Arylation and Vinylation Reactions of Benzo[*b*]furan *via* Organopalladium Intermediates

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The Heck reaction of benzo[*b*]furan with arylpalladium chloride leads to the formation of 2-arylbenzo[*b*]furan derivatives. In the presence of palladium acetate, benzo[*b*]furan reacts in benzene to give 2,2′-bibenzo[*b*]furyl, accompanied by 2-arylbenzo[*b*]furan. In the phenylation of [2-^{2}H]benzo[*b*]furan with phenylpalladium salts, it was confirmed that no hydride shift takes place in the reaction. In the presence of palladium acetate, benzo[*b*]furan also reacts with olefin to produce benzo[*b*]furyl-substituted olefins, accompanied by a small amount of 2,2′-bibenzo[*b*]furyl, and from the reaction of [β,β-$^2H_2$]styrene and benzo[*b*]furan in the presence of palladium acetate it was confirmed that no hydride shift occurs in the reaction.

It is considered that furan possesses a considerable aromatic character arising from the delocalization of four carbon π-electrons and two paired electrons donated by the oxygen atom. However, furan still has a character which clearly resembles a conjugated diene or enol ether. In order to study whether or not the Heck arylation[1] occurs in the reaction of benzo[*b*]furan (I) with arylpalladium compounds, the reaction of I with arylmercuric compounds (II) was performed in the presence of palladium salts. This report also contains the results of a study of the reaction of I and olefins in the presence of palladium acetate.

Results and Discussion

In the presence of palladium salts, I was allowed to react with II in polar solvents, such as ethanol. The substitution reaction on the C_2 of I has been observed to lead to the formation of 2-arylbenzo[*b*]furan (III), accompanied by a small amount of biaryl (IV). The reactions carried out are summarized in Table 1. The properties of the products are given in Table 2. Furthermore, in order to study whether or not a hydride shift takes place between the C_2 and C_3 of I in the Heck reaction of I, the reaction of [2-^{2}H]-benzo[*b*]furan (V) with arylpalladium compounds was performed in ethanol at room temperature. The results are summarized in Table II. If the reaction of V with arylpalladium compounds proceeds *via* a hydride shift, the reaction will produce product (III) containing some deuterium on the C_3. However, in the presence of palladium salts, the reactions of V with phenylmercuric

TABLE 1. THE ARYLATION OF BENZO[*b*]FURANS WITH ARYLPALLADIUM COMPOUNDS

Benzo[*b*]furans	Arylating agent	Product	Yield %[a]
Benzo[*b*]furan	Phenylmercuric acetate	2-Phenylbenzo[*b*]furan (III–1)	77
		Biphenyl[b]	7
Benzo[*b*]furan	*p*-Tolylmercuric chloride	2-*p*-Tolylbenzo[*b*]furan (III–2)	79
		Bi-*p*-tolyl[c]	6
Benzo[*b*]furan	*p*-Anisylmercuric chloride	2-*p*-Anisylbenzo[*b*]furan (III–3)	71
		Bi-*p*-anisyl[d]	8
Benzo[*b*]furan	*m*-Nitrophenylmercuric chloride	2-(*m*-Nitrophenyl)benzo[*b*]furan (III–4)	70
		3,3′-Dinitrobiphenyl[e]	5
5-Methylbenzo[*b*]furan	Phenylmercuric acetate	2-Phenyl-5-methylbenzo[*b*]furan (III–5)	75
		Biphenyl[b]	9
5-Methylbenzo[*b*]furan	*p*-Tolylmercuric chloride	2-*p*-Tolyl-5-methylbenzo[*b*]furan (III–6)	72
		Bi-*p*-tolyl[c]	6
5-Methylbenzo[*b*]furan	*p*-Anisylmercuric chloride	2-*p*-Anisyl-5-methylbenzo[*b*]furan (III–7)	66
		Bi-*p*-anisyl[d]	8
5-Methylbenzo[*b*]furan	*m*-Nitrophenylmercuric chloride	2-(*m*-Nitrophenyl)-5-methylbenzo[*b*]furan (III–8)	60
		3,3′-Dinitrobiphenyl	6

