Russian Journal of Organic Chemistry, Vol. 40, No. 6, 2004, pp. 802–812. Translated from Zhurnal Organicheskoi Khimii, Vol. 40, No. 6, 2004, pp. 841–853.

Dedicated to Full Member of the Russian Academy of Sciences O.N. Chupakhin on his 70th Anniversary

Palladium-Catalyzed Arylation of Sulfones

A. V. Mitin, A. N. Kashin, and I. P. Beletskaya

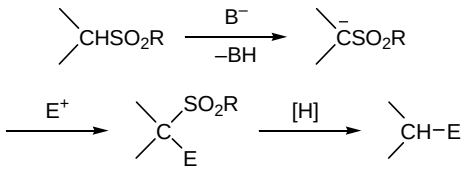
Faculty of Chemistry, Lomonosov Moscow State University, Vorob'evy gory 1, Moscow, 119992 Russia
e-mail: beletska@org.chem.msu.ru

Received February 22, 2004

Abstract—A procedure was developed for monoarylation of sulfones with aryl halides in the presence of palladium complexes. Optimal reaction conditions were found, and the scope of application of the proposed procedure was determined. The arylation occurs only with those sulfones which are relatively strong CH acids; the corresponding monoarylated sulfones are formed in moderate to high yields. The arylation of carbanions derived from the sulfones and some other CH acids requires the presence of an additional equivalent of base. The presence of the latter is also necessary in stoichiometric reactions of carbanions with the palladium complex $CF_3C_6H_4Pd(PPh_3)_2Br$; no reaction occurs in the absence of a base. A new mechanism of arylation was proposed, where the key stage is deprotonation of palladium intermediate $ArPdL_2CHXY$ which activates the reductive elimination stage.

Sulfones constitute an important class of organic synthons which are used for the preparation of a number of natural and biologically active compounds [1–3]. Wide application of sulfones in organic synthesis results from important properties of the sulfonyl group: being a strong electron acceptor, it facilitates deprotonation of the neighboring carbon atom thus favoring various transformations of the resulting stabilized carbanions; on the other hand, this group can readily be removed by reductive desulfonylation under mild conditions (Scheme 1).

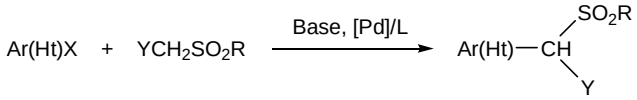
Scheme 1.



Alkyl-substituted sulfones are often synthesized following the known scheme where the key stage is alkylation of the corresponding carbanions. However, in most cases this scheme cannot be applied to introduction of an aryl or vinyl group. For this purpose, we proposed a procedure based on direct arylation with aryl halides under catalysis by palladium complexes [4] (Scheme 2).

The arylation of carbanions with aryl halides in the presence of palladium complexes is now the subject of extensive studies [5, 6]. In most cases, the arylation of such CH acids as ketones, amides, diethyl malonate, cyclic diketones, nitroalkanes, amides, esters, and protected amino acids can be achieved with the use of electron-donor and sterically hindered phosphine or carbene ligands [7]. Simple ligands like triphenylphosphine are efficient in the monoarylation of α-functionalized nitriles YCH_2CN [8]. On the whole, it still remains unclear how the nature of CH acid determines the possibility for its arylation.

Scheme 2.



Y is an electron-acceptor group.

In the present work we examined arylation of various sulfones (Tables 1–4) with aryl halides with the goal of determining the applicability limits of the above procedure, specifically those originating from CH acidity of the substrate. Also, the effect of the sulfone structure and reaction conditions on the product yield was considered. The results allowed us to propose a new mechanism of arylation of CH acids.

Table 1. Reactions of $PhSO_2CH_2CO_2Et$ and $C_6F_5CH_2SO_2CF_3$ with 4-bromobenzotrifluoride[a]

Run no.	Base (solvent)	Ligand[b]	Catalyst	Time, h	Conversion of ArBr, %	Yield,[c] %
			$PhSO_2CH_2CO_2Et$			
1	Cs_2CO_3 (dioxane)	BINAP	$Pd_2dba_3\cdot CHCl_3$[d]	3	0	–
2	K_3PO_4 (dioxane)	BINAP	$Pd_2dba_3\cdot CHCl_3$	12	34	–
3	*t*-BuOK (toluol)	BINAP	$Pd_2dba_3\cdot CHCl_3$	3	53	32
4	*t*-BuOK (dioxane)	BINAP	$Pd_2dba_3\cdot CHCl_3$	3	100	53
5	*t*-BuOK (dioxane)	DPPF	$Pd_2dba_3\cdot CHCl_3$	3	100	52
6	*t*-BuOK (dioxane)	Xanthphos	$Pd_2dba_3\cdot CHCl_3$	3	100	54
7	*t*-BuOK (dioxane)	PPh_3	$Pd_2dba_3\cdot CHCl_3$	3	100	57
8	NaHMDS (dioxane)[e]	PPh_3	$Pd_2dba_3\cdot CHCl_3$	3	100	70
9	NaH (dioxane)	PPh_3	$Pd_2dba_3\cdot CHCl_3$	3	100	82
10	NaH (dioxane)	DPPF	$Pd_2dba_3\cdot CHCl_3$	3	100	77
11	NaH (dioxane)	PPh_3	$4\text{-}CF_3C_6H_4Pd(PPh_3)_2Br$	3	100	80
12	NaH (dioxane)	PPh_3	$PdCl_2$	3	8	–
13	NaH (dioxane)	PPh_3	$[Pd(dmba)Cl]_2$[f]	3	31	17
			$C_6F_5CH_2SO_2CF_3$			
14	NaH (DME)	Ph_3As	$Pd_2dba_3\cdot CHCl_3$	5	66	55
15	NaH (DME)	PFu_3	$Pd_2dba_3\cdot CHCl_3$	5	65	54
16	NaH (DME)	PPh_3	$Pd_2dba_3\cdot CHCl_3$	5	63	51
17	NaH (DME)	DBPBP	$Pd_2dba_3\cdot CHCl_3$	5	51	40
18	NaH (DME)	$P(t\text{-}Bu)_3$	$Pd_2dba_3\cdot CHCl_3$	5	75	37
19	NaH (DME)	DPPBz	$Pd_2dba_3\cdot CHCl_3$	5	13	8

[a] The reaction was carried out at 70°C using 4 mol % of the palladium catalyst (2 mol % of $Pd_2dba_3\cdot CHCl_3$), ratio Pd/(L~L) = 1/1.5, Pd/L = 1/3; amounts of the reactants: CH acid, 0.16 mol; 4-bromobenzotrifluoride, 0.125 mmol; base, 0.375 mmol; solvent, 4 ml.

[b] DPPF is 1,1'-bis(diphenylphosphino)ferrocene, Xantphos is 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene, DBPBP is 2-(diphenylphosphino)biphenyl, and DPPBz is 1,2-bis(diphenylphosphino)benzene.

[c] According to the GLC data.

[d] dba is dibenzylideneacetone.

[e] HMDSH is hexamethyldisilazane.

[f] dmba is cyclometalated dimethylbenzylamine.

