CHEMISTRY LETTERS, pp. 229 - 232, 1985.

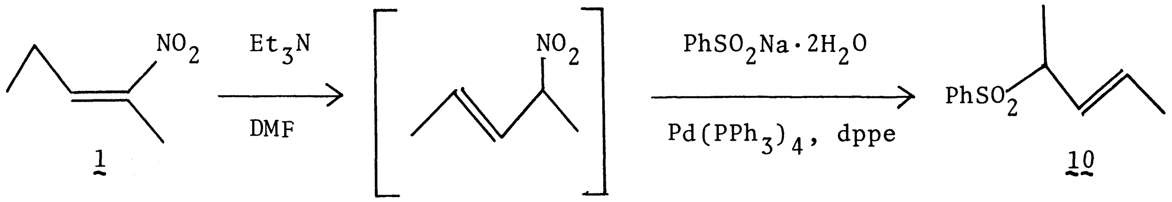
PALLADIUM CATALYZED SYNTHESIS OF ALLYLIC SULFONES. UTILIZATION OF α-NITRO OLEFINS AS ALLYLIC NITRO COMPOUNDS

Rui TAMURA,* Koji HAYASHI, Masato KAKIHANA, Masanori TSUJI, and Daihei ODA
Department of Chemistry, The National Defense Academy, Yokosuka 239

α-Nitro olefins reacted with sodium benzenesulfinate in the presence of tertiary amine and palladium(0) catalyst to afford allylic sulfones. The competition experiment showed that relative rate of the sulfonylation of an α-nitro olefin to that of the corresponding allylic acetate was about 2.2.

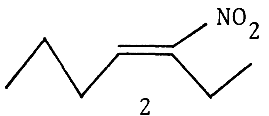
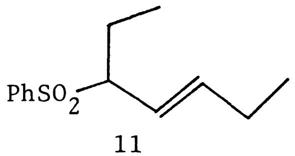
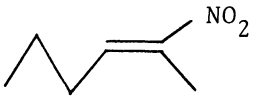
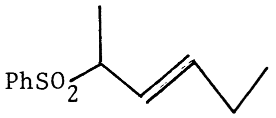
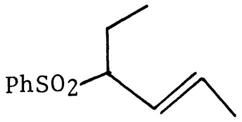
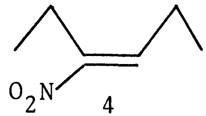
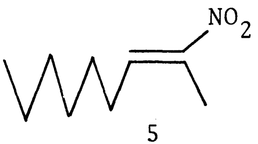
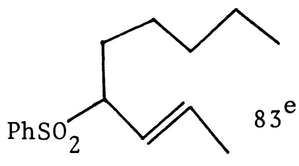
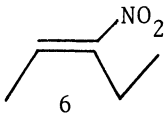
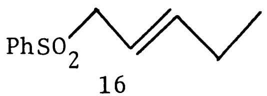
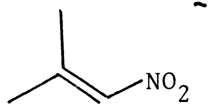
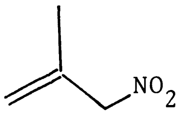
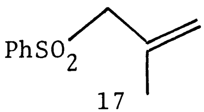
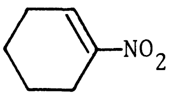
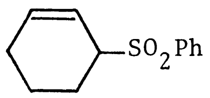
Allylic nitro compounds have been demonstrated to act as the electrophile for Pd(0) catalyzed allylic alkylation and amination reactions,1) however, there were reported only a few examples for the preparation of allylic nitro compounds.2) For instance, generally simple allylic nitro compounds are not obtainable under basic conditions because of the high stability of α-nitro olefins, the isomer of allylic nitro compounds. In order to overcome this inconvenience we have recently found that α-nitro olefins can be utilized as allylic nitro compounds for Pd(0) catalyzed allylic amination reaction.3) It is of value to use readily accessible α-nitro olefins as allylic nitro compounds and convert them to other classes of important synthetic intermediates. Here we wish to describe a facile method to prepare allylic sulfones directly from α-nitro olefins by use of a catalytic amount of palladium(0).