a) Yields are based upon the arylating agent.
b) Mp 68—69°C, (lit.[f] mp 69—70°C).
c) Mp 119—120°C, (lit.[f] mp 120°C).
d) Mp 170—171°C, (lit.[f] mp 170—172°C).
e) Mp 201—203°C, (lit.[g] mp 198.5—199.5°C).
f) E. Müller and T. Topel, *Ber.*, **72**, 273 (1939).
g) B. W. Williamson and W. H. Rodebush, *J. Amer. Chem. Soc.*, **63**, 3018 (1941).

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[1] R. F. Heck, *J. Amer. Chem. Soc.*, **90**, 5518 (1968); and subsequent papers.

Table 2. Properties and analyses of 2-arylbenzo[*b*]furans (III)

Compound	Mp °C (lit.)	Anal. Found (Calcd) %, C	H	N	IR spectrum (cm^{-1}) and NMR spectrum, ppm (no. of protons).
III-1	120—121 (120—121[a])				
III-2	128—129 (127—129[b])				
III-3	150—151 (151[c])				
III-4	129—130	70.33 (70.28)	3.82 (3.79)	5.86 (5.85)	IR 1530, 1360, 880. NMR δ 7.04 s (1) H on C_3, 7.15—8.14 m (8) aromatic ring protons.
III-5	131—133 (126—129[d])				
III-6	155—156	86.51 (86.44)	6.41 (6.34)		IR 875. NMR δ 2.39 s (3) $-CH_3$, 2.42 s (3) $-CH_3$, 6.88 s (1) H on C_3, 7.15—7.82 m (7) aromatic ring protons.
III-7	172—173 (172[e])				
III-8	157—159	71.29 (71.13)	4.48 (4.37)	5.62 (5.53)	IR 1528, 1355, 882. NMR δ 2.41 s (3) $-CH_3$, 7.04 s (1) H on C_3, 7.17—8.14 m (7) aromatic ring protons

a) P. Yates, *J. Amer. Chem. Soc.*, **74**, 5376 (1952).
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c) M. M. Bokadia, B. R. Brown, and W. Cummings, *J. Chem. Soc.*, **1960**, 3308.
d) F. Wessely and E. Zbiral, *Ann. Chem.*, **605**, 98 (1957).
e) K. K. Thomas and M. M. Bokadia, *J. Indian Chem. Soc.*, **45**, 265 (1968).

Table 3. The reactions of [2-^{2}H]-benzo[*b*]furan (V) with arylmercuric compounds (II)

Arylating agent	Products	Yields (%[a])	D-content of arylbenzo[*b*] furan (III)[b]
Phenylmercuric acetate	III-1 Biphenyl	74 6	0 %[c]
p-Tolylmercuric chloride	III-2 Bi-*p*-tolyl	76 6	0 %[c]
p-Anisylmercuric chloride	III-3 Bi-*p*-anisyl	71	0 %[c]

a) Yields are based upon arylating agent.
b) The deuterium-content of the products was calculated from the mass spectra analyses results.
c) The 60 MHz NMR spectra showed also an absence of *D* in the C_3.

acetate, *p*-tolylmercuric chloride, and *p*-anisylmercuric chloride all result in the formation of III; this indicates that the deuterium content is not at all different from the case of the hydride shift. This clearly shows that no hydride shift occurs in the reaction.