The conditions of arylation with 4-bromobenzotrifluoride were optimized using ethyl phenylsulfonylacetate and pentafluorobenzyl trifluoromethyl sulfone as model substrates (Table 1). The reaction occurs in ethers such as dioxane and 1,2-dimethoxyethane. In weakly polar toluene, the reaction was slow, presumably because of poor solubility of the corresponding CH acid salt (Table 1, run no. 3). Among the examined catalytic precursors, the most effective were $Pd_2dba_3\cdot CHCl_3$ and $4\text{-}CF_3C_6H_4Pd(PPh_3)_2Br$. Weak bases like Cs_2CO_3 and K_3PO_4 turned out to be ineffective, and the reaction occurred only in the presence of strong bases: sodium hydride, sodium hexamethyldisilazide, and potassium *tert*-butoxide. The latter promotes a side reaction leading to formation of the corresponding biaryl; as a result, the yield of the target product appreciably decreases (Table 1, run no. 7). The maximal yields were achieved with the use of sodium hydride (Table 1, run no. 9). The ligand nature was found to only slightly affect the process: the yield varied in the range from 37 to 55% in the series of ligands differing in their donor properties (Table 1, run nos. 14–18). Likewise, no appreciable difference was observed in the efficiency of bi- and unidentate ligands. An exception was bidentate 1,2-bis(diphenylphosphino)benzene (DPPBz) which is characterized by

Table 2. Palladium-catalyzed arylation of sulfones with 4-bromobenzotrifluoride[a]

Run no.	CH acid	pK_a[b]	Product	Time, h	Conversion of ArBr, %	Yield,[c] %
1	$PhSO_2Me$	29.0	–	5	12	0[d]
2	$PhSO_2CH_2C_6F_5$	–	–	5	13	0
3	$PhSO_2CH_2CO_2Et$	–	$4\text{-}F_3CC_6H_4CH(SO_2Ph)CO_2Et$	3	100	83
4	$PhSO_2CH_2SO_2CH_3$	–	$4\text{-}F_3CC_6H_4CH(SO_2Ph)SO_2Me$	3	100	82
5	$PhSO_2CH_2SO_2Ph$	12.2	$4\text{-}F_3CC_6H_4CH(SO_2Ph)_2$	3	100	85
6	$PhSO_2CH_2CN$	12.0	$PhCH(SO_2Ph)CN$	–	–	82[e]
7	$PhSO_2CH_2COPh$	11.4	$4\text{-}F_3CC_6H_4CH(SO_2Ph)COPh$	4.5	100	30
8	$PhSO_2CH_2NO_2$	7.1	$4\text{-}F_3CC_6H_4CH(SO_2Ph)NO_2$	4.5	100	72
9	$PhCH_2CH_2SO_2CH_2CO_2Et$	–	$4\text{-}F_3CC_6H_4CH(CO_2Et)SO_2CH_2CH_2Ph$	8	100	75
10	*cyclo*-$C_6H_{13}SO_2CH_2CO_2Et$	–	$4\text{-}F_3CC_6H_4CH(CO_2Et)SO_2C_6H_{13}$-*cyclo*	8	100	66
11	$4\text{-}F_3CC_6H_4CH(SO_2Ph)CO_2Et$	–	–	8	18	0
12	$PhSO_2CH(Me)CO_2Et$	–	–	8	17	0

[a] The reactions were carried out using 0.5 mmol of aryl halide, 0.65 mmol of CH acid, 2 mol % of $Pd_2dba_3 \cdot CHCl_3$ (4 mol % of Pd), 12 mol % of PPh_3, 1.5 mmol of NaH, and 4 ml of DME at 70°C under argon.

[b] pK_a in DMSO [10].

[c] Yield of the isolated product (by column chromatography).

[d] No reaction occurred in the presence of BuLi as base.

[e] In the reaction with bromobenzene [7].

a small bite angle; the use of that ligand afforded a strongly reduced yield (Table 1, run no. 19). Therefore, accessible and inexpensive triphenylphosphine was used in most experiments.

It is known that the reactivity of carbanions in the alkylation processes correlates with pK_a values of the conjugate CH acids: stronger CH acids produce less nucleophilic carbanions [9]. In order to estimate the relation between the reactivity of sulfones toward arylation and their structure we examined reactions of 4-bromobenzotrifluoride with a series of substituted sulfones whose CH acidity varies over a wide pK_a range [10].

The data in Table 2 show that the arylation readily occurs with sulfones having an additional functional group in the α-position, which are relatively strong CH acids (Table 2, run nos. 3–9). Even such a strong CH acid (pK_a = 7.1) as nitromethyl phenyl sulfone undergoes arylation (Table 2, run no. 8). In these reactions, the corresponding monoarylation products

Table 3. Palladium-catalyzed arylation of some trifluoromethyl sulfones with aryl halides[a]

Run no.	Trifluoromethyl sulfone	Aryl halide	Time, h	Conversion of ArBr, %	Yield,[b] %
1	CF_3SO_2Ph	$4\text{-}CF_3C_6H_4Br$	20	79	67
2	$CF_3SO_2C_6H_4Br\text{-}4$	$4\text{-}CF_3C_6H_4Br$	40	57	36
3	$CF_3SO_2C_6H_4Br\text{-}3$	$4\text{-}CF_3C_6H_4Br$	14	51	30
4	$CF_3SO_2C_6F_5$	$4\text{-}CF_3C_6H_4Br$	12	94	81
5	$CF_3SO_2C_6F_5$	$4\text{-}ClC_6H_4Br$	24	71	48
6	$CF_3SO_2CH_2CH_2Ph$	$4\text{-}CF_3C_6H_4Br$	24	31	–
7	$CF_3SO_2CH_2COOEt$	$4\text{-}CF_3C_6H_4Br$	24	20	–

[a] The reactions were carried out using 0.5 mmol of aryl halide, 0.65 mmol of CH acid, 2 mol % of $Pd_2dba_3 \cdot CHCl_3$ (4 mol % of Pd), 12 mol % of PPh_3, 1.5 mmol of NaH, and 4 ml of DME at 70°C under argon.

[b] Yield of the isolated product (by column chromatography).

Table 4. Palladium-catalyzed arylation of ethyl phenylsulfonylacetate and bis(phenylsulfonyl)methane[a]

Run no.	Aryl halide	Time, h	Product	Conversion of ArBr, %	Yield,[b] %
			$PhSO_2CH_2CO_2Et$		
1	PhBr	9	$PhCH(SO_2Ph)CO_2Et$	100	72
2	4-MeC_6H_4Br	8	4-$MeC_6H_4CH(SO_2Ph)CO_2Et$	91	74
3	4-$F_3CC_6H_4Br$	3	4-$F_3CC_6H_4CH(SO_2Ph)CO_2Et$	100	83
4	3-FC_6H_4Br	4	3-$FC_6H_4CH(SO_2Ph)CO_2Et$	100	64
5	4-$F_3CC_6H_4Cl$	27	4-$F_3CC_6H_4CH(SO_2Ph)CO_2Et$	75	25
6	4-$MeOC_6H_4Br$	20	4-$MeOC_6H_4CH(SO_2Ph)CO_2Et$	100	41
7	4-$MeOC_6H_4I$	3	4-$MeOC_6H_4CH(SO_2Ph)CO_2Et$	100	71
8	1-Bromonaphthalene	12	1-$C_{10}H_7CH(SO_2Ph)CO_2Et$	85	62
			$(PhSO_2)_2CH_2$		
9	4-$F_3CC_6H_4Br$	3	4-$F_3CC_6H_4CH(SO_2Ph)_2$	100	85
10	3-FC_6H_4Br	4	3-$FC_6H_4CH(SO_2Ph)_2$	100	81
11	1-Bromonaphthalene	6	1-$C_{10}H_7CH(SO_2Ph)_2$	100	77

[a] The reactions were carried out using 0.5 mmol of aryl halide, 0.63 mmol of CH acid, 1.4 mmol of NaH, 2 mol % of $Pd_2dba_3 \cdot CHCl_3$, 12 mol % of PPh_3, and 4 ml of DME at 70°C under argon.

[b] Yield of the isolated product (by column chromatography).

