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Aromatic Substitution of Olefins. XIX. Reaction of Five-membered Heterocyclic Aromatic Compounds with Styrene

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We reported on substitution reactions of olefins with benzene derivatives in the presence of palladium(II) salts to give aryl-substituted olefins, and demonstrated that a number of olefins undergo the substitution with benzene derivatives.[1] Ferrocene, a nonbenzenoid aromatic compound, undergoes the reaction with vinyl compounds to give alkenylferrocenes *via* direct substitution.[2] If the reaction is of general applicability, heterocyclic aromatic compounds such as furan, thiophene, selenophene, or *N*-methylpyrrole should react with an olefin to give alkenyl-substituted derivatives. We have found that styrene reacts with heterocyclic five-membered aromatic compounds to give styryl-substituted derivatives.

Results and Discussion

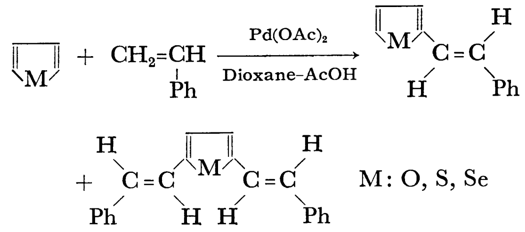
The heterocyclic compounds have greater aromatic reactivity than benzene.[3] Thus it is of interest to determine whether they also react with olefins.

A solution of furan, styrene (equal mole equiv. to furan), palladium(II) acetate (equal mole equiv. to furan) in acetic acid and dioxane was stirred under reflux for 8 hr, to give *trans,trans*-2,5-distyrylfuran (46%, all yields based on palladium(II) acetate) with *trans*-2-styrylfuran (15%). Reactions with other heterocycles such as thiophene, selenophene, or *N*-methylpyrrole were carried out under similar reaction conditions. The results are given in Table 1.

TABLE 1. REACTION OF STYRENE WITH FIVE-MEMBERED HETEROCYCLIC AROMATIC COMPOUNDS BY PALLADIUM(II) ACETATE[a]

Aromatics	Products and yield, %[b]	
Furan	*trans*-2-Styrylfuran	15
	trans,trans-2,5-Distyrylfuran	46
Thiophene	*trans*-2-Styrylthiophene	13
	trans,trans-2,5-Distyrylthiophene	36
Selenophene	*trans*-2-Styrylselenophene	9
	trans,trans-2,5-Distyrylselenophene	34
N-Methylpyrrole	*trans*-2-Styryl-*N*-methylpyrrole	11
	trans-3-Styryl-*N*-methylpyrrole	3
trans-2-Styryl-furan	*trans,trans*-2,5-Distyrylfuran	68
	trans,trans,trans-2,3,5-Tristyrylfuran	12

a) Equimolar amounts of aromatics, styrene, and palladium acetate were used, and all the reactions were carried out under reflux for 8 hr. b) Yields are based on palladium acetate.



It was found that these heterocycles can easily react with styrene to give styryl-substituted heterocycles. Distyryl-substituted cyclic compounds are formed as a major product except for the case of *N*-methylpyrrole, suggesting that the mono-substituted derivative derived from a single-step alkenylation of the heterocycle undergoes further alkenylation reaction with styrene. This may be due to the higher reactivity of the monostyryl-substituted compound in the present reaction. In fact, 2-styrylfuran reacts easily with styrene to afford 2,5-distyrylfuran in a good yield. This double-step alkenylation has not been observed in the reaction of benzenoid aromatic compounds with olefins.[1]

The substitution reaction appears to take place exclusively at positions 2 and 5 of the heterocycles except for *N*-methylpyrrole. This is consistent with the result obtained in electrophilic substitution reactions of these compounds.[4,5] *N*-Methylpyrrole seems to be of low reactivity since the aromatic character of the compound is destroyed by addition of acid.

The results provide a very convenient method for the synthesis of alkenylheterocyclic compounds.

Experimental

IR spectra were recorded on a Japan Spectroscopic Co. IR-E spectrometer. NMR spectra were obtained using a Japan Electron Optics JNM-4H-100 or JEOL C-60HL spectrometer, with tetramethylsilane as an internal standard.

Materials. Palladium (II) acetate was prepared from palladium sponge and acetic acid in the presence of concd. nitric acid. Selenophene (109—110°C) was prepared from butadiene and selenium metal according to the procedure of Yur'ev and Magdesieva.[6,7] Commercial aromatics and styrene were purified before use. Dioxane was refluxed with sodium metal and distilled. Acetic acid was dried over phosphorus pentoxide for 1 week and distilled. Light petroleum refers to a fraction of bp 38—60°C.

General Procedure for the Alkenylation of the Heterocycles. Solutions containing equimolar amounts of palladium(II)

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[1] Y. Fujiwara, I. Moritani, S. Danno, R. Asano, and S. Teranishi, *J. Amer. Chem. Soc.*, **91**, 7166 (1969).

[2] R. Asano, I. Moritani, A. Sonoda, Y. Fujiwara, and S. Teranishi, *J. Chem. Soc. C*, **1971**, 3691, and prior papers of this series.

[3] P. Linda and G. Marino, *Tetrahedron*, **23**, 1739 (1967).

[4] P. Linda and G. Marino, *J. Chem. Soc. B*, **1968**, 392.

[5] S. Clementi and G. Marino, *Tetrahedron*, **25**, 4599 (1969).

