was triturated with cold water (20 mL) and filtered. The filtrate was acidified with concentrated HCl to pH 2, and the precipitate was collected and crystallized from water to give 370 mg of **11**. See Table IV for physical and analytical data.

Registry No. **1a**, 874-14-6; **1b**, 4401-71-2; **1d**, 3013-92-1; **1e**, 31217-00-2; **1f**, 7033-39-8; **1g**, 36980-91-3; **1h**, 41613-26-7; **1n**, 36980-95-7; **1o**, 38009-11-9; **2a**, 108-13-4; **2i**, 107-95-1; **2j**, 5977-14-0; **2k**, 103-81-1; **2m**, 75993-39-4; **3a**, 35441-11-3; **3b**, 75993-40-7; **3d**, 75993-41-8; **3e**, 75993-42-9; **3f**, 75993-43-0; **3g**, 52600-58-5; **3i**, 18266-78-9; **3j**, 68999-74-6; **3k**, 10211-36-6; **3m**, 75993-44-1; **4**, 49785-67-3; **5**, 71350-47-5; **6a**, 68999-73-5; **6b**, 53422-09-6; **7**, 71350-48-6; **8a**, 6642-31-5; **8p**, 41740-15-2; **8q**, 41862-14-0; **9a**, 57821-20-2; **9g**, 74115-52-9; **9h**, 74115-55-2; **9n**, 74115-56-3; **9o**, 75993-45-2; **9x**, 74115-53-0; **9y**, 75993-46-3; **9z**, 74115-54-1; **10**, 74115-57-4; **11**, 53681-49-5; **12**, 75993-47-4.

Palladium-Catalyzed Alkenylation of Aromatic Heterocycles with Olefins. Synthesis of Functionalized Aromatic Heterocycles[1]

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Aromatic heterocycles such as furan, thiophene, benzofuran, benzothiophene, and *N*-acetylindole undergo facile palladium-assisted alkenylation with various olefins to produce mono- and/or dialkenylated heterocycles in high yield. With furan and thiophene, the reaction is regioselective, giving products substituted at the 2-position of the heterocycles, and is also stereoselective, giving *E* products when the substituent on the olefin is bulky. The reactions of benzofuran and *N*-acetylindole with olefins give cyclization products such as dibenzofuran and carbazole derivatives together with alkenylated products. The mechanistic implications with respect to these alkenylations are discussed.

The reaction with palladium salts has been intensively studied following the discovery of the Wacker process.[2] We have reported a new reaction which combines aromatic compounds and olefins via direct activation of the both olefinic and aromatic C–H bonds by palladium salts, giving aromatic-substituted olefins. This reaction provides a convenient synthetic method for a wide variety of olefins.[3]

Aromatic heterocycles like furan and thiophene are important starting materials for synthesis of various biologically and physiologically active compounds.[4] However, functionalization of these compounds, especially introduction of alkenyl groups to such heterocycles, is difficult and no general method is known for alkenylation. For example, one has to prepare alkenylated heterocycles via multistep procedures involving formylation and subsequent Wittig reactions.[5]

We have developed a new route to alkenylated aromatic heterocycles by the $Pd(OAc)_2$–$Cu(OAc)_2$ catalyst system. Herein we report the palladium-catalyzed one-step mono- and dialkenylations of five-membered aromatic heterocycles such as furan or thiophene[6] and the reactions of benzofuran, benzothiophene, and *N*-acetylindole with olefins like acrylonitrile, methyl acrylate, and styrene to give cyclization products such as dibenzofuran and carbazole derivatives along with alkenylated products.

Table I. Pd-Assisted Alkenylation of Furan and Thiophene with Olefins (CH_2=CHR)

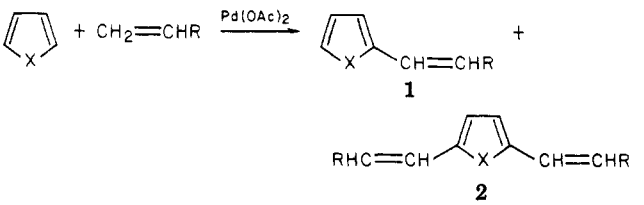
X	R	product, % yield[a] 1	2	stereochemistry
O	CN	23[b]	31[c]	*Z* and *E*
O	Ph	15	46	*E*
O	CO_2CH_3	26	19	*E*
S	CN	24[d]	11[e]	*Z* and *E*
S	Ph	13	36	*E*
S	CO_2CH_3	33	28	*E*

[a] Yields are based on palladium acetate. [b] *Z* and *E* 1:2 mixture. [c] *E,Z* and *E,E* 1:1 mixture. [d] *Z* and *E* 1:2 mixture. [e] *E,Z* and *E,E* 1:1 mixture.

Results and Discussion

Stoichiometric Alkenylation. The alkenylation reactions of furan and thiophene with olefins (CH_2=CHR) were carried out, using equimolar amounts of $Pd(OAc)_2$, the heterocycle, and the olefin in a solution of dioxane and acetic acid. The solution was stirred at 100 °C in the presence of air for usually 8 h. The results are given in Table I.

