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THE REACTION OF SOME β-NITROSTYRENES WITH BENZENE IN THE PRESENCE OF PALLADIUM(II) ACETATE1)

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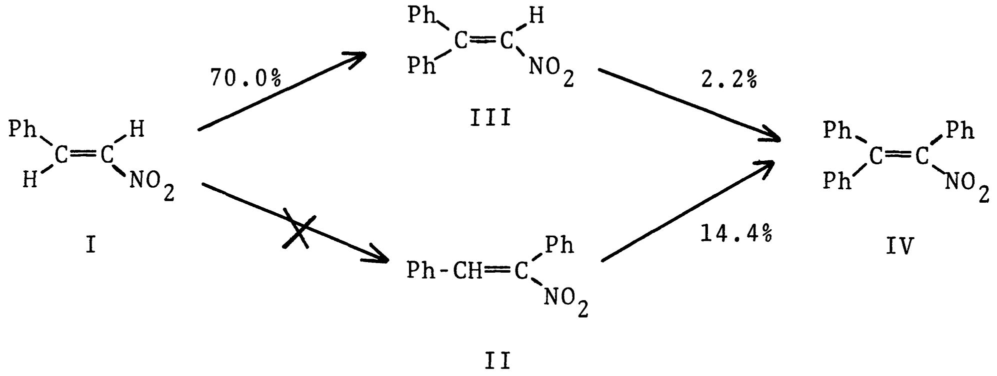
The phenylation of some β-nitrostyrenes, such as β-nitrostyrene, α-nitrostilbene, and 1,1-diphenylnitroethylene, in the presence of palladium(II) acetate is described. The phenylation reactions were affected very strongly by the nitro group, and tend to occur on the olefinic carbon atom adjacent to that bearing the nitro group.

Recently, Moritani et al. reported a novel aromatic substitution of olefins in the presence of palladium(II) acetate,2) and Heck reported the similar phenylation of olefins using palladium(II) salts and aromatic mercuric compounds.3) In a previous paper,4) we reported the formation of geometrical isomers of β-diphenylmethyl-β-nitrostyrene by the reaction of β-methyl-β-nitrostyrene with benzene in the presence of palladium(II) acetate, and reported a reaction pathway involving an intramolecular hydrogen transfer and two-step phenylation process. Although extensive studies on arylation of olefins using palladium(II) salts have been reported in the literature, this was to our knowledge the first case of direct diphenylation of an allylic methyl group, and also the first example of phenylation of nitro-olefins. It was therefore of interest to us to extend these phenylation reactions to other phenylated nitro-olefins, and the present paper deals with phenylation of β-nitrostyrenes such as β-nitrostyrene (I), α-nitrostilbene (II) and 1,1-diphenyl-2-nitroethylene (III).

An equimolar mixture of the β-nitrostyrene and palladium(II) acetate in a large excess of benzene and acetic acid was refluxed with stirring until the precipitation

Table 1. Phenylation of β-Nitrostyrenes

β-Nitrostyrenes		Reaction Time, hr	Phenylated Products yield, %			mp, °C
$C_6H_5CH=CHNO_2$	(I)	20	70.0	$(C_6H_5)_2C=CHNO_2$	(III)	88
$C_6H_5CH=C(C_6H_5)NO_2$	(II)	50	14.4	$(C_6H_5)_2C=C(C_6H_5)NO_2$	(IV)	175
$(C_6H_5)_2C=CHNO_2$	(III)	200	2.2			
$C_6H_5CH=CHCH_3$		50	24.0	$C_6H_5CH=C(C_6H_5)CH_3$		82



of black metallic palladium ceased. The results are summarized in Table 1.

Though β-nitrostyrene (I) has two hydrogen atoms which can be expected to be substituted by phenyl group, 1,1-diphenyl-2-nitroethylene (III) was the main product and no α-nitrostilbene (II), correspond to the β-phenylated compound of I, was obtained under the reaction conditions. The production of III from I in excellent yield is interesting, because β-methylstyrene gave the β-phenylated compound, trans-methylstilbene, in lower yield (24 %) under the same conditions and furthermore Fujiwara et al. reported that trans-stilbene reacted with benzene to give triphenylethylene in 28 % yield under similar conditions.5) This phenylation reaction seems very suitable for the synthesis of III, because the starting materials are readily available and the yield is satisfactory compared to those of methods reported in the literature.6)

The phenylation reaction of α-nitrostilbene (II) proceeded similarly, yielding

1,1,2-triphenyl-2-nitroethylene (IV) in 14.4 % yield, biphenyl, α-acetoxystilbene, and other materials containing a carbonyl group being produced as by-products. The low yield of IV and the formation of by-products may be due to steric hindrance of the nitro and the two phenyl groups on the double bond. IV was also obtained from 1,1-diphenyl-2-nitroethylene (III) under similar conditions, but the yield was only 2.2 % with about 70 % of III recovered unchanged, even when the reaction mixture was allowed to reflux for an extended period. It is interesting that the yield of the phenylation of III is lower than that of the phenylation of triphenylethylene, which like III is regarded as a trisubstituted ethylene, affording tetraphenylethylene in 13 % yield under similar conditions.5) These facts suggest that phenylation reactions of β-nitrostyrenes tend to occur on the olefinic carbon adjacent to that bearing the nitro group. Fujiwara et al. investigated the phenylation of a series of phenyl-substituted ethylenes in the presence of palladium(II) salts and showed that the yields were mainly affected by the steric factors.5) In the cases of β-nitrostyrenes investigated, however, it was shown that both steric and electronic factors, especially the latter, have an effect on the reactivity of the olefins.

It can thus be concluded that, owing to its powerful electronegativity, the nitro group of these β-nitrostyrenes affects very strongly the arylation using palladium(II) acetate.

References

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