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# Phenylations of β-Nitrostyrene Derivatives with Benzene by the Use of Palladium(II) Acetate

Kimiaki YAMAMURA and Setsuo WATARAI

*Institute of Chemistry, College of General Education, Kobe University, Tsurukabuto, Nada, Kobe, Hyogo 657*

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**Synopsis.** The phenylations of several β-nitrostyrene derivatives with benzene in the presence of palladium(II) acetate have been studied. The nitro group of the β-nitrostyrenes investigated affects the phenylations very strongly, because of its powerful electron-withdrawing nature, and a high reactivity and regiospecificity were observed.

Nucleophilic addition reactions to a carbon-carbon double bond conjugated with electron-withdrawing groups are well-known. We have ourselves previously reported the nucleophilic addition of ethanol to β-nitrostyrenes under very mild conditions.[1] Recently, Moritani and Fujiwara *et al.* reported a novel aromatic substitution reaction with olefins in the presence of palladium salts,[2] and also reported that an electron-withdrawing group on the olefinic carbon atom assists the phenylation reaction.[3] This prompted us to examine the phenylation reaction of β-nitrostyrenes by the use of palladium acetate.

A mixture of a β-nitrostyrene derivative and palladium acetate in a large excess of benzene and acetic acid was refluxed under stirring until the precipitation of black metallic palladium ceased. The results are summarized in Table 1. From β-nitrostyrene(I), 1,1-diphenyl-2-nitroethylene(III) was obtained predominantly; no α-nitrostilbene(II) was produced under the present reaction conditions. The selective formation of III from I in a good yield is interesting, since the treatment of *trans*-1-phenyl-1-propene under the same conditions gave *trans*-methylstilbene in a lower yield (24%) and *trans*-stilbene yielded triphenylethylene in a 28% yield on treatment with palladium acetate under similar conditions.[4] These facts indicate that, in this reaction, an electronic factor of the nitro group in I plays an important role. Both α-nitrostilbene (II) and 1,1-diphenyl-2-nitroethylene(III) reacted with benzene to give 1,1,2-triphenyl-2-nitroethylene(VII) (14.4 and 2.2% yields respectively), accompanied by considerable amounts of biphenyl and unidentified carbonyl compounds. The low yields of the phenylated compounds and the formation of appreciable amounts of by-products may be due to the steric hindrance of two phenyl groups and the nitro group. In fact, in their study of the phenylations of a series of phenyl-substituted ethylenes, Fujiwara *et al.* reported that the reactivity in olefin arylation using palladium salts was markedly influenced by a steric factor and that 1,1,2-triphenylethylene gave tetraphenylethylene in a 13% yield under similar conditions.[4] That the yield of VII from III was lower than those in the cases of II and triphenylethylene is interesting. This fact indicates that, in III, the nitro group on the carbon atom carrying the hydrogen which undergoes substitution interferes with the phenylation reaction. Ethyl α-nitrocinnamate(IV) reacted with benzene under similar conditions to afford the corresponding phenylated product, VIII, in a 47.3% yield; here the steric factor does not seem to be as important as had been expected. This is presumably due to the powerful electron-withdrawing nature of the nitro and carboethoxy groups on the same ethylenic carbon atom. With β-bromo-β-nitrostyrene(V), the expected phenylated compound, 1,1-diphenyl-2-bromo-2-nitroethylene, was not obtained; instead, III was obtained as the main product, together with small amounts of VII and (*Z*)-α-nitrostilbene(IX).

