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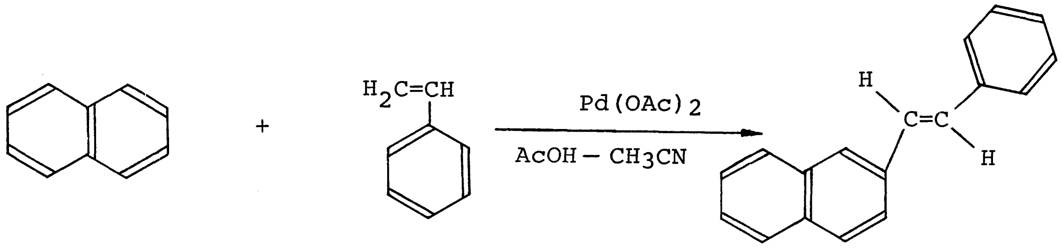
AROMATIC SUBSTITUTION OF OLEFINS. REACTIONS OF NAPHTHALENE AND TRICARBONYL(η-CYCLOBUTADIENE)IRON(0) WITH STYRENE IN THE PRESENCE OF PALLADIUM(II) ACETATE[1]

Yuzo FUJIWARA, Ryuzo ASANO, Ichiro MORITANI, and Shiichiro TERANISHI
Department of Chemistry, Faculty of Engineering Science, Osaka University
Machikaneyama, Toyonaka, Osaka 560

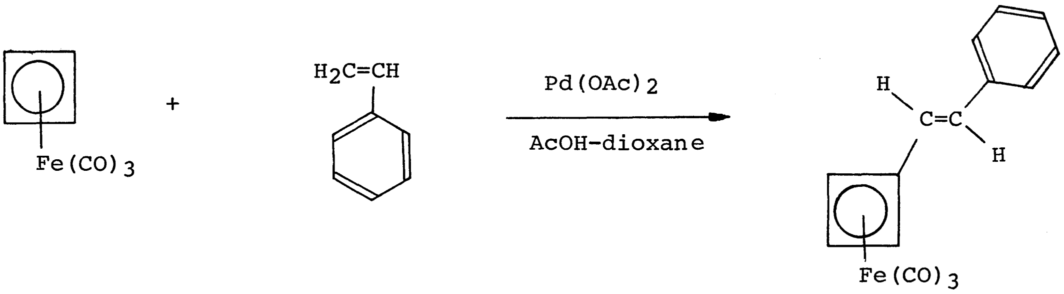
Naphthalene and tricarbonyl(η-cyclobutadiene)iron(0) have been found to react with styrene in the presence of palladium(II) acetate to give the styryl-substituted derivatives. This result shows that the present reaction possesses a high generality with which the reaction can be extended to such classes of the aromatic compounds.

We have discovered the substitution reaction of olefins with benzene derivatives in the presence of palladium(II) salts to give aryl-substituted olefins[2] and showed that a variety of olefins react with benzene derivatives.[3] In extension of this work, we expected that the fused-ring aromatic hydrocarbons such as naphthalene would also undergo the substitution and further nonbenzenoid aromatic compounds such as the cyclobutadienemetal complex should react with olefins if the reaction is a general aromatic substitution reaction.[4]

We report here the reactions of naphthalene and tricarbonyl(η-cyclobutadiene)-iron(0) with styrene to give styryl-substituted aromatic compounds. Thus, naphthalene on heating under reflux with stirring for 8 hr with styrene and $Pd(OAc)_2$ (equivalent amount to styrene) in acetonitrile and acetic acid, leads to trans-2-styrylnaphthalene[5] in a 40% yield (based on styrene), mp 143°C (lit.[6] mp 145-146°C), ir(Nujol): 1449, 980, 966, 822, 740, and 690 cm^{-1}, nmr(CCl_4): 2.00-3.10(m,12H) and 3.30-4.10τ(m,2H) which was assigned by comparison with an authentic sample.[6,7]



Tricarbonyl(η-cyclobutadiene)iron(0) can be considered to be a nonbenzenoid aromatic system in the sence that it easily undergoes electrophilic substitution reactions.[8] Thus, reaction of tricarbonyl(η-cyclobutadiene)iron(0)[9] (10 mmol) with styrene (10 mmol) and Pd(OAc)$_2$ (20 mmol) in a mixture of dioxane (160 ml) and acetic acid (40 ml) under reflux for 8 hr, followed by separation and purification on alumina column chromatography, gives a 6% yield (based on styrene) of light yellow oil, tricarbonyl(η-*trans*-styrylcyclobutadiene)iron(0), ir(neat): 2080, 1970, 960, 934, 831, 759, and 701 cm,$^{-1}$ nmr(CCl$_4$): 2.81(m,5H,phenyl), 3.55(d,1H,olefinic), 3.85(d,1H,J=16 Hz,olefinic), 5.73(s,2H,cyclobutadiene ring), and 5.96(s,1H,cyclobutadiene ring) τ, and a 16% yield of *trans*,*trans*-1,4-diphenylbutadiene.



These are the first examples for the direct substitution of the polynuclear aromatic compound and also the cyclobutadienemetal complex with the olefin. The results, together with those reported already,[3] show that the present aromatic substitution reaction is a general reaction occurring between olefins and both benzenoid and nonbenzenoid aromatic compounds.

References and Notes

1) Considered as part XXIII of this series.
2) Y. Fujiwara, I. Moritani, S. Danno, R. Asano, and S. Teranishi, J. Amer. Chem. Soc., *91*, 7166(1969); J. Chem. Soc.(C), 3691(1971).
3) For a review see I. Moritani and Y. Fujiwara, Synthesis, 524(1973), and references cited therein.
4) It has been known that a variety of olefins react with benzene derivatives without exception, and besides simple benzene derivatives, some nonbenzenoid aromatic compounds such as ferrocene, furan, thiophene and selenophene react with olefins.[3]
5) Interestingly, no 1-styryl isomer was formed probably due to the steric factor.
6) J. L. Everett and G. A. R. Kon, J. Chem. Soc., 1601(1948).
7) Similarly, anthracene, phenanthrene, and pyrene have been found to react with styrene to give the corresponding *trans*-styryl derivatives, mp being 211-212, 205-207, and 106°C, respectively, although the position of the substitution is not yet known.
8) M. P. Cava and M. J. Mitchell, 'Cyclobutadiene and Related Compounds,' Academic Press New York, N.Y., 1967.
9) Prepared according to the method of Pettit *et al*., J. Amer. Chem. Soc., *87*, 131 (1967).

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