4. U. M. Dzhemilev, R. V. Kunakova, R. L. Gaisin, G. A. Tolstikov, and V. V. Sidorova, Izv. Akad. Nauk SSSR, Ser. Khim., 696 (1981).

SYNTHESIS OF AROMATIC AND HETEROAROMATIC UNSATURATED SULFONES USING PALLADIUM COMPLEX CATALYSTS

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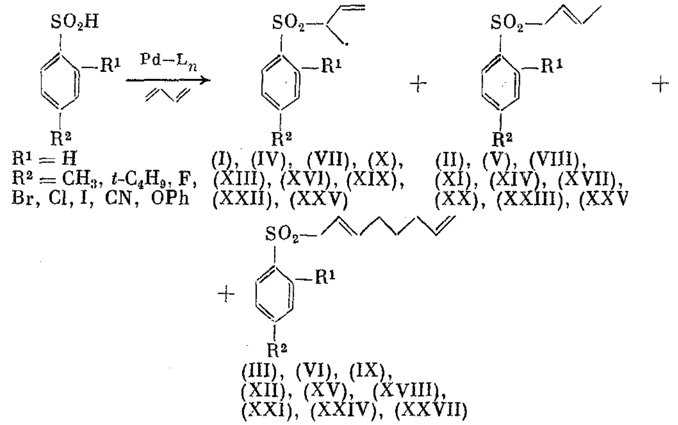
We have recently [1-5] developed a method for the preparation of difficultly available unsaturated sulfones, based on the reaction of sulfinic acids with 1,3-dienes under the action of palladium and nickel-containing complex catalysts.

To examine the possible use of different aromatic and heteroaromatic sulfinic acids in this reaction, in the present work, we studied the reaction of butadiene with substituted arylsulfinic acids, catalyzed by low-valence Pd complexes.

We have already found [1-5] that low-valence Pd complexes, obtained by reduction of Pd(acac)$_2$ by triethylalane in the presence of PPh$_3$, are the most active catalysts in the reaction of sulfinic acids with 1,3-dienes. With this catalytic system, benzene- and toluenesulfinic acids react with butadiene (60°C, 6 h) to give the corresponding butenyl and 2,7-octadienyl sulfones (I)-(VI) in yields of ~ 97%. Replacement of a methyl group in toluenesulfinic acids by F, Cl, Br, and I atoms, and also by tert-butyl, nitrile, and phenoxyl groups, practically does not influence the direction, the yield, and the composition of the products of their telomerization with butadiene. In all the experiments, both mono- (VII)-(XX) and diadducts (XXI)-(XXVII) are formed. The ratio of butenyl and octadienyl sulfones changed inappreciably from experiment to experiment, and is on the average 51:34:15, respectively (Table 1).



(I), (IV), (VII), (X), (XIII), (XVI), (XIX), (XXII), (XXV)

(II), (V), (VIII), (XI), (XIV), (XVII), (XX), (XXIII), (XXV

(III), (VI), (IX), (XII), (XV), (XVIII), (XXI), (XXIV), (XXVII)

R^1 = R^2 = H (I)—(III); R^1 = H, R^2 = CH$_3$ (IV)—(VI); R^1 = H, R^2 = t-C$_4$H$_9$ (VII)—(IX); R^1 = H, R^2 = F (X)—(XII); R^1 = H, R^2 = Cl (XIII)—(XV); R^1 = H, R^2 = Br (XVI)—(XVIII); R^1 = H, R^2 = I (XIX)—(XXI); R^1 = H, R^2 = CN (XXII)—(XXIV); R^1 = H, R^2 = OPh (XXV)—(XXVII).

Similar results were obtained in the study of the telomerization of naphthalenesulfinic acid with butadiene, leading to sulfones (XXVIII)-(XXX) with an overall yield of 91%. In contrast to the above acids, *o*-methoxybenzenesulfinic acid enters into telomerization with butadiene with the exclusive formation of (XXXII), (XXXIII). However, in its reactivity, *o*-chlorophenylsulfinic acid practically does not differ from the above acids, and reacts with butadiene to give sulfones (XXXIV)-(XXXVI) in an overall yield of 85%.