Heck proposed a reaction mechanism for the arylation using palladium salts and an arylmercury compound, in which the first step is the *cis*-addition of arylpalladium acetate to the olefinic double bond, followed by the *cis*-elimination of hydridopalladium acetate.[5] When this mechanism is applied to the case of V, the following reaction pathway is considered. The yield of IX was very slight compared with that of III. This can be explained by considering that the initial complex, XI, was produced in preference to XII, because the phenyl group would tend to be introduced at the carbon atom adjacent to that bearing the nitro group. VII might be derived *via* III and

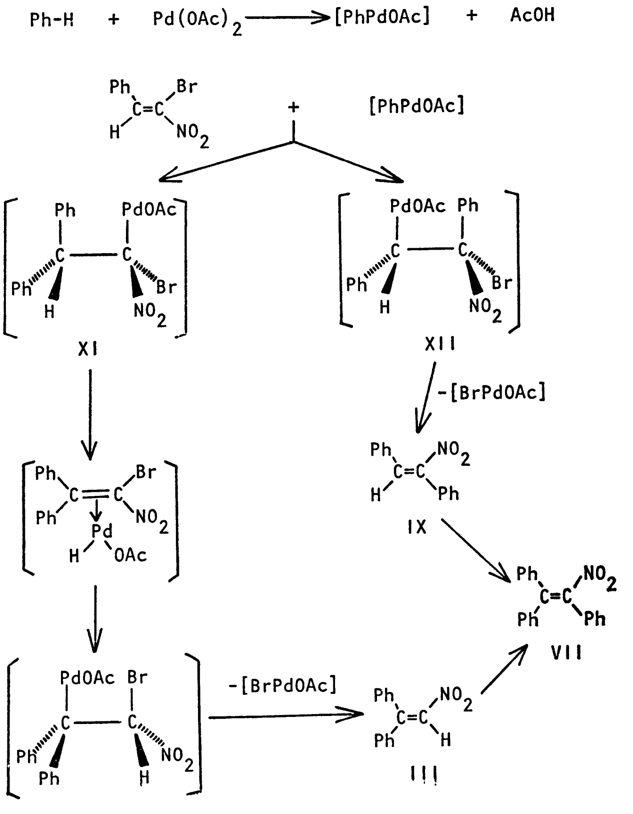
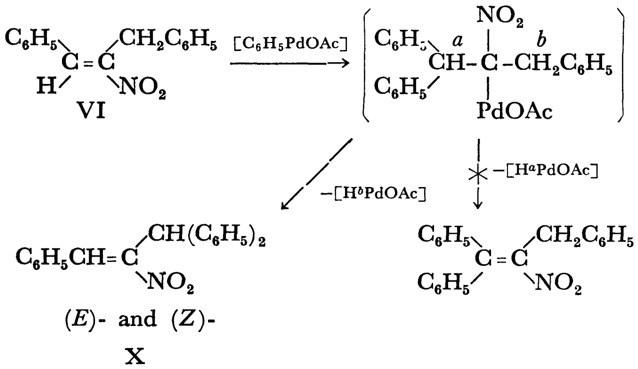


Table 1. Results of phenylation of β-nitrostyrenes

| Starting β-nitrostyrene | | Reaction time (hr) | Phenylated Product | | Yield (%)[a] |
|---|---|---|---|---|---|
| $PhCH=CHNO_2$ | I[b] | 20 | $Ph_2C=CHNO_2$ | III | 70.0 |
| $PhCH=CPhNO_2$ | II[b] | 50 | $Ph_2C=CPhNO_2$ | VII | 14.4 |
| $Ph_2C=CHNO_2$ | III | 250 | $Ph_2C=CPhNO_2$ | VII | 2.2 |
| $PhCH=C(COOEt)NO_2$ | IV[c] | 20 | $Ph_2C=C(COOEt)NO_2$ | VIII | 47.3 |
| $PhCH=CBrNO_2$ | V[b] | 30 | $Ph_2C=CHNO_2$ | III | 20.0[d] |
| $PhCH=C(CH_2Ph)NO_2$ | VI[b] | 20 | $PhCH=C(CHPh_2)NO_2$ | X | 66.0[e] |

a) Yields are of isolated and purified products. b) (*E*)-isomer. c) (*Z*)-isomer. d) Small amounts of (*Z*)-α-nitrostilbene(IX) and VII were also isolated. e) Total yield; (*E*)-: 34.0, (*Z*)-: 32.0 %.