Davidson and Trigg[2] have recently reported that reactions between aryl compounds and palladium salts give arylpalladium complexes, and a biaryl-formation reaction by palladium salts has also been reported.[3] We were interested in whether or not the arylation reaction of I also occurs in the reaction of I, benzene, and palladium acetate, and so the reaction of I with palladium acetate was performed in a solution of acetic acid and benzene for 6 hr. The reactions carried out are summarized in Table 4. Interestingly, in the case of the reaction with benzene, 2,2′-bibenzo[*b*]furyls (VI, homocoupling products) rather than III was formed as the major product, suggesting that the reactivity of I towards palladium acetate is far higher than that of benzene and that I is highly activated by palladium

Table 4. The reactions of benzo[*b*]furans (I) with benzene

Benzo[*b*]furans	Products	Yield %[a]
Benzo[*b*]furan	Biphenyl	4
	III-1	12
	2,2′-Bibenzo[*b*]furyl (VI-1)[b]	68
5-Methylbenzo[*b*]-furan	Biphenyl	5
	III-5	10
	5,5′-Dimethyl-2,2′-bibenzo[*b*]-furyl (VI-2)[c]	70
[2-^{2}H]-Benzo[*b*]-furan	Biphenyl	5
	III-1[d]	11
	VI-1[e]	70

a) Yields are based upon the used benzo [*b*] furans.
b) Mp 194—195°C, (lit.[f] mp 194.5—195.5°C).
c) Mp 217—218°C, IR spectrum: 883 cm^{-1}. NMR spectrum: δ 2.43 s (6) $-CH_3$, 7.01 s (2) furan ring protons, 7.12—7.44 ppm m (6). Found: C, 82.48; H, 5.41%; mol wt 255 (Rast). Calcd for $C_{18}H_{14}O_2$: C, 82.48; H, 5.34%; mol wt 262.
d, e) Deuterium contents of both compounds were 0 % from the mass spectra analyses results and the 60 MHz NMR spectra also showed an absence of D in the furan ring.
f) F. Toda and M. Nakagawa, This Bulletin, **33**, 223 (1960).

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2) J. M. Davidson and C. Trigg, *J. Chem. Soc.*, *A*, **1968**, 1324, 1331.

3) R. van Helden and G. Verberg, *Rec. Trav. Chim. Pays-Bas*, **84**, 1263 (1965); J. M. Davidson and C. Trigg, *Chem. Ind.*, **1966**, 457.

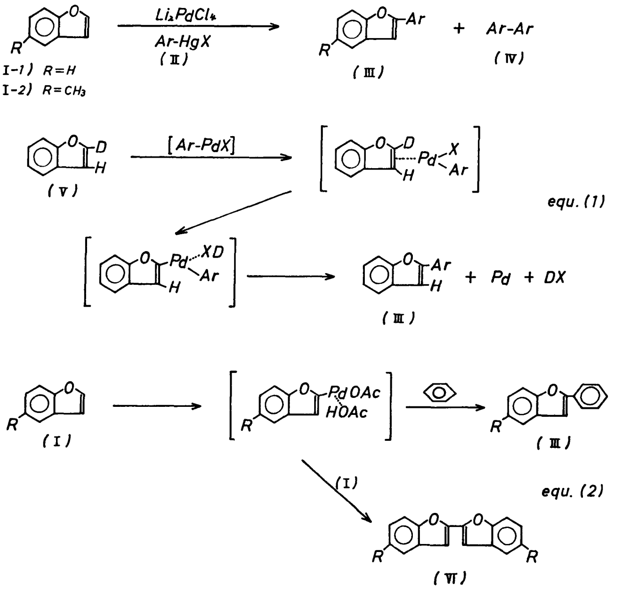

Fig. 1.

salts, thus forming benzo[*b*]furylpalladium salts. The reaction can be explained by Eq. (2) of Fig. 1. Furthermore, the reaction of V and benzene was carried out in the presence of palladium acetate and acetic acid. The deuterium analyses of the products clearly show that no hydride shift occurs in the formation of either VI or III.