As can be seen from Table I, furan and thiophene are easily alkenylated with olefins to give 2-alkenylated heterocycles (**1**) and 2,5-dialkenylated heterocycles (**2**) in good



1 **2**

X = O, S
R = CN, Ph, CO_2CH_3

yields. It is interesting that the dialkenylated product is

(1) Presented in part at the 9th International Conference on Organometallic Chemistry, University of Dijon, France, 1979.
(2) Smidt, J.; Hafner, W.; Jira, R.; Sieber, R.; Sedlemeier, J.; Sable, A. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 80. Maitlis, P. M. "The Organic Chemistry of Palladium"; Academic Press: New York, 1971; Vol. 1, 2.
(3) (a) Moritani, I.; Fujiwara, Y. *Tetrahedron Lett.* **1967**, 1119. (b) Fujiwara, Y.; Moritani, I.; Danno, S.; Asano, R.; Teranishi, S. *J. Am. Chem. Soc.* **1969**, *91*, 7166. (c) Moritani, I.; Fujiwara, Y. *Synthesis* **1973**, 524.
(4) For example, see: Katritzky, A. R., Ed. "Advances in Heterocyclic Chemistry"; Academic Press: New York, 1963-1972.
(5) Capron, B.; Paulmier, C.; Pastour, P. *Bull. Soc. Chim. Fr.* **1975**, 2575.
(6) For a preliminary report, see: Maruyama, O.; Yoshidomi, M.; Fujiwara, Y.; Taniguchi, H. *Chem. Lett.* **1979**, 1229.

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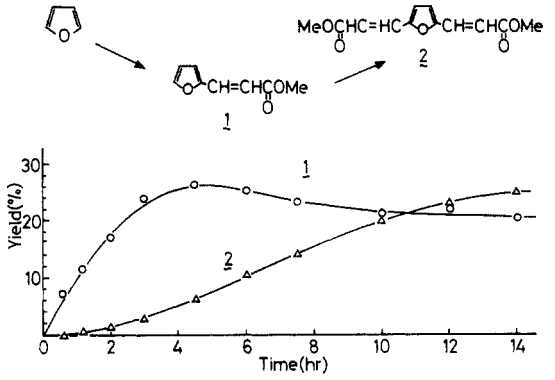


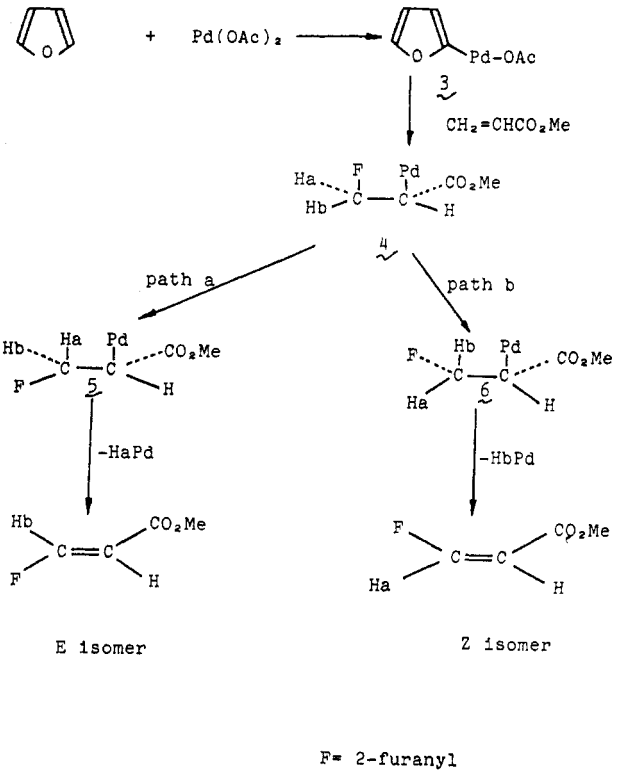
Figure 1. Plot of reaction time vs. the yields of methyl (*E*)-3-(2-furyl)acrylate (1) and (*E,E*)-dimethyl 3,3′-(2,5-furandiyl)bisacrylate (2). Reaction was carried out with stirring at 100 °C, using furan (2.8 mmol), methyl acrylate (2.8 mmol), $Pd(OAc)_2$ (2.8 mmol), dioxane (28 mL), and acetic acid (7 mL) and the yield was determined by GLC.

also obtained in each case whereas the reactions of benzene or ferrocene with olefins give only monoalkenylated products.[7] This may be due to the high reactivity of furan and thiophene in electrophilic substitution. It is reported that furan is 6.1×10^{11} times more reactive than benzene in bromination[8] and 10^3 times more reactive than benzene toward olefins in the palladium-assisted substitution reaction.[9] In order to study the reaction course of the dialkenylated product, we monitored the yield of the products vs. time in the reaction of furan with methyl acrylate and obtained the results shown in Figure 1.