IX. From 1,3-diphenyl-2-nitro-1-propene(VI), two unexpected compounds, (*E*)- and (*Z*)-1,3,3-triphenyl-2-nitro-1-propene(X), were obtained as the main products,[6] and at the end of reaction considerable amounts of the starting VI were recovered. When VI was treated with a 2-mol equiv. of palladium acetate under similar conditions, (*E*)- and (*Z*)-X were obtained in 34.0 and 32.0% yields respectively. The usual phenylated compound, 1,1,3-triphenyl-2-nitro-1-propene, was not obtained. The formation of X from VI may also be explained by the addition-elimination mechanism.[5]



In all of the β-nitrostyrenes investigated in this study, the reactivity and the direction of the introduction of the phenyl group are markedly influenced by the electronic factor of the nitro group. This finding is interesting because it has previously been reported that the direction of the introduction of an aromatic group to unsymmetrical olefins is influenced by the steric factor rather than by the electronic one.[7]

## Experimental

*Materials.* Palladium acetate was prepared according to the method of Stephenson *et al.*[8] All the β-nitrostyrene derivatives except 1,3-diphenyl-2-nitro-1-propene(VI) were prepared by the method described in a previous paper.[1]

*Preparation of VI.* A mixture of freshly distilled benzaldehyde (0.05 mol), 1-phenyl-2-nitroethane (0.05 mol), and butylamine(0.02 mol) in 100 ml of toluene was refluxed for 16 hr. After the evaporation of the solvent, the residue was chromatographed over silica gel. Pale yellow crystals of VI were thus obtained in a 51% yield; mp 52 °C. IR (KBr), 1639, 1514, 1495, 1447, 1325, 767, 740, 695 $cm^{-1}$; NMR ($CDCl_3$), δ 8.30(s 1H, vinyl), 7.42 (s 5H, phenyl), 7.27 (s 5H, phenyl), 4.27 (s 2H, methylene). Found: C, 75.37; H, 5.44: N, 5.90%.

*General Procedure for the Phenylation of β-Nitrostyrenes.* A mixture of the β-nitrostyrene derivative (0.01 mol) and palladium acetate (0.01 mol) in 150 ml of benzene and 40 ml of acetic acid was refluxed until the precipitation of palladium metal ceased. After the filteration of palladium metal, the reaction mixture was poured into water. The organic layer was separated, and the aqueous layer was extracted with benzene. The combined extract was washed with water, and then the solvent was evaporated. The residue was chromatographed over silica gel, using a mixture of hexane-benzene (1 : 1) as the eluent. The first elution gave biphenyl, while subsequent fractions gave the phenylated products. The structures of the products were determined by means of their IR, UV, and NMR spectra and by elemental analyses. The following results were obtained:

a) The phenylation of I afforded III in a 70.0% yield.

b) The phenylations of II and III afforded VII in 14.4 and 2.2% yields respectively; mp 175 °C (lit,[9] 175 °C).

c) The phenylation of IV afforded VIII in a 47.3% yield; yellow crystals, mp 74 °C. NMR ($CDCl_3$) δ 7.47—7.09 (m, 10H, phenyl), 4.13 (q 2H, methylene, $J$=8 Hz), 1.05 (t 3H, methyl). Found: C, 68.63; H, 4.95; N, 4.68%.

d) The phenylation of V afforded III in a 20.0% yield, accompanied by small amounts of VII and XI.

e) The phenylation of VI with a 2-mol equiv. of palladium acetate afforded a mixture of (*E*)- and (*Z*)-isomers of X in a 66.0% yield. The physical data have been reported in a previous paper.[6]

*Phenylation of* trans-1-*Phenyl*-1-*propene.* Under conditions similar to those described above, *trans*-1-phenyl-1-propene gave *trans*-methylstilbene in a 24% yield.

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