On the other hand, Fujiwara *et al.*[4] have described that a reaction mixture of palladium acetate, olefins, benzene derivatives, and acetic acid gives arylation products of olefins. Therefore, in order to investigate the reactivity of I towards olefins, the reaction of I, olefin, and palladium acetate was performed.[5] When a solution of I and olefin in acetic acid was heated at reflux in the presence of palladium acetate, benzo[*b*]furyl-substituted olefin (VII) was obtained as the major product, accompanied by VI. Neither the acetoxylation products of I nor those of olefins were obtained. The results of the reaction are summarized in Table 5. The products were identified by the observation of the IR and NMR spectra (Table 6). For example, the reaction of I-1 with styrene resulted in

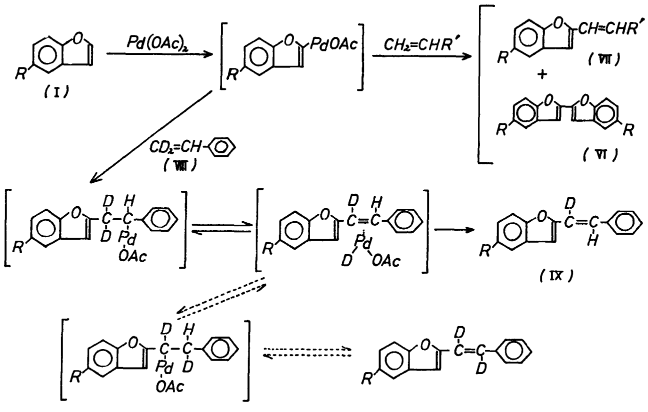

Fig. 2.

Table 5. The reactions of benzo[*b*]furan (I) with olefin

Benzo[*b*]furan	Olefin	Product	Yield %
I-1	Styrene	2-Styrylbenzo[*b*]furan (VII-1)	69
		VI-1	7
I-1	Ethyl acrylate	Ethyl 2-(2-benzo[*b*]furyl)-acrylate (VII-2)	70
		VI-1	5
I-1	Methyl methacrylate	Methyl 2-(2-benzo[*b*]furyl)-methacrylate (VII-3)	53
		VI-1	10
I-1	Ethyl crotonate	Ethyl 2-(2-benzo[*b*]furyl)-crotonate (VII-4)	60
		VI-1	8
I-1	Acrylonitrile	2-(2-Benzo[*b*]furyl)-acrylonitrile (VII-5)	72
		VI-1	8
I-2	Styrene	2-Styryl-5-methylbenzo[*b*]furan (VII-6)	70
		VI-2	6
I-2	Ethyl acrylate	Ethyl 2-(5-methyl-2-benzo[*b*]furyl)-acrylate (VII-7)	67
		VI-2	8
I-2	Methyl methacrylate	Methyl 2-(5-methyl-2-benzo[*b*]furyl)-methacrylate (VII-8)	58
		VI-2	8
I-2	Ethyl crotonate	Ethyl 2-(5-methyl-2-benzo[*b*]furyl)-crotonate (VII-9)	53
		VI-2	9
I-2	Acrylonitrile	2-(5-Methyl-2-benzo[*b*]furyl)-acrylonitrile (VII-10)	62
		VI-2	6
I-2	Methyl vinyl ketone	4-(5-Methyl-2-benzo[*b*]furyl)-3-buten-2-one (VII-11)	67
		VI-2	7
I-2	Acrolein	3-(5-Methyl-2-benzo[*b*]furyl)-2-propenal (VII-12)	55
		VI-2	8

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4) Y. Fujiwara, I. Moritani, S. Danno, R. Asano, and S. Teranishi, *J. Amer. Chem. Soc.*, **91**, 7166 (1969); S. Danno, I. Moritani, Y. Fujiwara, and S. Teranishi, *J. Chem. Soc.*, *B*, **1971**, 196.