Table 5. Palladium-catalyzed arylation of ethyl phenylsulfonylacetate and bis(phenylsulfonyl)methane with hetaryl bromides ans *trans*-β-bromostyrene[a]

Run no.	Aryl halide	Time, h	Product	Conversion, %	Yield,[b] %
			$PhSO_2CH_2CO_2Et$		
1	3-Bromopyridine	6	3-$C_5H_4NCH(SO_2Ph)CO_2Et$	94	51
2	*trans*-BrCH=CHPh	6	*trans*-$PhCH{=}CHCH(SO_2Ph)CO_2Et$	100	40
			$(PhSO_2)_2CH_2$		
3	3-Bromothiophene	8	3-$C_4H_3SCH(SO_2Ph)_2$	100	77
4	3-Bromopyridine	5	3-$C_5H_4NCH(SO_2Ph)_2$	97	90
5	3-Bromoquinoline	6	3-$C_9H_6NCH(SO_2Ph)_2$	100	76

[a] The reactions were carried out using 0.5 mmol of aryl halide, 0.63 mmol of CH acid, 1.4 mmol of NaH, 2 mol % of $Pd_2dba_3 \cdot CHCl_3$, 12 mol % of PPh_3, and 4 ml of DME at 70°C under argon.

[b] Yield of the isolated product (by column chromatography).

are formed mainly in high yields (72–85%). An exception is phenacyl phenyl sulfone (Table 2, run no. 7), for its sodium salt is poorly soluble; the yield of the arylation product is only 30%. Trifluoromethylsulfonyl group exerts a strong activating effect: substituted benzyl trifluoromethyl sulfones turned out to be reactive (Table 3), while analogous compounds with a phenylsulfonyl group failed to react (Table 2, run no. 2). It should be noted that, among the examined benzyl trifluoromethyl sulfones, the reaction occurred most readily with the sulfone containing an electron-acceptor perfluorophenyl group (Table 3, run no. 4).

Weak CH acids were completely inert in the arylation under the given conditions. We did not succeed in effecting the arylation of methyl phenyl sulfone even when butyllithium was used as a base, though the latter is known to quantitatively deprotonate the substrate (Table 2, run no. 1). Sulfones with a tertiary α-carbon atom also failed to react (Table 2, run nos. 9, 10). Obviously, the same factor is responsible for the observed selectivity; i.e., only one aryl group is introduced.

Unfortunately, the arylation of some sulfones was unsuccessful because of decomposition of the initial

compound. For example, $PhSO_2CH_2SiMe_3$ underwent desilylation to methyl phenyl sulfone instead of arylation. Ethyl pentafluorobenzylsulfonylacetate and ethyl benzylsulfonylacetate decomposed to give salts of the corresponding sulfinic acid, $C_6F_5CH_2SO_2H$ and $PhCH_2SO_2H$. The same products were obtained by the action of NaH or *t*-BuOK in the absence of a catalyst.

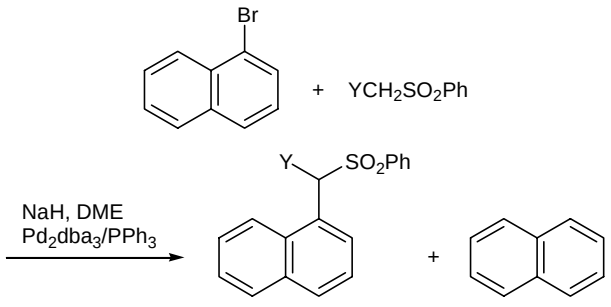
Under the optimal conditions we performed reactions of the most active CH acids, ethyl phenylsulfonylacetate and bis(phenylsulfonyl)methane with various aryl halides (Table 4) and hetaryl halides (Table 5). The reactions readily occurred with aryl bromides and aryl iodides, the latter being more reactive (Table 4, run nos. 6, 7). As a result, the corresponding monoarylation products were obtained in moderate to high yields.

Aryl chlorides are difficult to react with sulfones. Even with activated 4-chlorobenzotrifluoride, the reaction stops while the conversion is not complete, and the product yield is poor. Analogous results were obtained with the use of electron-donating sterically hindered phosphines [PCy_3 and 2,2'-bis(*tert*-butylphosphino)biphenyl] as ligands, though the same ligands were effective in other reactions of carbanions with aryl chlorides [5, 6].

trans-β-Bromostyrene also reacted with ethyl phenylsulfonylacetate (Table 5, run no. 2) to give the corresponding vinylation product without change of the position and configuration of the double bond. This reaction is the first example of palladium-catalyzed vinylation of CH acids.

In all the above reactions, no less than 2 equiv of a base should be used, for it is consumed for metalation of not only the initial CH acid but also the arylation product. Otherwise, i.e., with an equimolar amount of base, the conversion would not exceed 50%:

Scheme 3.

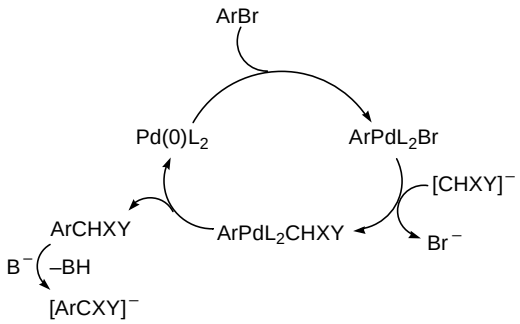


$Y = SO_2Ph$	77%	5%
$Y = CO_2Et$	62%	18%

a half of the initial carbanion would be consumed for deprotonation of the product which is a stronger CH acid than the initial sulfone. However, sodium hydride promotes side reduction of the aryl halide to the corresponding arene, so that the yield of the major product decreases [11] (Scheme 3).

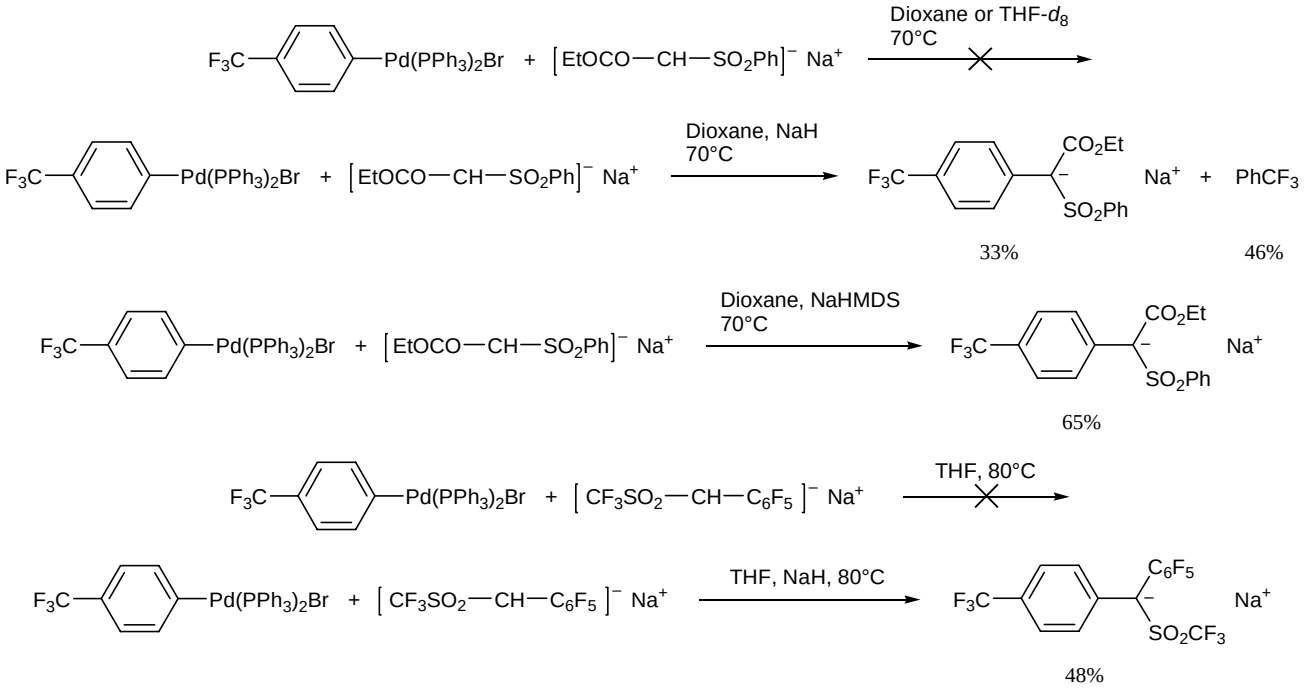
In order to avoid the reduction of aryl halide with sodium hydride we used two-fold amount of initial CH acid. Contrary to expectations, no reaction occurred at all. Analogous pattern was also observed in reactions with other CH acids, such as ethyl cyanoacetate and malonodinitrile. As follows from the data in Table 6, apart from carbanion, the presence of an additional amount of a strong base (NaH, *t*-BuOK, or NaHMDS) is necessary for the reaction to proceed. These results cannot be interpreted in terms of the known mechanism of cross-coupling with participation of carbanions (Scheme 4).