[6] Yu. K. Yur'ev and N. N. Magdesieva, *Sb. IREA* (*Rept. Inst. Pure Chem. Reagents, USSR*), No. 6, 6 (1962).

[7] B. A. Arbuzov and E. G. Kataev, *Dokl. Akad. Nauk SSSR*, **96**, 983 (1954), *Chem. Abstr.*, **49**, 8907 (1955).

Table 2. Properties of styrylheterocycles

Compound	Mp (°C) (lit, mp)	Found (%)			Calcd (%)			IR (Nujol, cm^{-1}) and NMR spectra
		C	H	Other	C	H	Other	
trans-2-Styrylfuran	52.5—54 (54—55)[a]	84.73	6.01		84.68	5.92		1148, 1011, 965, 955, 924, 885, 804, 760, 741, 695; τ (CCl$_4$) 2.50—2.93 (5H: 1H,m), 3.04(1H, d, J=16 Hz), 3.22 (1H,d, J=16 Hz), 3.60—3.83 (2H,m)
trans,trans-2,5-Distyrylfuran	144—145.5 (144—145.5)[a]	88.01	5.87		88.20	5.92		960, 792, 757, 696; τ(CCl$_4$) 2.47—2.94(10H,m), 2.97(2H,d, J=16 Hz), 3.23(2H,d, J=16 Hz), 3.73 (2H,s)
trans-2-Styrylthiophene	106.5—108 (112—113)[a]	77.61	5.62		77.38	5.41		965, 866, 845, 824, 760, 714, 698; τ (CCl$_4$) 2.54—3.16 (phenyl 5H: thiophenyl 3H, m), 3.00(1H, d, J=16 Hz), 3.15(1H,d, J=16 Hz)
trans,trans-2,5-Distyrylthiophene	192.5—194 (196—198)[a]	82.99	5.61	11.09 (S)	83.29	5.59	11.12 (S)	954, 800, 753, 696; τ(CDCl$_3$) 2.47—2.94(10H,m), 2.84 (2H, s), 2.92 (2H, d, J=16 Hz), 3.18 (2H, d, J=16 Hz)
trans-2-Styryl-selenophene	134—136	62.15	4.31		61.81	4.32		959, 825, 810, 759, 695; τ(CCl$_4$) 2.29 (1H,m), 2.51—3.04 (phenyl 5H: selenophenyl 2H: olefinic 1H, m), 3.29(1H,d)
trans,trans-2,5-Distyrylselenophene	220—221.5	71.48	4.67		71.64	4.81		948, 802, 753, 696; τ(CDCl$_3$) 2.43—3.01 (phenyl 10H: olefinic 2H,m), 2.81(2H,s), 3.25(2H,d)
trans-2-Styryl-*N*-methylpyrrole	74.5—75.5 (73.5—75)[a]	84.88	7.14	7.61 (N)	85.20	7.15	7.65 (N)	1625, 1296, 1057, 957, 786, 725, 696; τ (CCl$_4$) 2.56—2.94 (5H, m), 3.16 (1H,d, J=15 Hz), 3.28 (1H,d, J=15 Hz), 3.55 (1H, m), 3.69 (1H, m), 4.04 (1H,m), 6.32(3H,s)
trans-3-Styryl-*N*-methylpyrrole	97—98							1630, 1368, 1160, 1083, 968, 918, 788, 749, 715, 696; τ(CCl$_4$) 2.58—2.96 (5H,m), 3.15(1H,d, J=16 Hz), 3.39(1H,d, J=16 Hz), 3.41(1H,m), 3.57(1H,m), 3.76(1H,m), 6.36(3H,s)
trasn,trans,trans-2,3,5-Tristyrylfuran	150.5—151.5	89.57	6.04		89.80	5.92		1595, 1064, 953, 812, 754, 695; τ(CDCl$_3$) 2.30—3.26 (phenyl 15H: olefinic 6H,m), 3.37 (1H,s)

a) Ref. 8.

acetate, styrene, and the heterocycle in acetic acid and dioxane were stirred for 8 hr under reflux. The resulting mixture was filtered to remove palladium metal. The filtrate was poured into water and the mixture was extracted with chloroform. The chloroform extract was washed with aqueous sodium bicarbonate and water, dried (Na$_2$SO$_4$) and then the solvent was evaporated. The products were isolated by alumina column or gas chromatography and identified by comparison (mixed mp, IR, and NMR spectra) with authentic samples. Analytical results and the properties of the styrylheterocycles are given in Table 2. A specific example of the reaction follows.

Reaction of Furan with Styrene. A solution of styrene (1.56 g, 15 mmol), furan (1.02 g, 15 mmol) and palladium(II) acetate (3.37 g, 15 mmol) in dioxane (160 ml) and acetic acid (40 ml) was stirred for 8 hr under reflux (CaCl$_2$ guard tube). After the work-up the residue was chromatographed on a column of alumina (130 g). Elution with light petroleum (900 ml) and recrystallization yielded *trans*-2-styrylfuran (0.38 g, 15%), which was identified by comparison with an authentic sample.[8] Further elution with benzene (500 ml) and recrystallization from ethanol gave *trans,trans*-2,5-distyrylfuran (0.92 g, 46%) which was identified by comparison with an authentic sample.[8] Finally elution with with ether (500 ml) and methanol gave tarry material (0.22 g) which was not further examined. Glc of the solvent evaporated off showed the presence of styrene and a trace amount of β-acetoxystyrene (*cis* and *trans* mixture).

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[8] E. J. Seus, *J. Heterocycl. Chem.*, **2**, 318 (1965).