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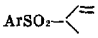
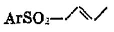
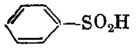
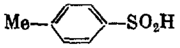
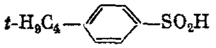
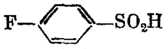
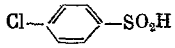
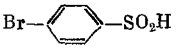
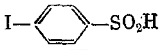
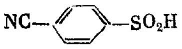
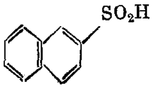
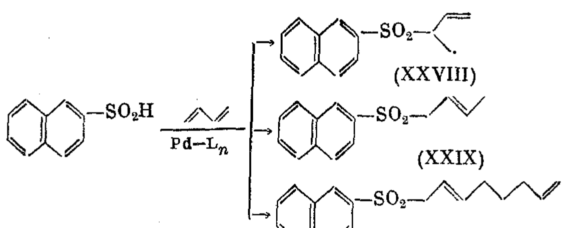
TABLE 1. Influence of Nature of Substituent in Arylsulfinic Acids on Yield and Composition of Products of Their Telomerization with Butadiene (catalyst: $Pd(acac)_2-PPh_3-AlEt_3$ (1:3:4), 60°C; toluene$-H_2O$ (4:1); butadiene − 200 mmoles, $PhSO_2H$ − 100mmoles)

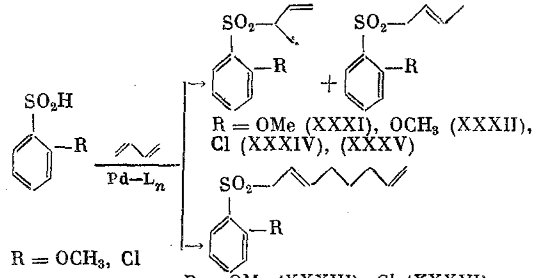
Sulfinic acid	Overall yield, %	Reaction products, %		
				
	97	53	39	8
	95	60	27	13
	93	50	45	5
	87	51	20	29
	85	52	26	22
	81	53	28	19
	80	55	30	15
	82	54	27	19
	80	46	36	18
	91	40	37	23



(XXVIII)

(XXIX)

(XXX)



R = OMe (XXXI), OCH_3 (XXXII), Cl (XXXIV), (XXXV)

R = OCH_3, Cl

R = OMe (XXXIII), Cl (XXXVI)

Therefore, taking as an example *o*-methoxybenzenesulfinic acid, we examined the influence of temperature and ratio of initial reagents (diene:acid) on the yield and composition of products of telomerization of this acid with butadiene.

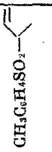
Table 2 shows that with increase in the concentration of butadiene in the reaction mixture, the fraction of octadienyl sulfone (XXXIII) increases. At a diene:acid = 1:1 ratio, monoadducts are preferentially formed. Increase in the telomerization temperature from 20 to 100°C leads not only to an increase in the overall yield of sulfones (XXXI)-(XXXIII), but also to a change in the isomeric composition of the monoadducts (XXXI), (XXXII). At a higher temperature, the fraction of branched sulfone (XXXI) increases.

It can be assumed that at elevated temperature under the telomerization conditions there is isomerization of the π-allyl complex (XXXVII) into σ-allyl complexes (XXXIX)-(XL), which are responsible for the forma-

TABLE 2. Influence of Ratio of Initial Monomers and Reaction Conditions on Yield and Composition of Products of Telomerization of *o*-Methoxyphenylsulfinic Acid with Butadiene (catalyst $Pd(acac)_2$ – 0.2 mmole, PPh_3 – 0.6 mmole, $AlEt_3$ – 0.8 mmole, 4 h, toluene–water, 4:1)

T., °C	Sulfinic acid–butadiene ratio (molar)	Overall yield of unsaturated sulfones, %	Composition of telomerization products, %		
			(XXXI)	(XXXII)	(XXXIII)
20	1 : 3	44	21	59	20
60	1 : 3	96	36	17	47
100	1 : 3	98	61	13	26
60	1 : 1	90	56,5	40,5	3
60	1 : 4	98	–	32	68
60	1 : 2	98	4	56	40

TABLE 3. Influence of Nature and Ratio of Catalyst Components on Yield and Composition of Products of Telomerization of Butadiene with Toluenesulfinic Acid ($Pd:RSO_2H$:butadiene, 1:100:200 (molar), 60°C, 4 h)

Ratio of catalyst components (molar)	Overall yield, %	Reaction products, %	
		 $CH_3C_6H_4SO_2$–	 $CH_3C_6H_4SO_2$–
$Pd(acac)_2 - PPh_3 - AlEt_3$ (1 : 10 : 3)	99	99	1
$Pd(acac)_2$–$L^*\cdot AlEt_3$ (1 : 1 : 2)	99	98	2
$Pd(acac)_2 - Et_2NH - AlEt_3$ (1 : 3 : 4)	92	61	39
$Pd(acac)_2 - C_5H_5N - AlEt_3$ (1 : 3 : 4)	92	60	40
$Pd(acac)_2 - p\text{-}NO_2C_6H_5 - AlEt_3$ (1 : 1 : 2)	90	70	30
$Pd(acac)_2 - AlEt_3$ (1 : 4)	53	63	37
$PdCl_2 - C_5H_5N - AlEt_3$ (1 : 3 : 4)	91	55	45