Scheme 4.



The role of base in the arylation of carbanions was studied by reacting carbanions derived from sulfones with a stoichiometric amount of the preliminarily prepared palladium complex $4\text{-}CF_3C_6H_4Pd(PPh_3)_2Br$ in the presence of a base and without it. These reactions simulate the stages of bromine replacement and reductive elimination in the catalytic series. Preliminarily prepared ethyl phenylsulfonylacetate sodium salt did not react with the complex $4\text{-}CF_3C_6H_4Pd(PPh_3)_2Br$ in the absence of a base on heating in dioxane or tetrahydrofuran for 12 h at 70°C. The ^1H and ^{19}F NMR spectra of the reaction mixture contained signals only from the initial compounds, and addition of hexane to the mixture resulted in precipitation of unchanged $4\text{-}CF_3C_6H_4Pd(PPh_3)_2Br$. After addition of NaHMDS or NaH, in 3 h at 70°C the corresponding monoarylation product was obtained in 65 and 33% yield, respectively. In the latter case, the arylation was accompanied by reduction of the complex to the free arene (yield

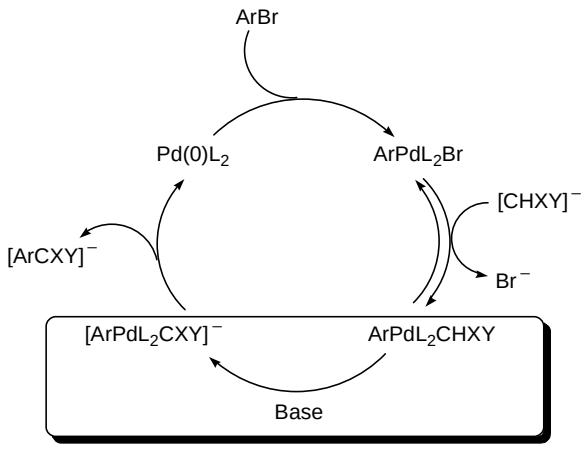
Scheme 5.



45%). Analogous effect of a base was observed in the arylation of carbanion derived from pentafluorobenzyl trifluoromethyl sulfone $C_6F_5CH_2SO_2CF_3$. In the presence of sodium hydride, the carbanion reacted with 4-$CF_3C_6H_4Pd(PPh_3)_2Br$ to afford 48% of the monoarylation product (according to the GLC data), while no such product was formed in the absence of a base (Scheme 5).

Thus the role of a base in the catalytic and stoichiometric arylation of carbanions is the same: the reaction occurs only in the presence of excess basic reagent. This may be explained on the assumption that the rate-determining stage in the arylation process is reductive elimination which is hindered for the neutral complex $ArPdL_2CHXY$ formed from carbanion. Deprotonation of $ArPdL_2CHXY$ by the action of a strong base gives anionic palladium complex $[ArPdL_2CXY]^-$ which then undergoes reductive elimination. Scheme 6 illustrates the catalytic series involving the above deprotonation stage.

Scheme 6.



It remains unclear why the bromine atom in the complex $ArPdL_2Br$ cannot be replaced by carbanion in a stoichiometric reaction. Presumably, the stage of halogen substitution in the palladium complex by a strongly stabilized carbanion is reversible and the equilibrium is displaced toward the initial carbanion. Therefore, only the subsequent reductive elimination shifts the equilibrium. The assumption that deprotonation of $ArPdL_2CHXY$ precedes the reductive elimination stage is consistent with the lack of arylation of sulfonyl CH acids with a tertiary α-carbon atom $[RSO_2CH(R')Y]$; deprotonation of the corresponding palladium complex is impossible. For the same reason, the other sulfones give rise exclusively to monoarylation products.

Obviously, the role of a base in the examined reactions consists in activation of the reductive elimination from $ArPdL_2CHXY$, and it does not affect *cis–trans* isomerization process. The presence of

Table 6. Effect of base in the palladium-catalyzed arylation of CH acids[a]

Run no.	CH acid	Reaction conditions	No excess base		Excess base (NaH)	
			time, h	conversion of ArBr, % (yield, %)	time, h	conversion of ArBr, % (yield, %)
1[b]	$PhSO_2CH_2CO_2Et$	Dioxane, 70°C, L = PPh_3	12	5 (0)	12	82 (61)
2	$PhSO_2CH_2CO_2Et$	Dioxane, 70°C, L = DPPF	8	2	4	100 (77)
3	$(PhSO_2)_2CH_2$	DME, 70°C, L = PPh_3	12	13	4	100 (86)
4	$C_6F_5CH_2SO_2CF_3$	DME, 70°C, L = PPh_3	12	0	12	87 (71)
5	$NCCH_2COOEt$	DME, 70°C, L = PPh_3	12	0	15	86 (72)
6	$NCCH_2CN$	DME, 70°C, L = PPh_3	12	0	6	100 (84)
7	$PhSO_2CH_2CO_2Et$	DME, 70°C, L = PPh_3[c]	4	0	4	100 (70)
8	$PhSO_2CH_2CO_2Et$	DME, 70°C, L = PPh_3[d]	4	0	4	100 (56)

[a] The reactions were carried out at 70°C in dioxane or DME; amounts of the reactants: 4-bromobenzotrifluoride, 0.5 mmol; $Pd_2dba_3 \cdot CHCl_3$, 2 mol %; L : Pd ratio 3 : 1; solvent, 4 ml; in the presence of excess base: NaH, 1.25 mmol; CH acid, 0.65 mmol; no excess base: NaH, 1.0 mmol; CH acid, 1.25 mmol.

[b] 1-Bromonaphthalene was used as aryl halide.

[c] Potassium *tert*-butoxide was used as base.

[d] Sodium hexamethyldisilazide was used as base.

excess basic reagent is also necessary in reactions with bidentate DPPF, where only the *cis*-complexes are involved (Table 6, run no. 2). The proposed arylation mechanism allows us to explain the unusual relation between the reactivity of sulfones and their pK_a values. As noted above, relatively weak CH acids, such as $MeSO_2Ph$, $PhCH_2SO_2Ph$, and $C_6F_5CH_2SO_2Ph$, fail to react; this is not the result of their difficult deprotonation, for the corresponding preliminarily prepared CH acid salts do not undergo arylation as well. Presumably, intermediate $ArPdL_2CHXY$ is a weaker CH acid than the initial sulfone; therefore, deprotonation of palladium intermediate is possible only when the corresponding CH acid is sufficiently strong.

Finally, the arylation can be completed by reaction with another electrophilic reagent rather than by protonation of the carbanion thus formed. To illustrate this possibility, we performed chlorination and allylation of aryl methyl sulfones by the action of *N*-chlorosuccinimide (NCS) and allyl or geranyl acetate, respectively. The reaction conditions and yields are given in Table 7.