As is apparent from Figure 1, the yield of methyl (*E*)-3-(2-furyl)acrylate (1, X = O; R = CO_2CH_3), the monoalkenylated product, increases with reaction time, reaches a maximum after ca. 5 h, and then gradually decreases. On the other hand, dimethyl (*E,E*)-3,3′-(2,5-furandiyl)bisacrylate (2, X = O; R = CO_2CH_3), the dialkenylated product, is not formed during the first 30 min of the reaction but after that induction period it gradually increases. This fact clearly indicates that the dialkenylated product (2) is formed by further alkenylation of the monoalkenylated one. In fact, when (*E*)-3-(2-furyl)acrylonitrile (1, X = O; R = CN) was reacted with acrylonitrile, the dialkenylated products, (*E,E*)-3,3′-(2,5-furandiyl)bisacrylonitrile (2, X = O; R = CN) and (*E,Z*)-3,3′-(2,5-furandiyl)bisacrylonitrile (2, X = O; R = CN) were obtained in 29% and 14% yields, respectively. Similarly, reaction of 3-(2-thiophenyl)acrylonitrile (1, X = S; R = CN) with acrylonitrile gave (*E,E*)-3,3′-(2,5-thiophenediyl)bisacrylonitrile (2, X = S; R = CN) and its *E,Z* isomer in 23% and 21% yields, respectively. Increasing the mole ratio of $Pd(OAc)_2$ and the olefin to the heterocycle results in the predominant formation of the dialkenylated products. For example, when 2 mol equiv of $Pd(OAc)_2$ and methyl acrylate to thiophene were used, 2 (X = S; R = CO_2CH_3) was obtained in 37% yield with 14% of 1 (X = S; R = CO_2CH_3).

The reaction is regioselective, occurring exclusively at the 2 (or 5) position of the heterocycles. In addition, when the substituent on the olefin is bulky, such as Ph and CO_2Me groups, the products have *E* stereochemistry. The possibility that both *E* and *Z* products are formed initially and the *Z* product undergoes isomerization to the *E* isomer

Scheme I



F= 2-furanyl

Table II. Reactions of Benzofuran and Benzothiophene with Acrylonitrile

heterocycle	product, % yield[a]
benzofuran	**7a**, 5%; **8a**, 16%; **9a**, 3%; **10a**, 9%
benzothiophene	**7b**, 5%; **8b**, 19%; **9b**, 2%; **10b**, 10%

[a] Isolated yields based on $Pd(OAc)_2$

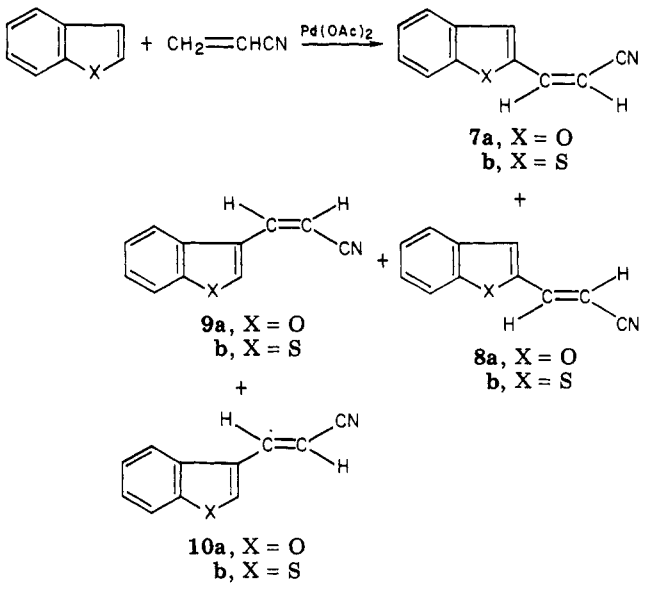
under the reaction conditions is ruled out since it is apparent from Figure 1 that no *Z* isomer is formed during the reaction. Thus, the *E* stereochemistry of the product can be explained by Scheme I.

Consider the reaction of furan with methyl acrylate. First, electrophilic attack of $Pd(OAc)_2$ at the 2-position of furan gives a furyl–Pd σ complex (3). 3 adds to methyl acrylate in *Z* manner to give an alkyl–Pd σ complex (4). For attainment of *Z* elimination of Pd–H, 4 may be transformed to the intermediate 5 or 6. In 6, however, there is greater steric repulsion between furyl and carbomethoxy groups than in 5 since the furyl group is located *Z* to the bulky carbomethoxy group. Therefore, 4 is transformed predominantly to the less sterically hindered intermediate 5 (path a), which affords the *E* product via *Z* elimination of a Pd–H species.[10] When the substituent on the olefin is as small as a CN group, no such stereoselectivity is observed.

The reactions of benzofuran and benzothiophene with acrylonitrile give (*Z*)-2-acrylonitrile derivatives (7) and their *E* isomers (8) and (*Z*)-3-acrylonitrile derivatives (9) and their *E* isomers (10). The yields are shown in Table II.