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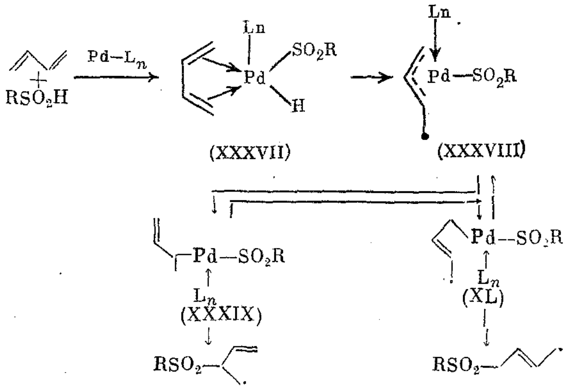
* L = 18-dibenzo-6-crown ether.

tion of the molecules of butenyl sulfones. Similar results were obtained for other sulfinic acids that we studied, listed in Table 1.



Further, to replace PPh_3 by more available activating additives, and also to clarify the influence of the nature of activator-ligands on the direction of the telomerization, we studied the influence of oxygen- and nitrogen-containing compounds on the activity and selectivity of action of palladium catalyst in these processes. The experiments were carried out on the example of the telomerization of butadiene with toluenesulfinic acid.

As the result, we found that fairly active palladium catalysts can be obtained when compounds such as diethylamine, pyridine, and nitrobenzene are used as activator ligands (Table 3). These ligands favor the exclusive formation of monoadducts (IV), (V). Catalysts modified by 18-dibenzo-6-crown ether or PPh_3 taken in a ratio of $Pd:PPh_3$ equal to 1:10, have the highest selectivity.

TABLE 4. Physical Constants and Characteristics of IR and PMR Spectra of Aromatic Sulfones

