

Palladium-catalysed Allylic Alkylations of Allylic Nitro-compounds

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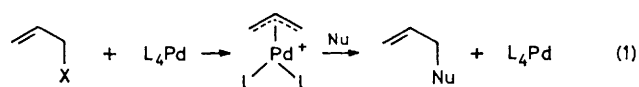
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In the presence of catalytic amounts of tetrakis(triphenylphosphine)palladium, allylic nitro-compounds undergo allylic alkylations with sodium dimethyl malonate.

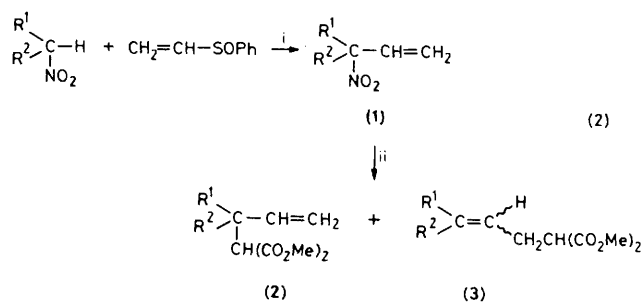
Palladium-catalysed allylic alkylations, equation (1), are extremely useful synthetic reactions, with allyl acetates (X = OAc) being among the most commonly used allylic compounds.¹ In this paper we report that allylic nitro-compounds (X = NO₂) undergo reactions with nucleophiles similar to that in equation (1).

Allylic nitro-compounds (1) were prepared *via* Michael addition of nitroalkanes to phenyl vinyl sulphoxide and subsequent thermolysis.² Treatment of (1) with *ca.* 2 mol % of tetrakis(triphenylphosphine)palladium in the presence of sodium dimethyl malonate at reflux in tetrahydrofuran (THF) led to a smooth alkylation as summarized in Table 1. Nucleophiles attacked predominantly at the less substituted end when R¹ = R². When R¹ and R² were different, compounds (3) were the sole products, with a predominance of the *E*-isomer.

As nitroalkanes are available from various sources, the present transformations may afford very useful organic syntheses. For example, the Diels-Alder adduct of nitroethylene and myrcene could be converted into (4), and then into (5) by the procedures of equation (2). Furthermore, various α,β -unsaturated sulphoxides can be used instead of phenyl vinyl sulphoxide. Thus, the desired allylic nitro-compounds may be prepared. Michael additions of nitromethane to 1-propenyl phenyl sulphoxide and methyl vinyl ketone gave the sulphoxide (6), which was converted into (7), and then into (8) by the same procedures.



X = OAc, OR, SO₂R



i, 1,5-Diazabicyclo[5.4.0]undec-5-ene (1 equiv.), room temp., 24 h, thermolysis (ref. 2); ii, NaCH(CO₂Me)₂, Pd(PPh₃)₄ (2 mol %), THF, 66 °C, 4 h.

Table 1. Preparation of allylic nitro-compounds (1) and the palladium-catalysed reaction of (1) with sodium dimethyl malonate.

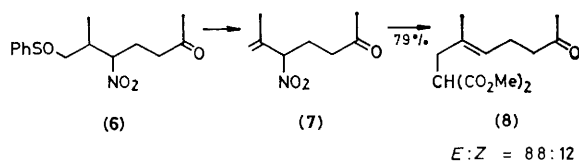
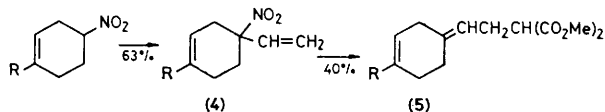
R ¹	R ²	% yield ^a of (1)	% yield ^b of [(2) + (3)]	Ratio ^c (3):(2)	E:Z ratio of (3) ^c
Me	Me	73	60	73:27	
	-[CH ₂] ₅ -	67	73	88:12	
Me	Me ₂ CHCH ₂	70	48	100:0	88:12
Me	CH ₃ CH ₂ C(=O)Me	74	51	100:0	62:38
Me	CH ₂ Ph	60	77	100:0	82:18

^a Isolated yield based on nitroalkanes. ^b Isolated yield. ^c Determined by g.l.c.

Thus, a nitro-group at an allylic position can be replaced with nucleophiles with the aid of Pd⁰. This may open a new area of organic nitro-chemistry, for the nitro-group generally

fails to serve as a leaving group in nucleophilic substitution reactions.³

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References

- 1 Various books and reviews are available for this subject, see: J. Tsuji, 'Organic Synthesis with Palladium Compounds,' Springer-Verlag, New York, 1980; B. M. Trost, *Acc. Chem. Res.*, 1980, **13**, 385; for allylic alkylation of allyl sulphones, see: B. M. Trost, N. R. Schmuff, and M. J. Miller, *J. Am. Chem. Soc.*, 1980, **102**, 5980.
- 2 R. Tanikaga, H. Sugihara, K. Tanaka, and A. Kaji, *Synthesis*, 1977, 299.
- 3 The nitro-group is replaced with nucleophiles, in some special cases, via one-electron transfer processes (S_{RN}1), see N. Kornblum, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 734.