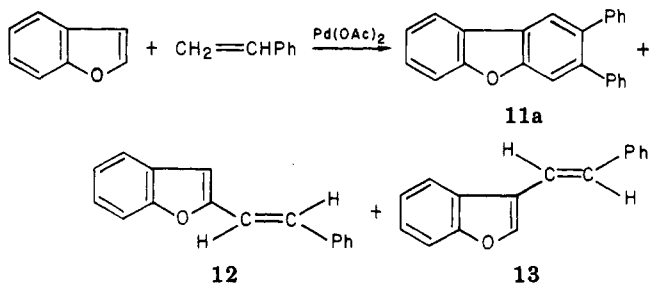
It is characteristic that the reaction of benzofuran gives 3-alkenylated products (**9a**, **10a**, total 12%) also with the 2-alkenylated products (**7a**, **8a**) and that of benzothiophene

(7) Reference 3b. Asano, R.; Moritani, I.; Sonoda, A.; Fujiwara, Y.; Teranishi, S. *J. Chem. Soc. C.* **1971**, 3691.
(8) Linde, P.; Marino, G. *Chem. Commun.* **1967**, 499.
(9) Fujiwara, Y.; Asano, R.; Moritani, I.; Teranishi, S. *J. Org. Chem.* **1976**, *41*, 1681.
(10) A cis addition of the organopalladium compound and a cis elimination of the palladium hydride mechanism has been shown in the reactions of organic halides with olefins: Dieck, H. A.; Heck, R. F. *J. Am. Chem. Soc.* **1974**, *96*, 1133.

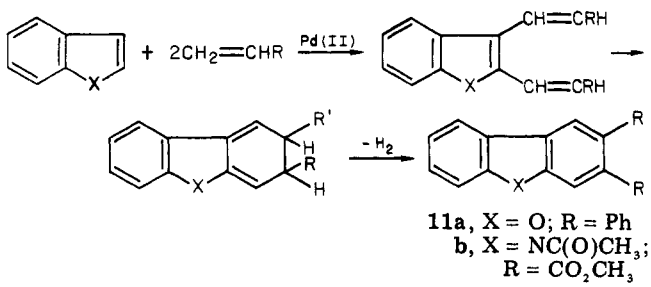


gives 2-alkenylated products (**7b**, **8b**, total 24%) as major products, while substitution at the 3- and 2-positions is generally less favorable for benzofuran and benzothiophene, respectively.[11] The reactivity of benzofuran and benzothiophene toward acrylonitrile is similar. This is compatible with the results in the usual electrophilic substitution reactions such as bromination and acetylation.[11]

Interestingly, the reaction of benzofuran with styrene gives 2,3-diphenyldibenzofuran (**11a**) in 26% yield, together with the usual alkenylated products, (*E*)-2-styrylbenzofuran (**12**, 16%) and (*E*)-3-styrylbenzofuran (**13**, 3%), and the coupling product, (*E,E*)-1,4-diphenylbutadiene (2%), and a trace amount of β-acetoxystyrene.



Similarly, the reaction of *N*-acetylindole with methyl acrylate gives *N*-acetyl-2,3-bis(carbomethoxy)carbazole (**11b**) in 9% yield with (*E*)-methyl 3-(1-acetyl-1*H*-indol-3-yl)acrylate (**14**, 20%), (*E*)-methyl 3-(1-acetyl-1*H*-indol-2-yl)acrylate (**15**, 4%), and a small amount of an unidentified monoalkenylated *N*-acetylindole (substitution site not determined). The formation of dibenzofuran and carbazole derivatives is the first example and can be explained in terms of dialkenylation of the heterocycles followed by an electrocyclic reaction and subsequent dehydrogenation. By this reaction one can prepare dibenzofuran and carbazole derivatives in one-step from olefins and benzofuran or indole.



Catalytic Alkenylation. The catalytic reactions of furan and thiophene with olefins were performed with 100 mol equiv of $Cu(OAc)_2$ to $Pd(OAc)_2$ at 100 °C with stirring for 8 h under air or oxygen. Table III summarizes the results. From the reaction of furan and acrylonitrile, for example, there were obtained 3-(2-furyl)acrylonitrile (**1**, X = O; R = CN; a mixture of *E* and *Z*) and 3,3′-(2,5-furandiyl)bisacrylonitrile (**2**, X = O; R = CN; a mixture of *E,E* and *Z,E*) in 1952% (39%) (yields in parentheses are based on the starting olefin) and 1070% (21%) yields based on $Pd(OAc)_2$, respectively. The total catalytic yield approaches ca. 3000%. In this catalytic alkenylation of heterocycles, reduced Pd(0) is reoxidized by $Cu(OAc)_2$. It is characteristic that mono- and dialkenylations of the heterocycles proceed in high yield without the use of dangerous oxygen high pressure, only atmospheric pressure of air or oxygen being sufficient. This is partly due to the higher reactivity (ca. 1000 times) of these heterocycles relative to benzene.

Byproducts. As byproducts, the reaction of styrene with benzofuran also gave a butadiene, the dimerized product, and an enol acetate, but yields of those were very low and no such products were formed in the reactions with other olefins under the reaction conditions.[3b] Butadienes and enol acetates are known to be obtained by the oxidative coupling of olefins and by the nucleophilic attack of acetate anion on olefins, respectively.[12] That the reactivity of aromatic compounds toward olefins is far higher than that of acetate anion suggests that aromatics are highly activated by palladium(II) compounds forming aromatic-Pd σ complexes.[3b] The aromatic-Pd σ complex formed would add to olefins to give alkenylated products predominantly via HPd elimination.