5) Recently, it has been reported briefly that the reaction of furan and styrene in the presence of palladium acetate resulted in the formation of 2-styrylfuran and 2,5-distyrylfuran: I. Moritani, R. Asano, Y. Fujiwara, and S. Teranishi, Abstracts of Papers Presented at the 26th Annual Meeting of the Chemical Society of Japan (1972), II, p. 1033.

the formation of 2-styrylbenzo[*b*]furan (VII-1), accompanied by a small amount of VI-1. These results indicate that this substitution reaction occurs on the C_2 atom of I and the β-carbon atom of styrene, and also that the reactivity of the benzo[*b*]furylpalladium compounds is far higher toward olefin than toward I. As with Fujiwara's arylation of olefin, it appears that an electron-donating group on olefinic carbon stoms decreases the yields.

Moreover, in order to study whether or not the reaction of I, olefins, and palladium acetate proceeds *via* a hydride shift, the reaction of I with [β,β-$^2H_2$]-styrenes (VIII) was performed in the presence of palladium acetate and acetic acid. If the hydride shift occurs in the reaction of I with VIII, the reaction will produce a mixture of mono- and di-deuterio-derivative of VII. However, the reaction of I with VIII resulted in the formation of monodeuterio-styrylbenzo[*b*]furans (IX), indicating that the deuterium content is completely different from the case of the hydride shift (D-content=150%). The reaction of V and undeuteriated styrene also produced VII-1, which was free from deuterium. Furthermore, the reaction of V and VIII resulted in the formation of IX. All these results clearly confirmed that no hydride shift takes place in the reaction, and suggested that a loss of hydrido-palladium species from the benzo[*b*]furylpalladium compound-olefin adduct involves the intermediate formation of a hydride-palladium π-complex and is much more likely than the readdition in the reverse direction.

Experimental

Analysis and Materials. All the melting points and boiling points are uncorrected. The infrared spectra were recorded by means of a Hitachi EPI-S IR spectrometer, while the NMR spectra were obtained by a Hitachi H-60 NMR spectrometer at 60 MHz in $CDCl_3$, using tetramethylsilane as the internal standard. Their chemical shifts are recorded as parts per million downfield from tetramethylsilane on the scale, together with the splitting pattern and the relative integrated area: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; d-d, double-doublet. The mass spectra were obtained on a Hitachi RMU-6d mass spectrometer, using a direct inlet and an ionization energy of 70 eV.

The palladium acetate was prepared according to the procedure of Wilkinson.[6] The [β,β-$^2H_2$]-styrene (VIII) was prepared from ethyl phenylacetate according to the method described by Schubert and Lamm.[7] The following compounds were synthesized by the methods described in the literature: benzo[*b*]furan[8] (I-1), bp 173—174°C; 5-methylbenzo[*b*]furan[9] (I-2) bp 197—199°C; *p*-tolylmercuric chloride,[10] mp 232—233°C; *p*-anisylmercuric chloride,[11] mp 173—174°C; *m*-nitrophenylmercuric chloride,[12] mp 218—221°C. The phenylmercuric acetate and the starting olefins were of a commercial grade.

Preparation of [2-^{2}H]-Benzo[b]*furan (V).* 2-Bromobenzo[*b*]furan was prepared from 2,3-dibromobenzo[*b*]furan in an 80% yield by the method described by Stoermer and Kahlert.[13] 2-Bromobenzo[*b*]furan (4.5 g, 0.179 mol) was reduced with lithium aluminum deuteride (4.5 g, 0.107 mol) in anhydrous tetrahydrofuran to [2-^{2}H]benzo[*b*]furan (V) (bp 173—174°C); 65% yield. NMR spectrum: δ 6.49 (s) H on the C_3; 7.06—7.51 (m) aromatic ring protons. The 60 MHz NMR spectrum showed the absence of H on the C_2, and a mass-spectral analysis indicated that the isotopic purity was 98.5%.

Found: C, 80.78; H, 5.97%. Calcd for C_8H_5DO: C, 80.57; H, 5.90%.