EXPERIMENTAL

Dioxane, tetrahydrofuran, and 1,2-dimethoxyethane were purified and dehydrated by standard procedures. Dioxane and DME were stored over potassium diphenylketyl under reduced pressure. The complex $Pd_2dba_3 \cdot CHCl_3$ was synthesized as described in [12]. Functionalized sulfones were prepared according to the procedures reported in [13, 14]. Trifluoromethyl sulfones were synthesized from the corresponding alkyl bromides and potassium trifluoromethanesulfinate [15]. Bromo(4-trifluoromethylphenyl)bis(triphenylphosphine)palladium(II) was synthesized following the procedure described in [16].

The ^1H, ^{13}C, and ^{19}F NMR spectra were recorded from solutions in $CDCl_3$ (unless otherwise stated) using a Varian VXR-400 spectrometer; the ^1H and ^{13}C chemical shifts were measured relative to tetramethylsilane as internal reference. The IR spectra were obtained from samples prepared as KBr pellets. The mass spectra (electron impact, 70 eV) were run on Cratos MS-30 and MS-890 instruments. GLC analysis was performed on a Hewlett– Packard 5890 Series II Plus chromatograph equipped with a flame-ionization detector and an HP-1 capillary column (25 m× 0.32 mm, film thickness 0.25 μm); helium was used as carrier gas.

Arylation of sulfones with aryl halides. A reactor was charged in a stream of argon with 0.65 mmol of sulfone, 15.8 mg (12 mol %) of triphenylphosphine, 10.4 mg (2 mol %) of $Pd_2dba_3 \cdot CHCl_3$, 10–20 mg of naphthalene (internal standard), 60 mg (1.5 mmol) of sodium hydride (a 60% suspension in oil), and 0.5 mmol of aryl halide. The reactor was cooled with liquid nitrogen and evacuated, and 4 ml of 1,4-dioxane was condensed thereto. The mixture was degassed by

Table 7. Arylation of sulfones with subsequent treatment with electrophile[a]

Sulfone	Aryl bromide	Electrophile	Product	Yield,[b] %
$PhCH_2CH_2SO_2CH_2CO_2Et$	4-$CF_3C_6H_4Br$	NCS[c]	4-$CF_3C_6H_4CCl(CO_2Et)SO_2CH_2CH_2Ph$	72
$PhSO_2CH_2SO_2CH_3$	4-$CF_3C_6H_4Br$	NCS[c]	4-$CF_3C_6H_4CCl(SO_2Me)SO_2Ph$	82
cyclo-$C_6H_{13}SO_2CH_2CO_2Et$	4-$CF_3C_6H_4Br$	NCS[c]	4-$CF_3C_6H_4CCl(CO_2Et)SO_2C_6H_{13}$-*cyclo*	62
$(PhSO_2)_2CH_2$	3-C_5H_4NBr	Allyl acetate[d]	3-$C_5H_4NC(SO_2Ph)_2CH_2CH{=}CH_2$	68
$PhSO_2CH_2CO_2Et$	4-$CF_3C_6H_4Br$	Allyl acetate[d]	4-$CF_3C_6H_4C(CO_2Et)(SO_2Ph)CH_2CH{=}CH_2$	80
$PhSO_2CH_2CO_2Et$	4-$CF_3C_6H_4Br$	Geranyl acetate[d]	4-$CF_3C_6H_4C(CO_2Et)(SO_2Ph)C_{10}H_{17}$	73

[a] The reactions were carried out with 0.5 mmol of aryl halide, 0.63 mmol of sulfone, 1.4 mmol of NaH, 2 mol % of $Pd_2dba_3 \cdot CHCl_3$, 12 mol % of PPh_3, and 4 ml of DME at 70°C under argon; when the arylation was complete, electrophilic reagent was added.

[b] Yield of the isolated product (by column chromatography).

[c] 1 mmol, 20°C, 12 h.

[d] 1 mmol, 40°C, 12 h.

triple freeze–thaw procedure, and the reactor was filled with argon. The reaction was carried out by stirring at 70°C, and its progress was monitored by GLC and TLC (Silufol UV-254). When the reaction was complete, the mixture was diluted with water acidified with 1 drop of concentrated hydrochloric acid and treated with diethyl ether (3×10 ml). The extract was evaporated, and the residue was subjected to chromatographic separation on silica gel (40–100 μm) using ethyl acetate–petroleum ether (bp 65–68°C) as eluent.

Ethyl phenyl(phenylsulfonyl)acetate $PhSO_2CH(Ph)CO_2Et$ was obtained from 78.5 mg of bromobenzene and 148 mg of ethyl phenylsulfonylacetate. Yield 110 mg, colorless crystals with mp 95–97°C. IR spectrum, ν, cm^{-1}: 1149, 1322 (SO_2); 1737 (CO_2). ^1H NMR spectrum, δ, ppm: 1.237 t (3H), 4.14–4.29 m, (2H), 5.095 s (1H), 7.29 t (2H), 7.33–7.40 m (3H), 7.43 t (2H), 7.58–7.64 m (3H). Found, %: C 63.47; H 5.11. $C_{16}H_{16}O_4S$. Calculated, %: C 63.14; H 5.30.

Ethyl phenylsulfonyl(4-trifluoromethylphenyl)acetate $PhSO_2CH(CO_2Et)C_6H_4CF_3$-4 was obtained from 112 mg of 4-bromobenzotrifluoride and 148 mg of ethyl phenylsulfonylacetate. Yield 154 mg, colorless crystals, mp 94–95°C (from hexane). IR spectrum, ν, cm^{-1}: 1151, 1330 (SO_2); 1726, 1737 (CO_2). ^{13}C NMR spectrum, δ_C, ppm: 13.8, 62.8, 74.7, 123.7 q, 125.4, 128.8, 129.8, 130.8, 131.7, 131.7 q, 134.5, 136.3, 164.2. Mass spectrum, *m/z*: 372 (M^+), 353, 326, 303, 231, 203, 186, 175, 159, 141. Found, %: C 55.04; H 4.18. $C_{17}H_{15}F_3O_4S$. Calculated, %: C 54.84; H 4.03.

Ethyl 4-methylphenyl(phenylsulfonyl)acetate $PhSO_2CH(CO_2Et)C_6H_4CH_3$-4 was obtained from 86 mg of 4-bromotoluene and 148 mg of ethyl phenylsulfonylacetate. Yield 118 mg, colorless crystals with mp 104–105°C. IR spectrum, ν, cm^{-1}: 1147, 1324 (SO_2); 1735 (CO_2). ^1H NMR spectrum, δ, ppm: 1.22 t (3H), 2.34 s (3H), 4.1–4.3 m (2H), 5.06 s (1H), 7.10 d (2H), 7.23 d (2H), 7.44 t (2H), 7.59–7.64 m (3H). Found, %: C 64.06; H 5.71. $C_{17}H_{18}O_4S$. Calculated, %: C 64.15; H 5.66.

Ethyl 3-fluorophenyl(phenylsulfonyl)acetate $PhSO_2CH(CO_2Et)C_6H_4F$-3 was obtained from 88 mg of 3-bromofluorobenzene and 148 mg of ethyl phenylsulfonylacetate. Yield 103 mg, colorless crystals, mp 83–84°C. IR spectrum, ν, cm^{-1}: 1149, 1326 (SO_2); 1735 (CO_2). ^1H NMR spectrum, δ, ppm: 1.23 t (3H), 4.14–4.23 m (2H), 5.09 s (1H), 7.27–7.70 m (4H). Found, %: C 60.04; H 4.68. $C_{16}H_{15}FO_4S$. Calculated, %: C 59.62; H 4.69.