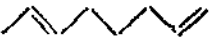
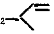
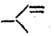
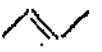
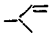
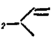
Sulfone	Bp, °C (p, mm Hg) Mp, °C	n_D^{20}	IR spectrum (ν, cm^{-1})				PMR spectrum (δ, ppm)							
			CH=CH$_2$	CH=CH	SO$_2$	aromatic ring	CH$_2$	CH$_3$—C— (CH$_3$—O)	CH$_2$—C=	CH$_3$—C=	CH—SO$_2$	=CH$_2$	—CH—CH— —CH=	C$_6$H$_5$
p-Me$_3$CC$_6$H$_4$SO$_2$— 	152–154 (1)	1,5383	910, 1005, 3090	–	1150, 1310	770, 850, 1600, 3030	–	1,3 s (12H)	–	–	3,6 m (1H)	4,8 m (2H)	5,1 m (1H)	7,7 m (4H)
p-Me$_3$CC$_6$H$_4$SO$_2$— 	160–163 (1)	1,5385	–	980, 1650, 3030	1150, 1320,	770, 850, 1600, 3030	–	1,3 s (9H)	1,5 d (3H)	–	3,7 d (2H)	–	5,3 m (2H)	7,7 (4H)
p-Me$_3$CC$_6$H$_4$SO$_2$— 	196–200 (1)	1,5405	920, 1000, 3080	980, 1640, 3040	1160, 1320	770, 850, 1600, 3030	1,5 m (2H)	1,3 s (9H)	–	2,0 (4H)	3,7 d (2H)	4,7 m (2H)	5,4 m (3H)	7,7 (4H)
o-MeOC$_6$H$_4$SO$_2$— 	138–141 (0,5)	1,5530	940, 1020, 3080	–	1130, 1320	780, 1600, 3030	–	1,3 d (3H) 3,8 s (3H)	–	–	3,8 m (1H)	4,8 (2H)	5,0 m (1H)	7,4 m (4H)
o-MeOC$_6$H$_4$SO$_2$— 	146–150 (0,5)	1,5540	–	980, 1660, 3030	1140, 1160, 1320	780, 1590, 3030	–	3,8 s (3H)	1,5 d (3H)	–	3,9 d (2H)	–	5,2 m (2H)	7,4 m (4H)
o-MeOC$_6$H$_4$SO$_2$— 	160–165 (0,5)	1,5535	920, 1005, 3080	975, 1630, 3026	1135, 1150, 1280, 1320	760, 1600, 3030	1,4 m (2H)	3,8 s (3H)	–	2,0 m (4H)	3,9 d (2H)	4,9 m (2H)	5,2 m (3H)	7,4 m (4H)
p-FC$_6$H$_4$SO$_2$— 	120–122 (0,5)	1,5245	930, 1000, 3080	–	1150, 1320	830, 1600, 3040	–	1,3 d (3H)	–	–	3,6 m (1H)	4,9 m (2H)	5,1 (1H)	7,2 m (2H) 7,9 m (2H)
p-FC$_6$H$_4$SO$_2$— 	126–128 (0,5)	1,5250		980, 1650, 3020	1160, 1335	820, 1610, 3040	–	–	1,6 d (3H)	–	3,6 d (2H)	–	5,4 m (2H)	7,2 m (2H) 7,9 m (2H)
p-FC$_6$H$_4$SO$_2$— 	147–149 (0,5)	1,5280	930, 3090, 1010	985, 1650, 3020	1160, 1330	830, 1600, 3040	1,5 m (2H)	–	–	1,9 m (4H)	3,6 d (2H)	4,9 m (2H)	5,4 m (3H)	7,2 m (2H) 7,9 m (2H)
p-ClC$_6$H$_4$SO$_2$— 	62–63	–	950, 1015, 3095	–	1135, 1160, 1280, 1320	830, 1585, 3040	–	1,3 d (3H)	–	–	3,6 t (1H)	–	5,0–6,0 m (3H)	7,5 m (4H)
p-ClC$_6$H$_4$SO$_2$— 	136–139 (0,5)	1,5520	–	980, 1660, 3045	1160, 1330	840, 1590, 3050	–	–	1,6 d (3H)	–	3,7 d (2H)	–	5,4 m (2H)	7,5 m (4H)
p-ClC$_6$H$_4$SO$_2$— 	172–174 (0,5)	1,5580	920, 1000, 3090	980, 1640, 3050	1160, 1320	840, 1580, 3040	1,3 m (2H)	–	–	1,9 m (4H)	3,7 d (2H)	4,8 m (2H)	5,4 m (3H)	7,6 m (4H)
o-ClC$_6$H$_4$SO$_2$— 	140–142 (0,5)	1,5565	940, 1020, 3090	–	1140, 1310	770, 1600, 3040	–	1,4 d (3H)	–	–	3,5 t (1H)	4,9 m (2H)	5,2 m (1H)	7,6 m (4H)
o-ClC$_6$H$_4$SO$_2$— 	175–178 (0,5)	1,5564	910, 1000, 3080	980, 1640, 3040	1150, 1310	760, 1600,	1,4 m (2H)	–	–	2,0 m (4H)	3,7 d (2H)	4,9 m (2H)	5,4 m (3H)	7,5 m (4H)
o-ClC$_6$H$_4$SO$_2$— 	145–150 (0,5)	1,5590	–	990, 1650, 3030	1160, 1320	770, 1600 3040	–	–	1,5 d (3H)	–	3,7 d (2H)	–	5,3 m (2H)	7,6 m (4H)
p-BrC$_6$H$_4$SO$_2$ — 	153–155 (0,5)	1,5610	920, 3010, 3080	–	1140, 1320	840, 1600, 3040	–	1,3 d (3H)	–	–	3,6 t (1H)	5,0 m (2H)	5,3 m (1H)	7,6 m (4H)
p-BrC$_6$H$_4$SO$_2$— 	159–161 (0,5)	1,5615	–	990, 1640, 3050	1160, 1330	840, 1600, 3040	–	–	1,6 d (3H)	–	3,8 (2H)	5,4 d (2H)	5,4 m (2H)	7,6 (4H)
p-BrC$_6$H$_4$SO$_2$— 	190–193 (0,5)	1,5680	920, 1000, 3090	980, 1650, 3030	1150, 1320	830, 1599, 3050	1,3 m (2H)	–	–	1,9 m (4H)	3,7 (2H)	4,9 m (2H)	5,3 m (3H)	7,6 m (4H)
p-IC$_6$H$_4$SO$_2$— 	170–173 (0,5)	1,5725	910, 1010, 3080	–	1160, 1320	840, 1600, 3040	–	1,3 d (3H)	–	–	3,8 (2H)	4,9	5,5 m (3H)	7,7 m (4H)
p-IC$_6$H$_4$SO$_2$— 	178–180 (0,5)	1,5730	–	990, 1640, 3010	1150, 1310	820, 1610, 3020	–	–	1,6 d (3H)	–	3,8 (2H)	–	5,4 m (2H)	7,7 m (4H)
p-IC$_6$H$_4$SO$_2$— 	222–225 (0,5)	1,5740	920, 1000, 3090	980, 1660, 3020	1160, 1320	840, 1610, 3030	1,5 m (2H)	–	–	2,0 (4H)	3,7 (2H)	4,9 m (2H)	5,3 m (3H)	7,6 m (4H)
p-CNC$_6$H$_4$SO$_2$— 	155–158 (0,5)	Oil	920, 1010, 3080	2230 (CN)	1130, 1300	820, 1590, 3010	–	1,3 d (3H)	–	–	3,6 m (1H)	4,8 m (2H)	5,1 m (1H)	7,7 m (4H)
p-CNC$_6$H$_4$SO$_2$— 	163–166 (0,5)	Same	–	980, 1650, 3030	1150, 1300	820, 1590, 3010	–	–	1,6 d (3H)	–	3,7 (2H)	–	5,3 m (2H)	"
p-CNC$_6$H$_4$SO$_2$— 	190–195 (0,5)	"	920, 1000, 3090	980, 1640, 3030	1150, 1300	820, 1590, 3010	1,3 m (2H)	–	–	2,0 м (4H)	3,6 (2H)	4,9 m (2H)	5,3 m (3H)	"
p-PhOC$_6$H$_4$SO$_2$— 	187–190 (0,02)	"	920, 1010, 3080	–	1150, 1300	820, 1590, 3010	–	1,3 d (3H)	–	–	3,6 t (1H)	5,0 m (2H)	5,3 m (1H)	7,7 m (9H)
p-PhOC$_6$H$_4$SO$_2$— 	192–195 (0,02)	"	–	980, 1640, 3030	1150, 1300	820, 1590, 3010	–	–	1,6 d (3H)	–	3,8 (2H)	–	5,4 m (2H)	7,7 m (9H)
p-PhOC$_6$H$_4$SO$_2$— 	225–230 (0,02)	"	920, 1000, 3090	980, 1650, 3030	1150, 1300	820, 1590 3010	1,3 m (2H)	–	–	2,0 m (4H)	3,8 (2H)	4,2 m (2H)	5,4 m (2H)	7,7 m (9H)