General Procedure for the Arylation of Benzo[b]*furans (I).* A lithium chloropalladite solution was prepared by stirring 0.84 g (0.02 mol) of anhydrous lithium chloride and 1.77 g (0.01 mol) of anhydrous palladium chloride overnight at room temperature in 100 ml of ethanol. To this lithium chloropalladite solution, a mixture of 0.01 mol of arylmercuric compound (II) and 0.02 mol of I was added, after which the mixture was stirred at room temperature for 12 hr. The products were isolated by filtration to remove a precipitated palladium and by distillation under reduced pressure to remove the solvent. The residue was dissolved in benzene and chromatographed on alumina. The first elution with benzene and recrystallization from ethanol afforded colorless crystals, which were identified as biphenyl derivatives by a mixed-melting-point determination. Further elution with benzene or chloroform and recrystallization from ethanol afforded the respective arylation product (III). The structures of the products were confirmed by a mixed-melting-point determination with an authentic sample and by the observation of the IR and NMR spectra. The results are summarized in Table 1, while the analytical results and the properties of the products are listed in Table 2.

General Procedure for the Arylation of [2-^{2}H]-Benzo[b]*furan (V).* In an ethanol (80 ml) solution of lithium chloropalladite (0.01 mol), a mixture of 0.01 mol of an arylmercuric compound (II) and 0.02 mol of V was stirred for 12 hr at room temperature. After the separation of the precipitated palladium, and after the evaporation of the solvent, the residual oil was separated by alumina chromatography. The 2-arylated benzo[*b*]furan thus produced was recrystallized from ethanol. The deuterium-content of the purified products was calculated from a mass-spectra analysis. (see Table 3).

General Procedure for the Reaction of Benzo[b]*furans (I) with Benzene.* In a solution of dry benzene (100 ml) and acetic acid (40 ml), was dissolved palladium acetate (2.24 g, 0.01 mol) and an equivalent amount of I. The mixture was heated gently under reflux at 80°C with stirring for 6 hr. After the separation of the precipitated palladium, the mixture was poured into water. The organic layer was separated, the aqueous layer was extracted with benzene, and the combined extracts were neutralized, washed, and dried ($MgSO_4$). After the evaporation of the solvent, the residue was dissolved in benzene and chromatographed on alumina. The first elution with benzene afforded colorless crystals which were identified as biphenyl by a mixed-melting-point determination. The second elution with benzene and recrystallization from ethanol afforded the 2-phenylbenzo[*b*]furans (III). Further elution with benzene or chloroform and

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10) F. C. Whitemore, F. H. Hamilton, and N. Thurman, "Organic Syntheses," Coll. Vol. I, p. 519 (1941).

11) O. Dimroth, *Ber,.* **35**, 2867 (1092).

12) C. Kapproth and F. Westheimer, *J. Amer. Chem. Soc.*, **72**, 4461 (1950).

13) R. Stoermer and B. Kahlert, *Ber.*, **35**, 1636 (1902).

TABLE 6. THE PROPERTIES AND ANALYSES OF 2-BENZO[*b*]FURYL OLEFIN DERIVATIVES (VII)