Ethyl 1-naphthyl(phenylsulfonyl)acetate $PhSO_2CH(CO_2Et)C_{10}H_7$-1 was obtained from 104 mg of 1-bromonaphthalene and 148 mg of ethyl phenylsulfonylacetate. Yield 110 mg, yellowish oily substance. ^{13}C NMR spectrum, δ, ppm: 13.8, 62.5, 69.15, 122.36, 123.7, 124.83, 125.85, 127.0, 128.38, 128.47, 128.57, 128.89, 129.85, 130.31, 131.74, 133.65, 133.98, 136.39, 165.14. Found, %: C 68.02; H 5.24. $C_{17}H_{18}O_5S$. Calculated, %: C 67.78; H 5.12.

Ethyl 4-methoxyphenyl(phenylsulfonyl)acetate $PhSO_2CH(CO_2Et)C_6H_4OMe$-4. Colorless crystals, mp 75–77°C. IR spectrum, ν, cm^{-1}: 1149, 1322 (SO_2); 1739 (CO_2). ^1H NMR spectrum, δ, ppm: 1.23 t (3H), 3.80 s (3H), 4.12–4.27 m (2H), 5.04 s (1H), 6.82 d (2H), 7.27 d (2H), 7.44 t (2H), 7.59–7.64 m (3H). Found, %: C 60.84; H 5.31. $C_{17}H_{18}O_5S$. Calculated, %: C 61.06; H 5.43.

Ethyl phenylsulfonyl(*trans*-2-phenylvinyl)acetate $PhSO_2CH(CO_2Et)CH{=}CHPh$-*trans* was obtained from 91 mg of *trans*-β-bromostyrene and 148 mg of ethyl phenylsulfonylacetate. Yield 70 mg, colorless oily substance. ^{1}H NMR spectrum, δ, ppm: 1.25 t (3H), 4.22 q (2H), 4.68 d (1H, J = 9.5 Hz), 6.15 d.d (1H, J_1 = 9.5, J_2 = 16 Hz), 6.58 d (1H, J = 16 Hz), 7.28–7.34 m (5H), 7.53 t (2H), 7.67 t (1H), 7.86 d (2H). ^{13}C NMR spectrum, δ_C, ppm: 13.9, 62.5, 74.6, 115.8, 126.9, 128.6, 128.8, 128.9, 129.7, 134.2, 135.3, 136.9, 139.5, 164.7. Found, %: C 65.79; H 5.51. $C_{18}H_{18}O_4S$. Calculated, %: C 65.43; H 5.49.

Ethyl phenylsulfonyl(3-pyridyl)acetate $PhSO_2CH(CO_2Et)Py$-3 was obtained from 79 mg of 3-bromopyridine and 148 mg of ethyl phenylsulfonylacetate. Yield 78 mg, colorless oily substance. ^{1}H NMR spectrum, δ, ppm: 1.23 t (3H), 4.15–4.28 m (2H), 5.122 s (1H), 7.30 t (1H), 7.49 t (2H), 7.63–7.69 m (3H), 7.97 t (1H), 8.415 s (1H), 8.62 d (1H). Found, %: C 59.34; H 5.01. $C_{15}H_{15}NO_4S$. Calculated, %: C 59.00; H 4.95.

Phenylsulfonyl(4-trifluoromethylphenyl)nitromethane $PhSO_2CH(NO_2)C_6H_4CF_3$-4 was obtained from 112 mg of 4-brombenzotrifluoride and 130 mg of ethyl phenylsulfonylacetate. Yield 123 mg, colorless crystals, mp 110–112°C. ^{1}H NMR spectrum, δ, ppm: 6.545 s (1H), 7.567 t (2H), 7.654 d (2H), 7.68 d (2H), 7.73–7.78 m (3H). Found, %: C 55.98; H 3.91. $C_{13}H_{11}NO_4S$. Calculated, %: C 56.31; H 4.00.

1-Phenyl-2-phenylsulfonyl-2-(4-trifluoromethylphenyl)ethanone $PhSO_2CH(COPh)C_6H_4CF_3$-4 was obtained from 112 mg of 4-bromobenzotrifluoride and 170 mg of phenylsulfonylacetophenone. Yield 61 mg, colorless crystals, mp 142.5–143.5°C. IR spectrum, ν, cm^{-1}: 1159, 1324 (SO_2); 1672 m (C=O). ^{1}H NMR spectrum, δ, ppm: 6.208 s (1H), 7.41–7.48 m (4H), 7.51–7.59 m (5H), 7.62–7.67 m (3H), 7.88 d (2H). Found, %: C 62.52; H 3.75. $C_{21}H_{15}F_3O_3S$. Calculated, %: C 62.37; H 3.73.

4-Trifluoromethylphenylbis(phenylsulfonyl)methane $4\text{-}CF_3C_6H_4CH(SO_2Ph)_2$ was obtained from 112 mg of 4-bromobenzotrifluoride and 175 mg of bis(phenylsulfonyl)methane. Yield 187 mg, colorless crystals, mp 210–211°C. Found, %: C 54.81; H 3.51. $C_{20}H_{15}F_3O_4S_2$. Calculated, %: C 54.54; H 3.43.

3-Fluorophenylbis(phenylsulfonyl)methane $3\text{-}FC_6H_4CH(SO_2Ph)_2$ was obtained from 88 mg of 3-bromofluorobenzene and 175 mg of bis(phenylsulfonyl)methane. Yield 158 mg, colorless crystals, mp 207.5–209°C. ^{1}H NMR spectrum, δ, ppm: 5.395 s (1H), 7.05–7.1 m (2H), 7.20–7.29 m (2H), 7.487 t (4H), 7.650 t (2H), 7.785 d (4H). Found, %: C 58.28; H 3.68. $C_{19}H_{15}FO_4S_2$. Calculated, %: C 58.45; H 3.87.

3-Thienylbis(phenylsulfonyl)methane $3\text{-}C_4H_3SCH(SO_2Ph)_2$ was obtained from 88 mg of 3-bromofluorobenzene and 175 mg of bis(phenylsulfonyl)methane. Yield 158 mg, colorless crystals, mp 185–186°C. ^{1}H NMR spectrum, δ, ppm: 5.606 s (1H), 7.00 d (1H), 7.22 d (1H), 7.315 s (1H), 7.47 t (4H), 7.63 t (2H), 7.77 d (4H). Found, %: C 54.27; H 3.91. $C_{17}H_{14}O_4S_3$. Calculated, %: C 53.95; H 3.73.

2-Pyridylbis(phenylsulfonyl)methane $2\text{-}PyCH(SO_2Ph)_2$ was obtained from 79 mg of 3-bromopyridine and 175 mg of bis(phenylsulfonyl)methane. Yield 168 mg, colorless crystals, mp 202–203°C. ^{1}H NMR spectrum, δ, ppm: 5.455 s (1H), 7.78 d (4H), 7.50 t (4H), 7.66 t (2H), 8.20 br (1H), 8.61 d (1H). Found, %: C 58.03; H 4.06; N 3.99. $C_{21}H_{15}F_3O_3S_2$. Calculated, %: C 57.89; H 4.05; N 3.75.

1-Naphthylbis(phenylsulfonyl)methane $1\text{-}C_{10}H_7CH(SO_2Ph)_2$ was obtained from 104 mg of 1-bromonaphthalene and 175 mg of bis(phenylsulfonyl)methane. Yield 163 mg, colorless crystals, mp 171–172°C (from MeOH). ^{1}H NMR spectrum, δ, ppm: 6.462 s (1H), 7.33–7.87 m (6H), 7.43 t (2H), 7.50 t (3H), 7.75 d (4H), 7.86 d (1H), 8.05 d (1H). Found, %: C 65.62; H 4.36. $C_{23}H_{18}O_4S_2$. Calculated, %: C 65.38; H 4.29.