Conclusion. By the present reaction the functionalization of heterocycles can be readily achieved. The reaction has the following characteristics: (a) since aromatic heterocyles such as furan itself undergo alkenylation with olefins to give mono- and dialkenylated products in just one step, there is no need to convert the heterocycles into their halides or aldehyde derivatives before alkenylation; (b) the reaction is regioselective, giving products substituted at the 2-position; (c) the reaction is stereoselective, giving *E* products when the substituent on the olefin is bulky; (d) in the reaction of benzofuran and benzothiophene with olefins, both 3- and 2-alkenylated products which are usually difficult to prepare from benzofuran and benzothiophene, respectively, can be formed; (e) from the reactions of benzofuran or indole with olefins, bibenzofuran and carbazole derivatives are formed via an electrocyclic reaction of dialkenylated products; (f) the reaction proceeds catalytically by the use of $Cu(OAc)_2$.

By use of this method a large number of alkenylated aromatic heterocycles can be synthesized in one step. The heterocycles functionalized by the reactive alkenyl group should serve as useful synthetic intermediates.

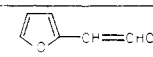
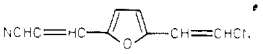
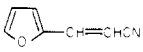
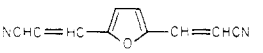
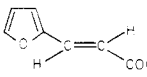
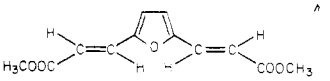
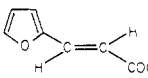
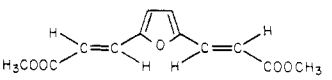
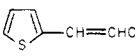
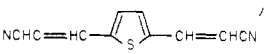
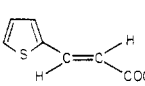
Experimental Section

General. NMR spectra were obtained with a Hitachi R-24S spectrometer, using Me_4Si as an internal standard. Mass spectra were taken with a Japan Electron Optics JMS-07 instrument.

(11) Clementi, S.; Linde, P.; Marino, G. *J. Chem. Soc. B* **1971**, 79.

(12) Tsuji, J. "Organic Synthesis with Palladium Compounds"; Springer-Verlag: New York, 1980. See also ref 2.

Table III. Catalytic Alkenylation of Furan or Thiophene with Olefins by $Pd(OAc)_2$-$Cu(OAc)_2$ [a]

heterocycle	olefin	$Pd(OAc)_2$, mmol	$Cu(OAc)_2$, mmol	product	% yield [b] based on $Pd(OAc)_2$ (olefin)
furan	acrylonitrile [c]	0.04	4.0	 [d]	1952 (39)
				 [e]	1070 (21)
furan	acrylonitrile [f]	0.04	1.0		1028 (21)
					665 (13)
furan	methyl acrylate [f]	0.04	4.1	 [g]	1039 (20)
				 [h]	458 (9)
furan	methyl acrylate [f]	0.04	0.2		325 (7)
					46 (1)
thiophene	acrylonitrile [c]	0.04	4.0	 [i]	361 (7)
				 [j]	16 (0.3)
thiophene	methyl acrylate [c]	0.04	4.0	 [k]	163 (3)

[a] Reactions were carried out at 100 °C with stirring for 8 h, using the heterocycle and the olefin (2.0 mmol each), dioxane (20 mL), and acetic acid (5 mL). [b] Yields are determined by GLC with the use of an internal standard. [c] Under air. [d] Mixture of 33% *Z* and 67% *E* isomers. [e] Mixture of 55% *E,E* and 45% *E,Z* isomers. [f] Under oxygen. [g] A trace amount of *Z* isomer was also detected by GLC. [h] A trace amount of the compound thought to be an *E,Z* isomer was also detected by GLC. [i] Mixture of 67% *E* and 33% *Z* isomers. [j] Mixture of 50% *E,E* and 50% *E,Z* isomers. [k] No dialkenylated product was obtained.