α-Nitro olefins (1.0 mmol), which are easily available from primary nitro alkanes and aldehydes4) or from alkenes,5) were allowed to react with $PhSO_2Na\cdot 2H_2O$ (2.0 mmol) in the presence of triethylamine (1.0 mmol), $Pd(PPh_3)_4$ (0.05 mmol), and 1,2-bis(diphenylphosphino)ethane (dppe) (0.05 mmol) in DMF (4 ml) at 70 °C for 2 h. After usual work-up, flash column chromatography (silica gel, 4:1 hexane/ethyl acetate) of the crude materials gave the corresponding allylic sulfones in fair to good yields (Eq. 1 and Table 1). The assignment of (E)-stereochemistry of the inner double bond of the products was established by analyzing the coupling constant for the olefinic protons deduced from their ^1H NMR spectra. In the absence



(1)

Table 1. Denitro-sulfonylation of α-Nitro Olefins[a]

Entry	α-Nitro olefin	Product[b]	Isolated yield/%
1	1	10	81 (51)[c] (41)[d]
2	 2	 11	71
3	 3	 12 65 : 35 13 	80[e]
4	 4	12 62 : 38 13	72[e]
5	 5	 14 73 : 27 15 	83[e]
6	 6	 16	60
7	 7 70 : 30 8 	 17	50
8	 9	 18	70

a) Reactions were carried out on 1.0 mmol scale with 2.0 equiv. of PhSO$_2$Na·2H$_2$O, 1.0 equiv. of triethylamine, and 5 mol% of Pd(PPh$_3$)$_4$ and dppe in DMF at 70 °C for 2 h unless otherwise noted. b) All products were fully characterized by infrared, ^{1}H and ^{13}C NMR spectra and elemental analyses. c) Without dppe. d) Without triethylamine. e) The isomeric ratios of 12 to 13, and 14 to 15 were determined by ^{1}H NMR and HPLC analyses.

of $Pd(PPh_3)_4$, the formation of allylic sulfones was not observed. In the reaction without triethylamine or dppe, the yield of allylic sulfones decreased (entry 1). Two regioisomers were obtained from 3, 4, and 5 (entries 3-5), respectively. These facts indicate that the reaction intermediate of the current sulfonylation should be the π-allylpalladium complex and that the nucleophilic attack of $PhSO_2^-$ occurred predominantly at the less hindered site (entries 3-5), or exclusively at the less substituted site to give the regio- and stereoselective product (entry 6).[6] A mixture of 7 and 8 was converted to the sole product (17), and the cyclic α-nitro olefin, 1-nitrocyclohexene (9), was also a good substrate for the sulfonylation (entry 8).

The approximate relative reactivity of α-nitro olefin 1 and the corresponding allylic acetate, 4-acetoxypent-2-ene (19), toward $PhSO_2^-$ was determined by two competition experiments, where 1.0 mmol of $PhSO_2Na \cdot 2H_2O$ was allowed to react with a mixture of 1 and 2 (1.0 mmol each) and that of 2 and 19 (1.0 mmol each), respectively, in the presence of triethylamine (1.0 mmol), $Pd(PPh_3)_4$ (0.05 mmol), and dppe (0.05 mmol) in DMF at 70 °C for 2 h. The order of the reactivity was 1 (1.0) $>$ 2 (0.77) $>$ 19 (0.45). Therefore the relative rate of the sulfonylation of 1 to that of the corresponding allylic acetate (19) is approximately 2.2. Thus, α-nitro olefins have proven to serve as excellent substrates for the Pd(0) catalyzed allylic sulfonylation reaction similarly to allylic acetates.[7]

We wish to thank professor Jiro Tsuji, Tokyo Institute of Technology, for helpful discussions. We also are grateful to professor Minoru Hirota and Mrs. Hiroko Suezawa, Yokohama National University, and professor Tamotsu Yamamoto, Kanto Gakuin University, for measuring NMR spectra.

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6) The Pd(0) catalyzed isomerization of the kinetically-controlled product, 3-benzenesulfonylpent-1-ene, to the thermodynamically stable **16** might occur; see Ref. 7a.

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(Received December 1, 1984)