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Aromatic Substitution of Olefins. XXI.* Reaction of o-Alkylstyrenes with Benzene in the Presence of Palladium(II) Acetate

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Synopsis. In aromatic substitution of olefins, steric factor of *o*-alkyl substituents of styrene was investigated. The formation of arylated products was found to be decreased by introduction of alkyl groups to *ortho* position of styrene.

In previous papers we reported on a new method for the synthesis of stilbene derivatives by the substitution of aromatics for vinylic hydrogen of styrenes in the presence of palladium(II) salts.¹⁾ It was demonstrated that a steric factor plays an important role. The phenylation reactivity was thus found to diminish markedly in the reactions of diphenylethylene and triphenylethylene with benzene as compared with the reaction of styrene with benzene.¹⁾

In order to elucidate the steric factor in the arylation reaction, we have investigated the reaction of some *ortho*-alkylstyrenes with benzene as well as the reactions of styrene with some alkylbenzenes.

The arylation reactions of o-alkylstyrenes with benzene (Reaction(1)) were carried out under normalized conditions.¹⁾ The results are summarized in Table 1. The reactions of o-methylstyrene(1b), 2,4,6-trimethyl-

styrene(1c), and 2,5-di-tert-butylstyrene(1d) with benzene gave 2b, 2c, and 2d, respectively, as the usual phenylated products besides small amounts of 1,1-diarylethylenes, 3b and 3c.²⁾ Introduction of alkyl groups into the ortho positions of styrene caused a decrease in the yield of arylation products. However, it does not seem likely that the second methyl substituent has any further effect on the arylation from a comparison of the reactions of 1b and 1c.

On the other hand, in the reaction of styrene with methyl substituted benzenes (Reaction(2)), the depressing effect on an additional methyl group was found to be more evident. The reaction of mesitylene with styrene was found to be more than five times slower than that of p-xylene with styrene (Table 2). It should be noted that a small amount of 1,1-diarylethylene was formed in the reaction of mesitylene as well.

A remarkable contrast is observed between the two similar reactions (1) and (2) which lead to the same reaction product 2c; arylation reaction of styrene with mesitylene appeared to be five times slower than that of 1c with benzene.

$$Ar-CH=CH_{2} + PhH \xrightarrow{Pd(OAc)_{2}} Ar \xrightarrow{Pd} C = C \xrightarrow{Ph} Ar \\ H + Ph \xrightarrow{Ar} C = CH_{2}$$

$$2a-d \qquad 3a-d$$

$$a, Ar=Phenyl \qquad b, Ar=o-Tolyl \qquad c, Ar=Mesityl \qquad d, Ar=2,5-Di-But$$

TABLE 1. REACTION OF ALKYLSTYRENES WITH BENZENE

la-d	Products and Yield % ^{b)}	$ \substack{NMR \\ \delta \; in \; CCl_4 } $	$\frac{\mathrm{UV}}{\lambda_{\mathrm{max}}(\log \epsilon)}$
1a ^{a)}	2a , 95		295 (4.40)
	3a , ND ^{c)}		
1b	2b , 50	2.41(s, 3H), 7.18(m, 11H)	294(4.35)
	3b , 3	1.97(s, 3H), 5.08(d, 1H)	247(4.05)
		5.62(d, 1H), 7.10(m, 9H)	
1c	2c, 55	2.20(s, 3H), 2.26(s, 6H)	280(4.32)
		6.40(d, 1H), 6.99(d, 1H)	
		6.71(s, 2H), 7.25(m, 5H)	
	3c, 5	2.07(s, 6H), 2.27(s, 3H)	243 (4.13)
		4.99(d, 1H), 5.87(d, 1H)	
		6.76(s, 2H), 7.15(s, 5H)	
1d	2d , 36	1.35(s, 9H), 1.45(s, 9H)	285(4.30)
		6.62(d, 1H), 7.17(m, 3H)	
		7.35(m, 5H), 7.69(d, 1H)	
	3d , ND		

a) Ref. 1. b) based on Pd(OAc)₂ used. c) none detected.

^{*} Part XX; R. Asano, I. Moritani, Y. Fujiwara, and S. Teranishi, This Bulletin, **46**, 2910 (1973).

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$$Ph-CH=CH_{2} + Ar'H \xrightarrow{Pd(OAc)_{2}} H \xrightarrow{Pd} C = C \xrightarrow{Ar'} H$$

$$4a-c \qquad 5a-c \qquad (2)$$

Table 2. Reaction of styrene with alkylbenzenes

Ar'H		Products and Yield %b)
Toluene	4a ^{a)}	5a , 61
<i>p</i> -Xylene	4 b a)	5b , 47
Mesitylene	4c	5c, 9
		$(0.5)^{c}$

a) Ref. 1. b) based pn Pd(OAc)₂ used. c) 1-Phenyl-1-mesitylethylene **3c** formed.

The results suggest that there is a greater steric hindrance at the site of the arylating species in the transition state involving a palladium-carbon σ bond.³⁾

Experimental

The IR and UV spectra were measured with Hitachi EPI-S2 and Hitachi EPS-2U spectrophotometers, respectively. The NMR spectra were recorded on a JEOL Co. C-60HL spectrometer with TMS as an internal standard. Vpc analyses were carried out with a JEOL JGC-20K gas chromatograph.

Starting olefins ${\bf 1b}$, ${\bf 1c}$, and ${\bf 1d}$ were prepared by known methods.⁴⁾

The arylation reactions were performed under normalized conditions: A mixed solution of olefin (50 mmol), palladium-(II) acetate (50 mmol), benzene (445 ml), and acetic acid (100 ml) was heated under reflux for 8 hr. After the usual work-up, 1) the product mixture was subjected to vpc analysis, (SE-30, Microwax). Samples for spectral measurement and elemental analysis were collected by means of a preparative vpc. The spectral data of these products are summarized in Table 1. The compounds showed satisfactory elemental analyses.

References

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- 2) Compounds **3b** and **3c** were identified by comparison of authentic samples prepared by the reaction of acetophenone with corresponding arylmagnesium bromide followed by dehydration; L. I. Smith, "Organic Syntheses," Coll. Vol. II, p. 95 (1943); R. C. Fason, M. D. Armstrong, W. E. Wallance, and J. W. Kneisley, *J. Amer. Chem. Soc.*, **66**, 681 (1944).
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- 4) C. G. Overberger and J. H. Saunders, "Organic Syntheses," Coll. Vol. III, p. 204 (1955); Hirschberg, J. Amer. Chem. Soc., 71, 3241 (1949); Eisenlahr and Schluz, Ber., 57, 1816 (1924).