Table IV. Properties of Alkenylated Furans and Thiophenes

alkenylated heterocycle	IR (Nujol), cm^{-1}; NMR ($CDCl_3$) δ
(*E*)- and (*Z*)-3-(2-furyl)acrylonitrile [a]	(neat) 2200, 1622, 956; 5.63 (d, *J* = 17 Hz, 1 H), 5.11 (d, *J* = 12 Hz, 1 H), 6.3–7.6 (m, 4 H)
(*E,E*)-3,3′-(2,5-furandiyl)bisacrylonitrile [b]	2200, 1605, 950; 5.89 (d, *J* = 17 Hz, 2 H), 6.70 (s, 2 H), 7.12 (d, *J* = 17 Hz, 2 H)
(*E,Z*)-3,3′-(2,5-furandiyl)bisacrylonitrile	2200, 1605, 950; 5.40 (d, *J* = 12 H, 1 H), 6.02 (d, *J* = 16 Hz, 1 H), 6.6–7.4 (m, 4 H)
(*E*)-methyl 3-(2-furyl)acrylate	(neat) 1639, 928; 3.73 (s, 3 H), 6.13–6.60 (m, 3 H), 7.41 (d, *J* = 15.6 Hz, 1 H), 7.40–7.45 (m, 1 H)
(*E,E*)-dimethyl 3,3′-(2,5-furandiyl)acrylate [c]	1725, 1629, 961; 3.79 (s, 6 H), 6.38 (d, *J* = 16 Hz, 2 H), 6.68 (s, 2 H), 7.40 (d, *J* = 16 Hz, 2 H)
(*E*)-methyl 3-(2-thiophenyl)acrylate	1715, 979; 3.69 (s, 3 H), 6.08 (d, *J* = 16 Hz, 1 H), 6.7–7.3 (m, 3 H), 7.61 (d, *J* = 16 Hz, 1 H)
(*E,E*)-dimethyl 3,3′-(2,5-thiophenediyl)bisacrylate [d]	1715, 950; 3.74 (s, 3 H), 6.16 (d, *J* = 16 Hz, 2 H), 7.07 (s, 2 H), 7.62 (d, *J* = 16 Hz, 2 H)
(*E*)- and (*Z*)-3-(2-thiophenyl)acrylonitrile [e]	2207, 1600, 953; 5.20 (d, *J* = 17 Hz), 6.9–7.1 (m)
(*E,E*)-3,3′-(2,5-thiophenediyl)bisacrylonitrile	5.62 (d, *J* = 16 Hz, 2 H), 7.10 (s, 2 H), 7.33 (d, *J* = 16 Hz, 2 H)
(*E,Z*)-3,3′-(2,5-thiophenediyl)bisacrylonitrile	5.35 (d, *J* = 12 Hz, 1 H), 5.73 (d, *J* = 17 Hz, 1 H), 7.0–7.7 (m, 4 H)

[a] Mixture of 33% *Z* and 67% *E* isomers: Patterson, J. M. "Organic Syntheses"; Wiley: New York, 1973; Collect. Vol. V, p 585. [b] Mp 170–173 °C (chloroform–hexane). [c] Mp 142.5–143.5 °C (benzene). [d] Mp 119–121 °C (hexane). [e] Mixture of 67% *E* and 33% *Z* isomers: *Chem. Abstr.* **1968**, *68*, 3854.

Palladium acetate was prepared from palladium sponge and glacial acetic acid by the method of Wilkinson et al.[13] Furan and thiophene were dried over sodium sulfate and distilled. Acrylonitrile and methyl acrylate were dried over molecular sieves and distilled. Dioxane was refluxed with sodium metal and distilled. *N*-Acetylindole was prepared from indole and acetyl chloride according to the literature.[14] Other starting materials were commercial grade.

General Procedure for the Catalytic Alkenylation of the Five-Membered Heterocycles. Into a 50-mL centrifuge tube containing a magnetic stirring bar were added the heterocycle (2 mmol), the olefin (2 mmol), $Pd(OAc)_2$ (0.04 mmol), $Cu(OAc)_2$ (4 mmol), dioxane (20 mL), and acetic acid (5 mL) and the tube

(13) Stephenson, T. A.; Morehouse, S. M.; Powel, A. R.; Heffer, J. P.; Wilkinson, G. *J. Chem. Soc.* **1965**, 3632.

(14) Illi, V. O. *Synthesis* **1979**, 387.

was sealed under air or oxygen with a No-Air stopper to avoid evaporation of the volatile starting materials. Then the mixture was heated with stirring for 8 h at 100 °C. The mixture was filtered to remove Pd and Cu metals, and after the usual workup, the products were analyzed by GLC and some products were separated by column (alumina) chromatography. Yields were determined by GLC directly with the use of an internal standard. Identities with the products formed were proved by IR or NMR and retention time comparison with authentic samples. Properties of the alkenylated five-membered heterocycles are listed in Table IV. Those of the products obtained from reactions of furan and thiophene with styrene were already described.[15]

General Procedure for the Stoichiometric Alkenylation of the Heterocycles. Solutions containing equimolar amounts of $Pd(OAc)_2$, the olefin, and the heterocyles in acetic acid and dioxane were stirred for 8 h at 100 °C. The resulting mixture was filtered to remove Pd 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 and dried and the solvent was evaporated. The products were isolated by column chromatography. Specific examples of the reaction are given in detail below.

Reaction of Benzofuran with Acrylonitrile. A solution of benzofuran (356 mg, 3 mmol), acrylonitrile (161 mg, 3 mmol), $Pd(OAc)_2$ (675 mg, 3 mmol), acetic acid (8 mL), and dioxane (32 mL) was stirred for 8 h under reflux. After workup as described above, the residue was chromatographed on a column of silica gel. Elution with hexane–carbon tetrachloride (1:4) yielded colorless crystals which were assigned as (*Z*)-3-(3-benzofuranyl)acrylonitrile (**9a**): 3% yield (yields given in this paper are based on $Pd(OAc)_2$); mp 68–68.8 °C (hexane); IR (Nujol) 2210 and 858 cm^{-1}; NMR ($CDCl_3$) δ 5.43 (d, J = 12 Hz, 1 H), 7.0–7.8 (m, 5 H), 8.50 (s, 1 H); mass spectrum, m/e 169 (M^+); UV (cyclohexane) λ_{max} 236, 241 nm.