Compound	Mp °C (lit.)	Anal. Found % (Calcd)		IR spectrum (cm^{-1}) and NMR spectrum (ppm, no. of proton, splitting patterns).
		C	H	
VII-1	121—122	87.29 (87.24)	5.55 (5.49)	IR 960, 875. NMR δ 6.62 1 s furan ring proton C_3, 6.89 1 d $-CH=C\mathbf{H}-Ph$, 7.12—7.68 10 m aromatic ring protons plus $-C\mathbf{H}=CH-Ph$.
VII-2	77—78 (76—77.5[a])			
VII-3	99—100	72.35 (72.21)	5.66 (5.59)	IR 1718, 1640, 880, 810. NMR δ 2.14 3 s $-CH=\underset{\mathbf{CH}_3}{C}-COOMe$, 3.82 3 s $-COOC\mathbf{H}_3$, 6.68 1 s furan ring proton on C_3, 7.20—7.78 5 m aromatic ring protons plus $-C\mathbf{H}=\underset{CH_3}{C}-COOMe$
VII-4	97—98	73.08 (73.03)	6.17 (6.13)	IR 1715, 1620, 894, 803 NMR δ 1.32 3 t $-COOCH_2C\mathbf{H}_3$, 2.53 3 d $-\underset{C\mathbf{H}_3}{C}=CHCOOEt$, 4.21 2 q $-COOCC\mathbf{H}_2CH_3$, 6.62 1 s furan ring proton on C_3, 6.92 1 t $-\underset{CH_3}{C}=C\mathbf{H}-COOEt$ 7.14—7.60 4 m aromatic ring protons.
VII-5	102—103	78.20 (78.09) (N 8.31	4.24 (4.17) (8.28))	IR 2220, 1620, 948, 890. NMR δ 5.90 1 d $-CH=C\mathbf{H}-CN$, 6.61 1 s furan ring proton on C_3, 7.21—7.76 5 m aromatic ring protons plus $-C\mathbf{H}=CH-CN$.
VII-6	130—131	87.23 (87.15)	6.11 (6.02)	IR 964, 878. NMR δ 2.41 3 s $-C\mathbf{H}_3$, 6.56 1 s furan ring proton on C_3, 6.86 1 d $-CH=C\mathbf{H}-Ph$, 7.08—7.52 9 m aromatic ring protons plus $-C\mathbf{H}=CH-Ph$.
VII-7	55—56	73.09 (73.03)	6.16 (6.13)	IR 1723, 1640, 965, 873. NMR δ 1.37 3 t $-COOCH_2C\mathbf{H}_3$, 4.28 2 q $-COOC\mathbf{H}_2CH_3$, 6.56 1 d $-CH=C\mathbf{H}-COOEt$, 6.62 1 s furan ring proton on C_3, 7.17—7.89 4 m aromatic ring protons plus $-C\mathbf{H}=CH-COOEt$
VII-8	97—98	73.14 (73.03)	6.25 (6.13)	IR 1720, 1637, 882, 810. NMR δ 2.34 3 d $-CH=\underset{\mathbf{CH}_3}{C}-COOMe$, 2.42 3 s $-C\mathbf{H}_3$, 3.31 3 s $-COOC\mathbf{H}_3$, 6.70 1 s furan ring proton on C_3, 7.14—7.56 4 m aromatic ring protons plus $-C\mathbf{H}=\underset{CH_3}{C}-COOMe$.
VII-9	95—96	73.82 (73.75)	6.60 (6.65)	IR 1718, 1632, 896, 881. NMR δ 1.32 3 t $-COOCH_2C\mathbf{H}_3$, 2.41 3 s $-C\mathbf{H}_3$, 2.50 3 d $-\underset{C\mathbf{H}_3}{C}=CH-COOEt$, 4.26 2 q $-COOC\mathbf{H}_2CH_3$, 6.60 1 s furan ring proton on C_3, 6.84 1 q $-\underset{CH_3}{C}=C\mathbf{H}-COOEt$, 7.16—7.38 3 m aromatic ring protons.
VII-10	79—80	78.77 (78.67) (N 8.84	5.08 (4.95) (8.73))	IR 2220, 1625, 944, 887. NMR δ 2.39 3 s $-C\mathbf{H}_3$, 5.87 1 d $-CH=C\mathbf{H}-CN$, 6.67 1 s furan ring proton on C_3, 7.05—7.49 3 m aromatic ring protons 7.60 1 d $-C\mathbf{H}=CH-CN$
VII-11	96—97	78.10 (77.98)	6.13 (6.04)	IR 1680, 1620, 875. NMR δ 2.34 3 s $-COC\mathbf{H}_3$, 2.41 3 s $-C\mathbf{H}_3$, 6.69 1 s furan ring proton on C_3, 6.84 1 d $-CH=C\mathbf{H}COCH_3$, 7.15—7.39 4 m aromatic ring proton plus $-C\mathbf{H}=CHCOCH_3$,
VII-12	99—100	77.52	5.48	IR 2790, 1680, 1620, 960, 870. NMR δ 2.42 3 s $-C\mathbf{H}_3$, 6.63 1 s furan ring proton on C_3, 6.87 1 d-d $-CH=C\mathbf{H}-CHO$, 7.21—7.63 4 m aromatic ring proton plus $-C\mathbf{H}=CH-CHO$, 9.71 1 d $-CH=CH-C\mathbf{H}O$.