3-Quinolylbis(phenylsulfonyl)methane $3\text{-}C_9H_6NCH(SO_2Ph)_2$ was obtained from 105 mg of 3-bromoquinoline and 175 mg of bis(phenylsulfonyl)methane. Yield 161 mg, colorless crystals, mp 228–229°C. ^{1}H NMR spectrum, δ, ppm: 5.655 s (1H), 7.477 t (4H), 7.60–7.68 m (3H), 7.77–7.86 m (6H). Found, %: C 62.57; H 4.22; N 3.08. $C_{22}H_{17}NO_4S_2$. Calculated, %: C 62.39; H 4.05; N 3.31.

Methylsulfonyl(phenylsulfonyl)(4-trifluoromethylphenyl)methane $4\text{-}CF_3C_6H_4CH(SO_2Ph)\text{-}SO_2Me$ was obtained from 112 mg of 4-bromobenzotrifluoride and 175 mg of methylsulfonyl(phenylsulfonyl)methane. Yield 155 mg, colorless crystals, mp 195–196°C. ^{1}H NMR spectrum, δ, ppm: 3.443 s (3H), 5.376 s (1H), 7.44–7.51 m (4H), 7.59 d (2H), 7.62–7.70 m (3H). Found, %: C 47.81; H 3.58. $C_{15}H_{13}F_3O_4S_2$. Calculated, %: C 47.61; H 3.46.

Ethyl (4-trifluoromethylphenyl)(2-phenylethylsulfonyl)acetate $4\text{-}CF_3C_6H_4CH(COOEt)SO_2CH_2\text{-}CH_2Ph$ was obtained from 112 mg of 4-bromobenzotrifluoride and 166 mg of ethyl (2-phenylethyl-

sulfonyl)acetate. Yield 150 mg, colorless crystals, mp 133–134°C (iz EtOH). 1H NMR spectrum, δ, ppm: 1.321 t (3H), 3.252 m (2H), 3.548–3.645 m (2H), 4.272–4.369 m (2H), 4.956 s (1H), 7.183 d (2H), 7.230–7.343 m (3H), 7.682 s (4H). Found, %: C 57.11; H 4.89. $C_{19}H_{19}F_3O_4S$. Calculated, %: C 56.99; H 4.78.

Ethyl cyclohexylsulfonyl(4-trifluoromethylphenyl)acetate 4-$CF_3C_6H_4CH(COOEt)SO_2C_6H_{13}$-*cyclo* was obtained from 112 mg of 4-bromobenzotrifluoride and 152 mg of ethyl cyclohexylsulfonylacetate. Yield 125 mg, colorless oily substance. ^{1}H NMR spectrum, δ, ppm: 1.20–1.70 m (9H), 1.90–2.00 m (2H), 2.20–2.35 m (2H), 3.50–3.65 t.d (1H), 4.37–4.47 m (2H), 5.71 s (1H), 7.70 d (2H), 7.90 d (2H). Found, %: C 54.09; H 5.74. $C_{17}H_{21}F_3O_4S$. Calculated, %: C 53.96; H 5.59.

Phenyl(4-trifluoromethylphenyl)(trifluoromethylsulfonyl)methane 4-$CF_3C_6H_4CH(Ph)SO_2CF_3$ was obtained from 112 mg of *p*-bromobenzotrifluoride and 112 mg of benzyl trifluoromethyl sulfone. Yield 123 mg, colorless oily substance. ^{1}H NMR spectrum, δ, ppm: 7.10–7.19 m (3H), 6.985 d (2H), 5.673 s (1H). Found, %: C 48.71; H 2.98; S 8.93. $C_{15}H_{10}F_6O_2S$. Calculated, %: C 48.92; H 2.74; S 8.71.

Pentafluorophenyl(4-trifluoromethylphenyl)-(trifluoromethylsulfonyl)methane 4-$CF_3C_6H_4CH(C_6F_5)SO_2CF_3$ was obtained from 112 mg of *p*-bromobenzotrifluoride and 112 mg of pentafluorobenzyl trifluoromethyl sulfone. Yield 184 mg, colorless oily substance. ^{1}H NMR spectrum, δ, ppm: 7.785 d (2H), 7.730 d (2H), 6.055 s (1H). Found, %: C 48.71; H 1.33; S 6.79. $C_{15}H_5F_{11}O_2S$. Calculated, %: C 39.32; H 1.10; S 7.00.

(3-Bromophenyl)(4-trifluoromethylphenyl)(trifluoromethylsulfonyl)methane 4-$CF_3C_6H_4CH(SO_2CF_3)C_6H_4Br$-3 was obtained from 112 mg of *p*-bromobenzotrifluoride and 190 mg of 3-bromobenzyl trifluoromethyl sulfone. Yield 66 mg, colorless oily substance. ^{1}H NMR spectrum [$(CD_3)_2CO$], δ, ppm: 8.107 d (2H), 8.041 s (1H), 7.914 m (3H), 7.530 t (1H), 7.723 d (1H), 6.66 s (1H). Found, %: C 40.20; H 2.21; S 6.99. $C_{15}H_5F_{11}O_2S$. Calculated, %: C 40.29; H 2.03; S 7.16.

(4-Bromophenyl)(4-trifluoromethylphenyl)(trifluoromethylsulfonyl)methane 4-$CF_3C_6H_4CH(SO_2CF_3)C_6H_4Br$-3 was obtained from 112 mg of *p*-bromobenzotrifluoride and 190 mg of 4-bromobenzyl trifluoromethyl sulfone. Yield 79 mg, colorless oily substance. ^{1}H NMR spectrum [$(CD_3)_2CO$], δ, ppm: 8.107 d (2H), 8.041 s (1H), 7.90 d (2H), 7.50 d (2H), 6.66 s (1H). Found, %: C 40.46; H 2.32; S 6.92. $C_{15}H_5F_{11}O_2S$. Calculated, %: C 40.29; H 2.03; S 7.16.

Reaction of sulfones with aryl halides, followed by treatment with electrophile. A reactor was charged in a stream of argon with 0.5 mmol of the corresponding sulfone, 15.8 mg (12 mol %) of triphenylphosphine, 10.4 mg (2 mol %) of $Pd_2dba_3 \cdot CHCl_3$, 10–20 mg (1.5 mmol) of naphthalene (internal standard), 60 mg of sodium hydride (a 60% suspension in oil), and 0.5 mmol of aryl halide. The reactor was cooled with liquid nitrogen and evacuated, and 4 ml of 1,4-dioxane was recondensed thereto. The mixture was degassed by triple freeze–thaw procedure, and the reactor was filled with argon. The mixture was then stirred at 70°C, the progress of the reaction being monitored by GLC and TLC (Silufol UV-254). When the reaction was complete, the mixture was cooled with ice water, 1 mmol of electrophilic reagent (*N*-chlorosuccinimide or allyl acetate) was added, and the mixture was stirred at 30°C (TLC, Silufol UV-254). The mixture was diluted with water and treated with diethyl ether (3×10 ml). The extract was filtered and evaporated, and the residue was subjected to chromatography on silica gel (40–100 μm) using ethyl acetate–petroleum ether (bp 65–68°C) as eluent.

Chloro(methylsulfonyl)(phenylsulfonyl)(4-trifluoromethylphenyl)methane 4-$CF_3C_6H_4CCl(SO_2Ph)(SO_2Me)$ was obtained from 112 mg of 4-brombenzotrifluoride, 118 mg of methylsulfonyl(phenylsulfonyl)methane, and 133 mg of NCS. Yield 168 mg, colorless crystals, mp 135–136°C (from EtOH). ^{1}H NMR spectrum, δ, ppm: 3.582 s (3H), 7.412 t (2H), 7.512 d (2H), 7.63–7.68 m (3H), 8.08 d (2H). Found, %: C 43.81; H 3.10. $C_{15}H_{12}ClF_3O_4S_2$. Calculated, %: C 43.64; H 2.91.