Further elution with carbon tetrachloride–chloroform (4:1) gave a mixture of (*Z*)-3-(2-benzofuranyl)acrylonitrile (**7a**, 5%) and its *E* isomer (**8a**, 14%). Recrystallization from hexane gave **8a** only: canary yellow crystals; mp 89–90 °C (hexane); IR (Nujol) 2210, 977, 878 cm^{-1}; NMR ($CDCl_3$) δ 6.00 (d, 1 H, J = 17 Hz), 6.90 (s, 1 H), 7.0–7.8 (m, 5 H); mass spectrum, m/e 169 (M^+); UV (cyclohexane) λ_{max} 316, 331 nm. NMR spectral analysis of the mother liquor showed that this liquor contained (*Z*)-3-(2-benzofuranyl)acrylonitrile (**7a**): NMR of **7a** and **8a** mixture ($CDCl_3$) δ 5.42 (d, 1 H, J = 12 Hz), 6.00 (d, 1 H, J = 17 Hz), 6.90 (s, 1 H), 6.93 (s, 1 H), 7.0–7.8 (m, 5 H).

Further elution with carbon tetrachloride–chloroform (2:3) yielded (*E*)-3-(3-benzofuranyl)acrylonitrile (**10a**, 9%): colorless crystals; mp 105.6–107.4 °C (sublimation followed by recrystallization from hexane); IR (Nujol) 2210, 960, 850 cm^{-1}; NMR ($CDCl_3$) δ 5.93 (d, 1 H, J = 17 Hz), 7.1–7.8 (m, 5 H), 7.84 (s, 1 H); mass spectrum, m/e 169 (M^+); UV (cyclohexane) λ_{max} 235, 241 nm. Finally elution with chloroform gave a small amount (24 mg) of the compound thought to be 3,3′-(2,3-benzofuranyl)-bisacrylonitrile: IR ($CHCl_3$) 2210, 954 cm^{-1}; NMR ($CDCl_3$) δ 6.07 (d, J = 17 Hz), 6.17 (d, J = 17 Hz), 7.1–7.9 (m).

Reaction of Benzofuran with Styrene. Reaction was carried out with stirring under reflux for 8 h, using benzofuran (1.18 g, 10 mmol), styrene (1.04 g, 10 mmol), $Pd(OAc)_2$ (2.25 g, 10 mmol), dioxane (107 mL), and acetic acid (27 mL). The products were separated and analyzed by silica gel column and gas chromatography to give 2,3-diphenyldibenzofuran (**11a**, 26%), (*E*)-2-styrylbenzofuran (**12**, 16%), (*E*)-3-styrylbenzofuran (**13**, 3%), (*E,E*)-1,4-diphenylbutadiene (2%), and a trace amount of β-acetoxystyrene. **11a**: yellow crystals; mp 138–138.5 °C; IR (Nujol) 686, 740, 955 cm^{-1}; NMR ($CDCl_3$) δ 6.8–7.9 (m); mass spectrum, m/e 320 (M^+). **12**: colorless crystals; mp 124.5–126 °C (EtOH) (lit.[16] mp 123 °C); IR (Nujol) 945 cm^{-1}. This compound was identified by comparison with an authentic sample prepared from 2-formylbenzofuran and benzyltriphenylphosphonium chloride.[16] **13**: colorless crystals; mp 118–119 °C (EtOH); IR (Nujol) 963 cm^{-1}. This was identified by comparison with the sample prepared from 3-formylbenzofuran and benzyltriphenylphosphonium chloride.

Reaction of Benzothiophene with Acrylonitrile. Reaction was carried out with stirring under reflux for 8 h, using benzothiophene (403 mg, 3 mmol), acrylonitrile (159 mg, 3 mmol), $Pd(OAc)_2$ (674 mg, 3 mmol), dioxane (32 mL), and acetic acid (8 mL). The products were (*Z*)-3-(2-benzothiophenyl)acrylonitrile (**7b**, 5%), (*E*)-3-(2-benzothiophenyl)acrylonitrile (**8b**, 19%), (*Z*)-3-(3-benzothiophenyl)acrylonitrile (**9b**, 2%), (*E*)-3-(3-benzothiophenyl)acrylonitrile (**10b**, 10%), and a trace amount of the compound thought to be 3,3′-(2,3-benzothiophenyl)bisacrylonitrile; mass spectrum, m/e 236 (M^+). **7b**: mp 107–109 °C (hexane); NMR ($CDCl_3$) δ 5.35 (d, 1 H, J = 12 Hz), 7.1–8.0 (m, 6 H); mass spectrum, m/e 185 (M^+); UV (cyclohexane) λ_{max} 321 nm. **8b**: mp 102–104.4 °C (sublimation); NMR ($CDCl_3$) δ 5.61 (d, 1 H, J = 17 Hz), 7.1–7.9 (m, 6 H); mass spectrum, m/e 185 (M^+); UV (cyclohexane) λ_{max} 318 nm. **9b**: mp 108.5–111 °C (sublimation); NMR ($CDCl_3$) δ 5.50 (d, 1 H, J = 12 Hz), 7.1–8.0 (m, 5 H), 8.51 (s, 1 H); mass spectrum, m/e 185 (M^+); UV (cyclohexane) λ_{max} 229, 232 nm. **10b**: mp 106–110 °C (sublimation and recrystallization from hexane); NMR ($CDCl_3$) δ 5.75 (d, 1 H, J = 17 Hz), 7.0–7.9 (m, 6 H); mass spectrum, m/e 185 (M^+); UV (cyclohexane) λ_{max} 229, 232 nm.