TABLE 4 (Continued)

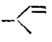
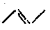
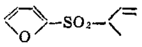
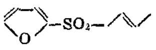
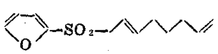
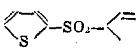
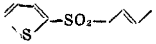
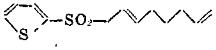
Sulfone	Bp, °C (p, mm Hg) Mp, °C	n_D^{20}	IR spectrum (ν, cm^{-1})				PMR spectrum (δ, ppm)							
			CH=CH$_2$	CH=CH	SO$_2$	aromatic ring	CH$_2$	CH$_3$—C— (CH$_3$—O)	CH$_3$—C=	CH$_2$—C=	CH—SO$_2$	=CH$_2$	—CH—CH— —CH=	C$_6$H$_5$
$C_{10}H_7SO_2$— 	190–195 (0,02)	″	920, 1020, 3080	–	1150, 1300	755, 820, 870, 1590, 3040	–	1,3 d(3H)	–	–	3,6т (1H)	5,0 (2H)	5,3 (1H)	7,8m(2H)
$C_{10}H_7SO_2$— 	195–198 (0,02)	″	–	980, 1660, 3020	1150, 1300	755, 820, 870, 1590, 3040	–	–	1,6d(3H)	–	3,8 (2H)		5,3m(2H)	7,8m(7H)
$C_{10}H_7SO_2$— 	228–232 (0,02)	Oil	920, 1020, 3080	980, 1660, 3020	1150, 1300	755, 820, 870, 1590, 3040	1,3m(2H)	–	–	2,0m(4H)	3,8 (2H)		5,3m(3H)	7,8m(7H)
	149–152 (1)	″	920, 1020, 3080	–	1130, 1320	740, 890, 1510, 1600 3120	–	1,3 d(3H)	–	–	3,6m(1H)	5,0m(2H)	5,3m(1H)	7,2m(3H)
	158–162 (1)	″	–	980, 1640, 3630	1130, 1320	740, 890, 1510, 1600, 3120	–	–	1,6 d(3H)	–	3,6m(2H)	–	5,4m(2H)	7,2m(3H)
	190–195 (1)	″	920, 1020, 3080	980, 1640, 3030	1130, 1320	740, 890, 1510, 1600, 3120	1,3m(2H)	–	–	2,0m(4H)	3,6m(2H)	5,0 (2H)	5,3m(3H)	7,2m(3H)
	147–150 (1)	″	920, 1020, 3080	–	1150, 1330	735, 1035, 1490, 3090	–	1,3d(3H)	–	–	3,7t (2H)	4,9m(2H)	5,4m(1H)	7,3m(3H)
	155–160 (1)	″	–	980, 1640, 3030	1150, 1330	735, 1035, 1490, 3090	–	–	1,6 d(3H)	–	3,7t (2H)	–	5,4m(2H)	7,3m(3H)
	198–200 (1)	″	920, 1020, 3080	980, 1640, 3030	1150, 1330	735, 1035, 1490, 309(	1,3m(2H)	–	–	2,0m(4H)	3,7 t(2H)	4,9m(2H)	5,4m(3H)	7,3 (3H)

