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THE REACTION OF β-METHYL-β-NITROSTYRENE WITH BENZENE IN THE PRESENCE OF PALLADIUM(II) ACETATE

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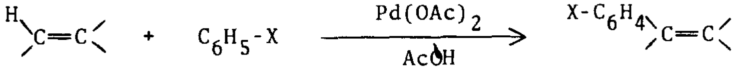
We wish to report the formation of geometrical isomers of diphenylation products (*E*)- and (*Z*)-β-diphenylmethyl-β-nitrostyrene by the reaction of β-methyl-β-nitrostyrene with benzene in the presence of palladium acetate.

Recently, Moritani and Fujiwara *et al*. reported a novel arylation of olefins with benzene derivatives in the presence of palladium acetate.[1)]



$$\mathrm{H}{>}\mathrm{C}{=}\mathrm{C}{<} \; + \; \mathrm{C_6H_5\text{-}X} \xrightarrow[\mathrm{AcOH}]{\mathrm{Pd(OAc)_2}} \mathrm{X\text{-}C_6H_4}{>}\mathrm{C}{=}\mathrm{C}{<}$$

This prompted us to examine phenylation of β-nitrostyrenes as a part of a series of studies on β-substituted β-nitrostyrenes.[2)]

When a mixture of β-methyl-β-nitrostyrene (I), an equimolar amount of palladium acetate, benzene (large excess), and acetic acid was refluxed for 6 hr, the expected compound, 1,1-diphenyl-2-nitropropene (II), was obtained in only very low yield and instead yellow crystals (III), mp 151°, and pale yellow crystals (IV), mp 103°, were obtained as the major products. On the other hand, when I was treated with 3 mol equiv. of palladium acetate for 50 hr, II was no longer produced, but III and IV were obtained in 37.3 and 24.4% yields respectively.

Both III and IV correspond to the same molecular formula $C_{21}H_{17}O_2N$ and are readily interconvertible under the conditions of their formation. Spectral data for III and IV are shown in Table 1. They show that III and IV could be geo-

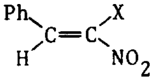
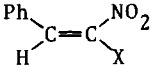
Table 1. Spectral Data for Reaction Products, III and IV

Compd.	IR (KBr) cm^{-1}	UV (in EtOH) mμ (ε)	NMR (in $CDCl_3$)[a] δ, at 60 MHz
III	1637, 1596, 1516, 1496, 1447, 1348(sh), 1328, 825, 788, 765, 695	299 (9300)	8.25(1H,s), 7.32(5H,s), 7.23(10H,s), 5.87(1H,s)
IV	1601, 1525, 1496, 1449, 1356, 749, 696	234 (16100) 286 (4000)	7.28(1H,s), 7.23(5H,s), 6.13(1H,d, J=1.50 Hz), 5.66(1H,d, J=1.50 Hz)

a) TMS was used as an internal standard.

Table 2. Chemical Shifts of α-Vinyl Protons in III, IV, and Related β-Substituted β-Nitrostyrenes

(δ value, at 60 MHz, in $CDCl_3$)

Substituent X (Compds. No.)	Configuration	
	 ppm	 ppm
H	8.02	
CH_3	8.03	
C_6H_5	8.25	6.83
$CO\cdot OC_2H_5$	8.08	7.56
$CO\cdot C_6H_5$	8.36	< 7.90[a]
$CH\cdot(C_6H_5)_2$ (III)	8.25	
(IV)		6.13

a) This signal overlapped with the ring proton region (δ, 7.30—7.90 ppm).

metrical isomers of β-diphenylmethyl-β-nitrostyrene. Table 2 shows the chemical shifts of the α-vinyl proton of III and IV, together with those for some related β-nitrostyrenes whose configurations were already known from their UV and IR spectra.[2] In the eight related β-nitrostyrenes examined, the α-vinyl proton is less shielded in the *cis* than in the *trans* configuration with respect to the nitro group, regardless of the other β-substituent. This fact suggests that the α-vinyl proton of *trans*-β-nitrostyrene systems may experience a large diamagnetic anisotropy effect from the nitro group in the *cis* position. Thus, from a comparison of the chemical shifts of a α-vinyl protons of III and IV, it is reasonable to assign the former as (*E*)-β-diphenylmethyl-β-nitrostyrene with a *trans*-β-nitrostyrene moiety and the latter as (*Z*)-β-diphenylmethyl-β-nitrostyrene with a *cis* one.

The formation of III and IV is noteworthy because it is the first example of phenylation of allylic methyl group with palladium acetate.

Two reasonable routes from I to III and IV are possible (Chart 1). Path A involves an intramolecular hydrogen transfer[3] from II to II', whereas path B involves an addition-elimination process.[4] Thus, whereas II is the intermediate in path A, it is a by-product in path B.

Path A seems to be more likely, because compound II, mp 56° (lit.[5] 56°), was isolated when a mixture of I and palladium acetate in benzene and acetic acid was refluxed for 6 hr, and further reflux of the reaction mixture resulted in a decrease of II and an increase of III and IV. In addition, compound II afforded III and IV when treated with 2 mol equiv. of palladium acetate.

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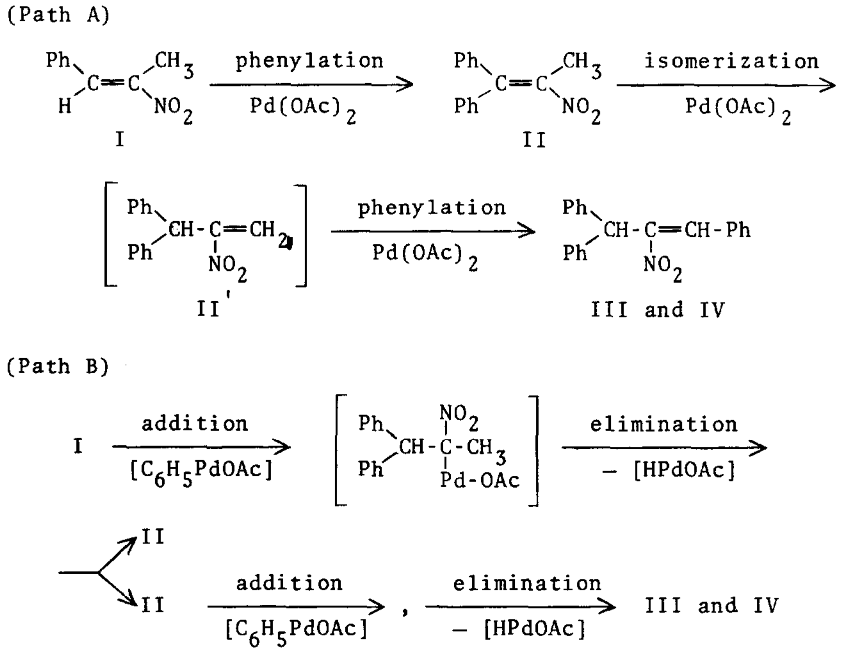

Chart 1

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