Reaction of *N*-Acetylindole with Methyl Acrylate. Reaction was carried out with stirring under reflux for 8 h, using *N*-acetylindole (317 mg, 2 mmol), methyl acrylate (180 μL, 2 mmol), Pd $(OAc)_2$ (448 mg, 2 mmol), dioxane (20 mL), and acetic acid (5 mL). The products were *N*-acetyl-2,3-bis(carbomethoxy)carbazole (**11b**, 9%), (*E*)-methyl 3-(1-acetyl-1*H*-indol-3-yl)-acrylate (**14**, 20%), (*E*)-methyl 3-(1-acetyl-1*H*-indol-2-yl)acrylate (**15**, 4%), and a small amount of an unidentified monoalkenylated *N*-acetylindole (substitution site not determined). **11b**: mp 154–155 °C (hexane–benzene); IR (Nujol) 1695, 1100, 1059, 780, 754 cm^{-1}; NMR ($CDCl_3$) δ 2.84 (s, 3 H), 3.86 (s, 6 H), 7.1–8.2 (m, 4 H), 8.27 (s, 1 H), 8.52 (s, 1 H). **14**: mp 181–183 °C (benzene); IR (Nujol) 1690, 1625, 1013, 974, 751 cm^{-1}; NMR ($CDCl_3$) δ 2.63 (s, 3 H), 3.78 (s, 3 H), 6.46 (d, 1 H, J = 16 Hz), 7.1–8.0 (m, 5 H), 7.58 (s, 1 H), 8.2–8.5 (m, 1 H); mass spectrum, m/e 243 (M^+). **15**: NMR ($CDCl_3$) δ 2.74 (s, 3 H), 3.83 (s, 3 H), 6.32 (d, 1 H, J = 17 Hz), 6.92 (s, 1 H), 7.0–8.3 (m, 5 H), 8.05 (d, J = 17 Hz).

Registry No. (*E*)-1 (X = O; R = CN), 6125-63-9; (*Z*)-1 (X = O; R = CN), 6137-73-1; (*E*)-1 (X = O; R = Ph), 21676-00-6; (*E*)-1 (X = O; R = CO_2CH_3), 58293-85-9; (*E*)-1 (X = S; R = CN), 26250-47-5; (*Z*)-1 (X = S; R = CN), 51791-11-8; (*E*)-1 (X = S; R = Ph), 26708-50-9; (*E*)-1 (X = S; R = CO_2CH_3), 57502-38-2; (*E,E*)-**2** (X = O; R = CN), 72643-68-6; (*E,Z*)-**2** (X = O; R = CN), 72643-71-1; (*E,E*)-**2** (X = O; R = Ph), 41082-14-8; (*E,E*)-**2** (X = O; R = CO_2CH_3), 72643-70-0; (*E,E*)-**2** (X = S; R = CN), 72643-69-7; (*E,Z*)-**2** (X = S; R = CN), 72643-72-2; (*E,E*)-**2** (X = S; R = Ph), 41123-26-6; (*E,E*)-**2** (X = S; R = CO_2CH_3), 76010-70-3; **7a**, 76010-71-4; **7b**, 76010-72-5; **8a**, 76010-73-6; **8b**, 76010-74-7; **9a**, 76010-75-8; **9b**, 76010-76-9; **10a**, 76010-77-0; **10b**, 76010-78-1; **11a**, 76010-79-2; **11b**, 76010-80-5; **12**, 65487-87-8; **13**, 76010-81-6; **14**, 19626-93-8; **15**, 76010-82-7; benzofuran, 271-89-6; acrylonitrile, 107-13-1; 3,3′-(2,3-benzofuranyl)bisacrylonitrile, 76010-83-8; styrene, 100-42-5; (*E,E*)-1,4-diphenylbutadiene, 538-81-8; benzothiophene, 95-15-8; 3,3′-(2,3-benzothiophenyl)bisacrylonitrile, 76010-84-9; *N*-acetylindole, 576-15-8; methyl acrylate, 96-33-3; furan, 110-00-9; thiophene, 110-02-1; $Pd(OAc)_2$, 33571-36-7.

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