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Palladium Catalyzed Allylation of Nitroalkanes with Allyl Chlorides

Short Communication

Piotr Aleksandrowicz, Hanna Piotrowska*, and **Wojciech Sas**

Institute of Organic Chemistry and Technology,
Technical University (Politechnika), PL-00-662 Warsaw, Poland

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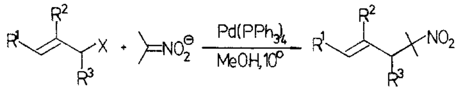
The palladium catalyzed synthesis of allylnitro compounds from allyl chlorides and nitroalkanes is described.

[Keywords: C-Allylation; Palladium (O) catalysis]

Palladium-katalysierte Allylierung von Nitroalkanen mit Allylchloriden
(Kurze Mitteilung)

Die Palladium-katalysierte Darstellung von Allylverbindungen aus Allylchloriden und Nitroalkanen wird beschrieben.

Nitroalkane monoanions react with alkyl and allyl halides yielding exclusively the unstable O-alkylation products[1]. We found that allyl halides may be used as C-allylation agents when palladium catalyst is present in the reaction medium.



The model reaction was carried out in methanol at 10 °C using the salt of 2-nitropropane, an allylic chloride and tetrakis(triphenylphosphine) palladium. The latter was generated *in situ* in the reaction medium from dichlorobis(triphenylphosphine) palladium, two equivalents of triphenylphosphine, and a salt of 2-nitropropane acting as

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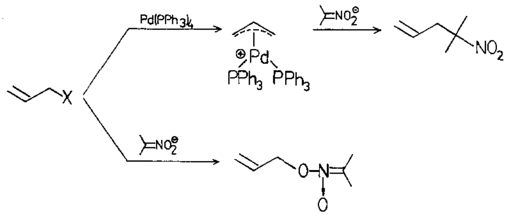
reducing agent[2]. Allyl bromide and phenylsulfonate were also applied in this reaction.

We investigated also the reaction of allyl chloride with primary nitroalkanes. When equimolar amounts of the nitronate salt and allyl chloride were reacted under the conditions described above, ca. 50% of the chloro compound was consumed and monoallyl derivatives were formed predominantly. However, when an excess of primary nitroalkane was used the resulting mixture contained more than 95% of the monoallyl derivative. The yields of monoallyl compounds in this process exceeded 50%, therefore the reaction might be of some preparative value. The results are compiled in Table 2. It should be noted that the reaction of primary nitroalkanes with allyl alcohol-ethyl acetate gives almost exclusively the diallyl derivatives[2].

It seems that the formation of C-allylation products of nitroalkanes proceeds through π-allyl complexes according to the mechanism proposed by *Trost*[3] for the alkylation of carboanions with allylic acetates.



This mechanism consists of two steps: first the activation step i. e. the formation of π-allyl complex after which the palladium moiety is substituted with the nitronate anion.

The fact crotyl chloride and 3-chlorobutene-1 yield the same allylation product (Table 1, entry 5, 6) is in good agreement with this proposal.

When allylic chlorides are used in the allylation reaction the yields are lower than with corresponding allylic acetates or phenyl allyl ethers. This might be caused by direct O-allylation, a process competitive to C-allylation catalyzed by palladium compounds. O-allylation is possible in the case of allyl chloride, and not possible when allyl acetates or ethers are the allylating agents. This competitive reaction is more pronounced when more reactive allyl bromide or harder allyl benzenesulfonate are used thus causing a decrease of the yield of the C-allylation product.

Table 1

No.	Allyl derivative				Product			Yield[a]	Boiling point
	R^1	R^2	R^3	X	R^1	R^2	R^3	(%)	(°C/mm Hg)
1	H	H	H	Cl	H	H	H	50	73/30
2	H	H	H	Br	H	H	H	27	73/30
3	H	H	H	$C_6H_5SO_3$	H	H	H	15	73/30
4	H	CH_3	H	Cl	H	CH_3	H	8[b]	84-85/29
5	CH_3	H	H	Cl	CH_3	H	H	35	88-89/27
6	H	H	CH_3	Cl	CH_3	H	H	30	88-89/27

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[a] 11 hours at 10 °C.

[b] 23% yield was obtained when the reaction was carried out at 50 °C.

Table 2

R-NO_2	Nitro compound/ allyl chloride (molar ratio)	Temp. (°C)	Mono: diallyl-derivative (molar ratio)	Estimated yield of monoallyl derivative (GLC)
1. $R = C_2H_5$	1:1	10	68:32	23[a]
2. n-C_3H_7	1:1	10	80:20	40[b]
3. n-C_4H_9	1:1	10	81:19	32[c]
4. C_2H_5	5:1	18	95:5	57
5. n-C_3H_7	5:1	18	97:3	60
6. n-C_4H_9	5:1	18	98:2	50

The boiling points (°C/mm Hg) of monoallyl and diallyl derivatives (uncorr.) are:

[a] 50-52/28 and 98-100/24.

[b] 68-70/30 and 98-100/20.

[c] 82-84/30 and 58-60/0.3, respectively.

Experimental

Typical procedure exemplified by preparation of 4-methyl-4-nitro-pentene-1:

2-Nitropropane sodium salt (0.05 mol), prepared *in situ* from the nitroalkane and stoichiometric amount of sodium methoxide, dichlorobis(triphenylphosphine)palladium (0.00128 mol) and triphenylphosphine (0.00256 mol) in methanol (50 ml) were heated to boiling and cooled slowly (30 min) to 10 °C. Allyl chloride (0.05 mol) was added dropwise at 10 °C during 3 h, and the mixture stirred for 11 h at 10 °C. Water work-up was used and 4-methyl-4-nitropentenen-1 was obtained with 50% yield.

References

[1] The Chemistry of Nitro and Nitroso Groups (*Feuer H.*, ed.). Interscience. 1969.

[2] *Aleksandrowicz P.*, *Piotrowska H.*, *Sas W.*, Tetrahedron **38**, 1321 (1982).

[3] *Trost B. M.*, Tetrahedron **33**, 2619 (1977).

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