a) T. Pan and T.C. Wang, *J. Chinese Chem.Soc. Ser. II*, **8**, 374 (1961).

TABLE 7. THE REACTION OF BEZNO[*b*]FURAN WITH[β,β-$^2H_2$]-STYRENE (VIII)

Benzo[*b*]furan	Olefin	Product (yield %)	D-content*)	NMR data (δ, ppm)
I–1	VIII	VI–1 (6)	0%	
		VII–1 (70)	98%a)	6.62 1 s furan ring proton on C, 6.89 1 s –CD=C**H**–Ph, 7.14—7.65 9 m aromatic ring protons.
I–2	VIII	VI–2 (6)	0%	
		VII–6 (68)	96%a)	2.41 3 s –CH_3, 6.58 1 s furan ring proton on C_3, 6.86 1 s –CD=C**H**–Ph, 7.09—7.55 8 m aromatic ring protons.
V	Styrene	VI–1 (7)	0%	
		VII–1 (72)	0%	6.62 1 s furan ring proton on C_3, 6.89 1 d –CH=C**H**–Ph, 7.12—7.68 10 m aromatic ring protons plus –C**H**–CH–Ph.
V	VIII	VI–1 (7)	0%	
		VII–1 (70)	96%a)	6.62 1 s furan ring proton on C_3, 6.89 1 s –CD=C**H**–Ph, 7.14—7.65 9 m aromatic ring protons.

*) The deuterium-content of the products was calculated from the mass-spectral analyses results, and on the basis that D-content of product containing one olefinic deuterium is 100%.

a) Neither of the 60 NMR nmr spectra of the products showed also evidence of D in the β-carbon of styryl group.

recrystallization from ethanol afforded colorless crystals which were identified as 2,2′-bibenzo[*b*]furyls (VI). The results are summarized in Table 4.

The Reaction of [2-^{2}H]-Benzo[b]*furan (V) with Benzene.* In the presence of palladium acetate, the reaction of V, benzene, and acetic acid was carried out by the same procedure as that used in the reaction of I with benzene. The products were purified by chromatography on alumina and recrystallization from ethanol. The results are summarized in Table 4. The isotopic purity of the products was calculated on the basis of a mass-spectral analysis and from the NMR results.

General Procedure for the Reaction of Benzo[b]*furan (I) with Olefins.* A mixture of palladium acetate (10 mmol), olefin (10 mmol), and I (10 mmol) was stirred in acetic acid (100 ml) for 6 hr at reflux. The resulting mixture was filtered to remove palladium metal, and, after the evaporation of the solvent under reduced pressure, the residue was poured into water. The organic layer was extracted with ether, and the ether layer was treated with an aqueous sodium bicarbonate solution, washed with water to free it from acetic acid, and then dried over anhydrous magnesium sulfate. After the evaporation of the solvent, the products were isolated by column chromatography. The first elution with benzene and the subsequent recrystallization from ethanol afforded colorless crystals which were identified as the 2-benzo[*b*]furyl-substituted olefin derivative (VII). Further elution with chloroform and recrystallization from ethanol afforded VI. The structures of the products were confirmed by means of the IR and NMR spectra. The results are summarized in Table 5, while the analytical results and the properties of the products are listed in Table 6.

The reactions of I with VIII, of V with styrene, and of V with VIII proceeded in a manner similar to that described above. The isotopic purity of the products was calculated on the basis of a mass-spectral analysis and from the NMR results. The results are summarized in Table 7.

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