TABLE 5. Data of Elemental Analysis of Sulfones

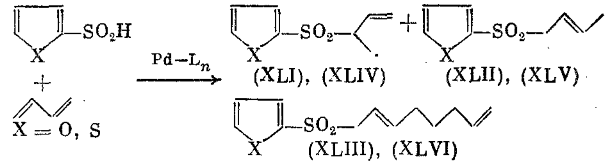
Compound	Empirical formula	Found/calculated, %				
		C	H	N	S	Hal
3-(p-tert-Butylphenylsulfonyl)-3-methyl-1-propene (VII)	$C_{14}H_{20}SO_2$	66,71/66,67	7,92/7,94	—	12,65/12,70	—
1-(p-tert-Butylphenylsulfonyl)-2-butene (VIII)	$C_{14}H_{20}SO_2$	66,71/66,67	7,92/7,94	—	12,65/12,70	—
8-(p-tert-Butylphenylsulfonyl)-1,7-octadiene (IX)	$C_{18}H_{26}SO_2$	70,56/70,59	8,55/8,50	—	10,40/10,46	—
3-(p-Fluorophenylsulfonyl)-3-methyl-1-propene (X)	$C_{10}H_{11}SO_2F$	56,17/56,07	5,07/5,14	—	14,90/14,95	—
1-(p-Fluorophenylsulfonyl)-2-butene (XI)	$C_{10}H_{11}SO_2F$	56,17/56,07	5,07/5,14	—	14,90/14,95	8,58/8,88
8-(p-Fluorophenylsulfonyl)-1,7-octadiene (XII)	$C_{14}H_{17}SO_2F$	62,79/62,69	6,29/6,34	—	11,80/11,94	6,90/7,09
3-(p-Chlorophenylsulfonyl)-3-methyl-1-propene (XIII)	$C_{10}H_{11}SO_2Cl$	52,16/52,06	4,70/4,77	—	13,80/13,88	15,25/15,40
1-(p-Chlorophenylsulfonyl)-2-butene (XIV)	$C_{10}H_{11}SO_2Cl$	52,16/52,06	4,70/4,77	—	13,80/13,88	15,25/15,40
8-(p-Chlorophenylsulfonyl)-1,7-octadiene (XV)	$C_{14}H_{17}SO_2Cl$	59,15/59,05	5,89/5,98	—	11,20/11,25	12,40/12,48
3-(p-Bromophenylsulfonyl)-3-methyl-1-propene (XVI)	$C_{10}H_{11}SO_2Br$	43,74/43,64	4,10/4,00	—	11,60/11,64	29,00/29,09
1-(p-Bromophenylsulfonyl)-2-butene (XVII)	$C_{10}H_{11}SO_2Br$	43,74/43,64	4,10/4,00	—	11,60/11,64	29,09/29,00
8-(p-Bromophenylsulfonyl)-1,7-octadiene (XVIII)	$C_{14}H_{17}SO_2Br$	51,16/51,06	5,20/5,17	—	9,70/9,73	24,22/24,32
3-(p-Iodophenylsulfonyl)-3-methyl-1-propene (XIX)	$C_{10}H_{11}SO_2I$	37,30/37,27	3,50/3,42	—	9,90/9,94	39,24/39,44
1-(p-Iodophenylsulfonyl)-2-butene (XX)	$C_{10}H_{11}SO_2I$	37,30/37,27	3,50/3,42	—	9,90/9,94	39,24/39,44
8-(p-Iodophenylsulfonyl)-1,7-octadiene (XXI)	$C_{14}H_{17}SO_2I$	44,73/44,68	4,60/4,52	—	8,45/8,51	33,68/33,78
3-(p-Cyanophenylsulfonyl)-3-methyl-1-propene (XXII)	$C_{11}H_{11}NSO_2$	59,60/59,73	4,90/4,98	6,45/6,33	11,38/11,48	—
1-(p-Cyanophenylsulfonyl)-2-butene (XXIII)	$C_{11}H_{11}NSO_2$	59,60/59,73	4,90/4,98	6,45/6,33	11,38/11,48	—
8-(p-Cyanophenylsulfonyl)-1,7-octadiene (XXIV)	$C_{15}H_{17}NSO_2$	65,20/65,45	6,22/6,18	5,20/5,09	11,70/11,64	—
3-(p-Phenoxyphenylsulfonyl)-3-methyl-1-propene (XXV)	$C_{16}H_{16}SO_3$	66,92/66,67	5,50/5,56	—	11,01/11,11	—
1-(p-Phenoxyphenylsulfonyl)-2-butene (XXVI)	$C_{16}H_{16}SO_3$	66,92/66,67	5,50/5,56	—	11,01/11,11	—
8-(p-Phenoxyphenylsulfonyl)-1,7-octadiene (XXVII)	$C_{20}H_{22}SO_3$	70,80/70,18	6,37/6,43	—	13,90/14,04	—
3-(β-Naphthylsulfonyl)-3-methyl-1-propene (XXVIII)	$C_{14}H_{14}SO_2$	68,20/68,29	5,71/5,69	—	13,11/13,01	—
1-(β-Naphthylsulfonyl)-2-butene (XXIX)	$C_{14}H_{14}SO_2$	68,20/68,29	5,71/5,69	—	13,11/13,01	—
8-(β-Naphthylsulfonyl)-1,7-octadiene (XXX)	$C_{18}H_{20}SO_2$	72,13/72,00	6,60/6,67	—	10,60/10,67	—
3-(o-Methoxyphenylsulfonyl)-3-methyl-1-propene (XXXI)	$C_{11}H_{14}SO_3$	58,50/58,41	6,10/6,19	—	14,06/14.16	—
1-(o-Methoxyphenylsulfonyl)-2-butene (XXXII)	$C_{11}H_{14}SO_3$	58,50/58,41	6,10/6,19	—	14,06/14,16	—
8-(o-Methoxyphenylsulfonyl)-1,7-octadiene (XXXIII)	$C_{15}H_{20}SO_3$	64,00/64,29	7,25/7,14	—	11,50/11,43	—
3-(o-Chlorophenylsulfonyl)-3-methyl-1-propene (XXXIV)	$C_{10}H_{11}SO_2Cl$	52,16/52,06	4,70/4,77	—	13,80/13,88	15,10/15,40
1-(o-Chlorophenylsulfonyl)-2-butene (XXXV)	$C_{10}H_{11}SO_2Cl$	52,16/52,06	4,70/4,77	—	13,80/13,88	15,10/15,40
8-(o-Chlorophenylsulfonyl)-1,7-octadiene (XXXVI)	$C_{14}H_{17}SO_2Cl$	59,15/59,05	5,90/5,98	—	11,19/11,25	12,28/12,48
3-(2-Furylsulfonyl)-3-methyl-1-propene (XLI)	$C_8H_{10}SO_3$	55,70/55,61	5,42/5,38	—	17,10/17,20	—
1-(2-Furylsulfonyl)-2-butene (XLII)	$C_8H_{10}SO_3$	55,70/55,61	5,42/5,38	—	17,10/17,20	—
8-(2-Furylsulfonyl)-1,7-octadiene (XLIII)	$C_{12}H_{16}SO_3$	60,15/60,00	6,60/6,67	—	13,20/13,3	—