Ethyl chloro(2-phenylethylsulfonyl)(4-trifluoromethylphenyl)acetate 4-$CF_3C_6H_4CCl(COOEt)SO_2CH_2CH_2Ph$ was obtained from 112 mg of 4-bromobenzotrifluoride and 128 mg of ethyl (2-phenylethylsulfonyl)acetate. Yield 156 mg, colorless oily substance. ^{1}H NMR spectrum, δ, ppm: 1.344 t (3H), 3.197 t (2H), 3.68–3.88 m (2H), 4.414 q (2H), 7.21–7.29 m (5H), 7.334 t (2H), 7.725 d (2H), 7.864 d (2H). Found, %: C 52.56; H 4.19. $C_{19}H_{18}ClF_3O_4S$. Calculated, %: C 52.48; H 4.17.

Ethyl chloro(cyclohexylsulfonyl)(4-trifluoromethylphenyl)acetate [4-$CF_3C_6H_4CCl(COOEt)SO_2C_6H_{13}$-*cyclo* was obtained from 112 mg of 4-bromobenzotrifluoride, 118 mg of ethyl cyclohexylsulfonylacetate, and 133 mg of NCS. Yield 128 mg, colorless

oily substance. ^{1}H NMR spectrum, δ, ppm: 1.354 t (3H), 1.17–2.35 m (10H), 3.80–3.92 t.d (1H), 4.37–4.47 m (2H), 7.695 d (2H), 7.905 d (2H). Found, %: C 49.56; H 4.99. $C_{17}H_{20}ClF_3O_4S$. Calculated, %: C 49.46; H 4.88.

4,4-Bis(phenylsulfonyl)-4-(3-pyridyl)-1-butene CH_2=CHCH_2C(Py-3)$(SO_2Ph)_2$ was obtained from 79 mg of 3-bromopyridine, 148 mg of bis(phenylsulfonyl)methane, and 100 mg of allyl acetate. Yield 140 mg, colorless oily substance. ^{1}H NMR spectrum, δ, ppm: 8.19–8.21 m (1H), 8.61 d (1H), 7.78 d (4H), 7.66 t (2H), 7.50 t (4H), 5.0–5.6 m (3H), 2.35–2.62 m (2H). Found, %: C 61.23; H 4.84; N 3.50. $C_{21}H_{19}NO_4S_2$. Calculated, %: C 61.00; H 4.63; N 3.39.

Ethyl 1-phenylsulfonyl-1-(4-trifluoromethylphenyl)-3-pentenoate CH_2=CH$CH_2C(SO_2Ph)$-$(CO_2Et)C_6H_4CF_3$-4 was obtained from 112 mg of 4-bromobenzotrifluoride, 114 mg of ethyl phenylsulfonylacetate, and 100 mg of allyl acetate. Yield 165 mg, colorless oily substance. ^{1}H NMR spectrum, δ, ppm: 7.6–7.9 m (8H), 7.43 t (1H), 5.0–5.6 m (3H), 4.41–4.43 m (2H), 2.35–2.62 m (2H), 1.23 t (3H). Found, %: C 58.26; H 4.68. $C_{20}H_{19}F_3O_4S$. Calculated, %: C 58.24; H 4.64.

Ethyl 4,9-dimethyl-1-phenylsulfonyl-1-(4-trifluoromethylphenyl)-3,7-decadienoate was obtained from 112 mg of 4-bromobenzotrifluoride, 114 mg of ethyl phenylsulfonylacetate, and 196 mg of geranyl acetate. Yield 185 mg, colorless oily substance. ^{1}H NMR spectrum, δ, ppm: 7.6–7.9 m (8H), 7.44 t (1H), 5.0–5.1 m (2H), 4.41–4.43 m (2H), 1.5–2.6 m (18H). Found, %: C 63.49; H 6.38. $C_{27}H_{31}F_3O_4S$. Calculated, %: C 63.76; H 6.14.

Study of the reaction of $ArPdL_2CH$ complexes with carbanions. Preliminarily washed with hexane and dried sodium hydride, 11 mg (a 60% suspension in oil), was added with stirring under argon to a solution of 57 mg (0.25 mmol) of ethyl phenylsulfonylacetate and 10 mg of durene (internal standard) in 10 ml of dioxane or THF-d_8. The mixture was stirred until hydrogen no longer evolved, filtered under argon, and transferred into a reactor; a sample of the mixture was analyzed by ^{1}H and ^{19}F NMR spectroscopy. To the resulting carbanion solution we added with stirring under argon 214 mg (0.25 mmol) of the complex 4-$CF_3C_6H_4Pd(PPh_3)_2Br$. The solution was stirred for 12 h at 70°C (oil bath) under argon. According to the GLC, TLC, and ^{1}H and ^{19}F NMR data, no reaction occurred. An additional amount of sodium hydride (preliminarily washed with hexane and dried, 11 mg of a 60% suspension in oil) was added, ad the mixture was stirred for 3 h at 70°C under argon. According to the GLC, TLC, and ^{1}H and ^{19}F NMR data, the reaction was complete.

REFERENCES

1. Prilezhaeva, E.N., *Poluchenie i svoistva organicheskikh soedinenii sery* (Synthesis and Properties of Organic Sulfur Compounds), Belen'kii, L.I., Ed., Moscow: Khimiya, 1998, p. 115.
2. Najera, C. and Yus, M., *Tetrahedron*, 1999, vol. 55, p. 10546.
3. *Houben–Weyl. Methoden der organische Chemie*, Stuttgart: Georg Thieme, 1985, E11.
4. Kashin, A.N., Mitin, A.V., Beletskaya, I.P., and Wife, R., *Tetrahedron Lett*., 2002, vol. 43, p. 2539.
5. Culkin, D.A. and Hartwig, J.F., *Acc. Chem. Res*., 2003, vol. 36, p. 234.
6. Prim, D., Campagne, J.-M., Joseph, D., and Andrioletti, B., *Tetrahedron*, 2002, vol. 58, p. 2041.
7. Sakamoto, T., Katoh, E., Kondo, Y., and Yamanaka, H., *Chem. Pharm. Bull*., 1990, vol. 38, p. 1513.
8. Uno, M., Seto, K., and Takahashi, S., *J. Chem. Soc., Chem. Commun*., 1984, p. 932.
9. Bordwell, F.G. and Hughes, D.L., *J. Org. Chem*., 1980, vol. 45, p. 3314; Bordwell, F.G. and Hughes, D.L., *J. Org. Chem*., 1980, vol. 45, p. 3320.
10. Bordwell, F.G., Vanier, W.S., Matthews, W.S., Hendrickson, J.B., and Skipper, P.L., *J. Am. Chem. Soc*., 1975, vol. 97, p. 7160.
11. Nelson, R.B. and Gribble, G.W., *J. Org. Chem*., 1974, vol. 39, p. 1425.
12. Ishii, Y., *Ann. N.Y. Acad. Sci*., 1972, vol. 239, p. 114; Ukai, T., Kawazura, H., and Ishii, Y., *J. Organomet. Chem*., 1974, vol. 65, p. 253.
13. Kohler, E.P. and Tishler, M., *J. Am. Chem. Soc*., 1935, vol. 57, p. 217.
14. Ashley, W.C. and Shriner, R.L., *J. Am. Chem. Soc*., 1932, vol. 54, p. 4410.
15. Hendrickson, J.B., Giga, A., and Wareing, J., *J. Am. Chem. Soc*., 1974, vol. 96, p. 2275.
16. Fitton, P. and Rick, E.A., *J. Organomet. Chem*., 1971, vol. 28, p. 279.