TABLE 5 (Continued)

Compound	Empirical formula	Found/calculated, %				
		C	H	N	S	Hal
3-(2-Thienylsulfonyl)-3-methyl-1-propene (XLIV)	$C_8H_{10}S_2O_2$	47,60 47,52	4,88 4,95	–	31,81 31,68	–
1-(2-Thienylsulfonyl)-2-butene (XLV)	$C_8H_{10}S_2O_2$	47,60 47,52	4,88 4,95	–	31,81 31,68	–
8-(2-Thienylsulfonyl)-1,7-octadiene (XLVI)	$C_{12}H_{16}S_2O_2$	56,34 56,25	6,15 6,25	–	25,11 25,00	–

Table 3 shows that oxygen- and nitrogen-containing activator-ligands are not inferior in their effectiveness to conventional phosphines and phosphites. The high selectivity with respect to the monoadduct when 18-dibenzo-6-crown ether or an excess of PPh_3 are included in the composition of the palladiumcatalyst is clearly due to the formation of active catalytic Pd complexes, which under telomerization conditions can coordinate with not more than one molecule of the diene.

To bring heteroaromatic sulfinic acids into the telomerization reaction, we studied the reaction of 2-thiophene- and 2-furansulfinic acids with butadiene in the presence of $Pd(acac)_2-PPh_3-AlEt_3$ (1:3:4) catalytic system. As the result we obtained a mixture of butenyl (XLI), (XLII), (XLIV), (XLV), and octadienyl sulfones (XLIII), (XLVI) in high yields.



X = O (XLI), (XLII), (XLIII), S (XLIV), (XLV), (XLVI)

EXPERIMENTAL

The arylsulfinic acids were prepared according to [6]. The mixtures of sulfones were analyzed on a "Chrom-4" chromatograph, using flame-ionization detector, a 1.2-m column with SE-30, carrier gas He. The PMR spectra were obtained on the "Tesla-487B" apparatus in $CDCl_3$, with HMDS as internal standard. The IR spectra were recorded on the UR-20 spectrophotometer (film or mineral oil). The mass spectra were run on the MX-13-06 apparatus with an energy of ionizing electrons of 70 eV and an ionization chamber temperature of 200°C.

General Method of Telomerization of Arylsulfinic Acids with Butadiene. A 0.8-mmole portion of $AlEt_3$ was added with stirring in an Ar current to a solution of 0.2 mmole of $Pd(acac)_2$, 0.6 mmole of PPh_3 in 2 ml of absolute toluene cooled to −10 to −15°C, and the mixture was held for 5-10 min at −10°C. Sulfinic acid, 20 mmoles, and 60 mmoles of butadiene in a mixture of toluene and water (4:1) were placed in a 20-ml steel autoclave cooled to −10°C, then the catalyst solution was added, and the mixture was heated for 4 h at 80°C. The mixture was cooled, and washed successively with 5% NH_4OH and H_2O. The organic layer was separated and dried over $MgSO_4$. After removal of solvent, the residue was distilled in vacuo or crystallized.

The physical constants and spectral characteristics of the aryl sulfones obtained are shown in Tables 4 and 5.

CONCLUSIONS

1. The nature and structure of the substituent in arylsulfinic acids slightly influence the direction of their telomerization with butadiene, and in almost all experiments this leads to a mixture of butenyl and octadienyl sulfones.

2. Low-valence palladium complexes, modified by secondary amines, nitrobenzene, or 18-dibenzo-6-crown ether, are effective catalysts of the telomerization of aromatic sulfinic acids with butadiene.

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STEREOCHEMISTRY OF SULFENYLCHLORINATION OF β-DEUTEROSTYRENES

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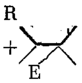
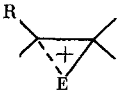
UDC 541.63:542.944+542.945.2:547.538.141

Changes in many fundamental characteristics of electrophilic addition reactions (AD$_E$-reactions) of alkenes are caused by difference in the degrees of participation of the reagent in the stabilization of the electron-deficient center of the transition state (TS) and (or) the intermediate [1-3]. In terms of a structural scheme, the degree of participation is usually reflected by the ratio of contributions to the addition reaction of the TS (intermediates) of open (I) and cyclic (II), (III) types


(I)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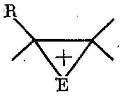
(III)

The stereochemical criterion of the passage of the Ad$_E$ reactions through a TS (intermediates) of cyclic (II), (III), and open (I) forms, is considered to be trans-stereospecific and nonstereospecific addition, respectively. Most of the reactions of alkenes with sulfur-containing electriphiles proceed by the first of these paths.

A disturbance of the stereospecificity of the trans-addition of the electrophiles to the alkenes is usually related to the high electron-donor ability of the substituents attached at the reaction center, causing that the reaction proceeds through the TS (intermediates) of an open type.

However, the picture is complicated by the fact that the stereochemical regularities of the addition of the electrophiles to the double bonds was studied mainly on models of nonterminal alkenes [1, 4, 5], and therefore the disturbance of the stereospecificity of the trans-addition can to a great extent be caused by the repulsive interaction of the vicinal groups in the TS (intermediates) of the cyclic type (II), (III). Therefore, strictly speaking, from the configuration of the products of the addition to alkenes with vicinal substituents, we cannot conclude on the contribution of the electronic effects to the stereodirectivity of the Ad$_E$-reactions of alkenes.

In the present work, we studied the influence of the electronic properties of substituents in the reagents on the stereodirectivity of the addition of arylsulfenyl chlorides to β-deuterostyrenes under conditions excluding the mutual interconversion of the stereoisomers (kinetic control). We also studied the case of conversion of the stereoisomers under the conditions usually used for Ad$_E$-processes.

To solve our problem, we synthesized stereoisomeric Z- and E-β-deuterostyrenes (IVa-d) and (Va-d) (Table 1) and examined their reactions with sulfenyl chlorides (VIb, c, e, g) in $CDCL_3$ and CD_3COOD (ratio of reagents 1:1)

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