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Invited Review

Metal complex catalysis in the synthesis of organic sulfur compounds

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Contents

1. Introduction

Despite the fact that homogeneous metal complex catalysts are commonly used in synthetic organic chemistry, it is only in recent years that these catalysts have attracted attention with respect to their potential application in the preparation of organic sulfur compounds (OSC). This is largely because OSC were traditionally considered to be catalytic poisons.

In 1978 the first communication appeared concerning the potential uses of palladium complex catalysts in the synthesis of higher allylsulfones from 1,3-dienes and arenesulfinic acids. That work was the starting point in our research and, undoubtedly, in that of many other organic chemists, developing unconventional approaches in the use of homogeneous metal-complex catalysts in the synthesis of important OSC with unique structures.

In the last ten years, a series of complex catalysts of unusually high efficiency was found, as well as new catalytic reactions, and regio- and stereoselective methods were developed for the heterocyclization of dienes, trienes and acetylenes with elemental sulfur and with small molecules containing two-, four-, or six-valent sulfur. This has provided single-step syntheses of linear and cyclic mono-, di-, trisulfides, sulfoxides, sulfones, sulfamides, thiophanes, thiophenes, 1,4-dithianes, 1,4-dithienes, thioamides and their derivatives, based on

available unsaturated hydrocarbons of petroleum origin. The alternative methods found so far for the preparation of OSC are rather complicated multi-step processes.

A good deal of information has been accumulated, particularly by Soviet workers, on the use of homogeneous metal-complex catalysts in the syntheses of various OSC.

This survey considers the most important results obtained by Soviet and other authors in the last ten years.

2. Reactions of conjugated dienes with sulfur-containing nucleophiles, catalyzed by transition metal complexes

By the middle of the 1970s homogeneous metal-complex catalysis had been developed in potentially important research directions such as the linear and cyclic oligomerizations of unsaturated compounds, metathesis, oxosynthesis, olefin oxidations, homogeneous hydration including asymmetric hydration, hydrocyanation of olefins and dienes, catalytic activation of small molecules and atoms, cross-coupling of allylic electrophiles with organometallic reagents, etc. However, we cannot find any literature from this period concerning the use of homogeneous metal-complex catalysts (HMCC) in the synthesis of organic sulfur compounds.

In 1976, taking as the starting point our own results and the data available world-wide on directed organic

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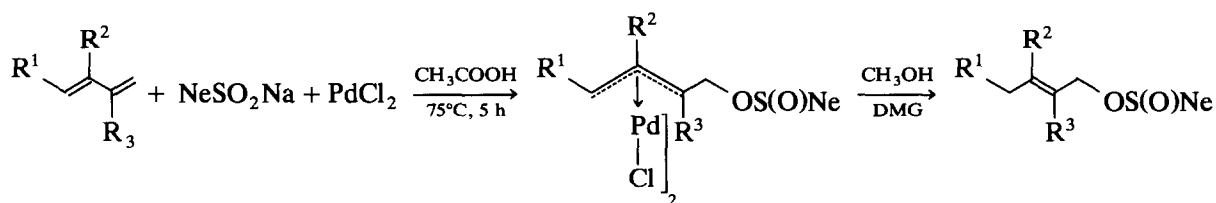
Ne–neophile–CH_2CMe_2Ph

$R^1 = C_2H_5$, $R^2 = R^3 = H$ (80%)

$R^1 = H$, $R^2 = R^3 = CH_3$ (80%)

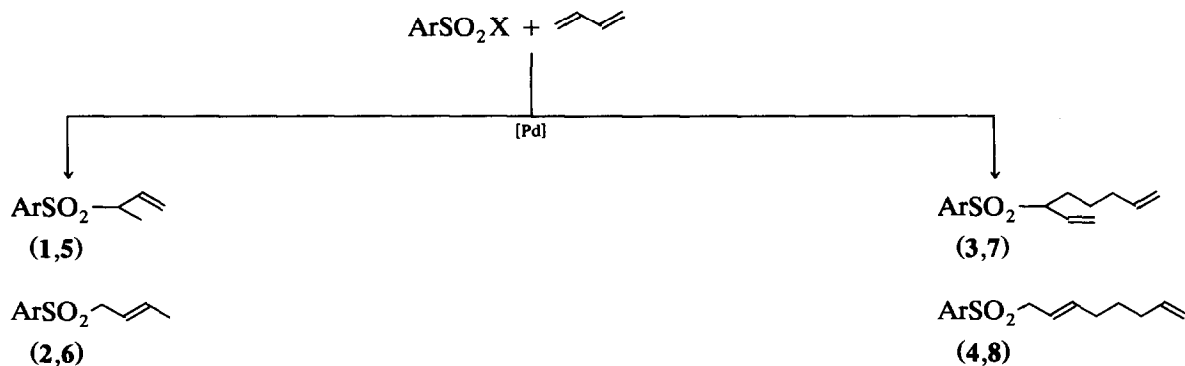$R^1 = R^2 = H$, $R^3 = CH_2CH_2CH=CMe_2$ (52%)

Scheme 1.

synthesis assisted by transition metal complexes, we initiated a research programme aimed at developing a scientific foundation for the synthesis of organic sulfur compounds (OSC), using homogeneous metal-complex catalysis. Our primary goal was to establish new catalytic reactions and unconventional methods of heterocyclization, as well as to find new complex homogeneous catalysts capable of activating conjugated dienes and acetylenes in reactions with S-nucleophiles and with compounds containing two-, four- or six-valent sulfur.

2.1. Telomerization of conjugated dienes with sulfinic acids in the presence of metal-complex catalysts

In 1978, two independent research groups reported on the use of palladium complexes for the synthesis of allylsulfones from 1,3-dienes and sulfinic acids [1,2] by stoichiometric and catalytic methods. Allylsulfones are synthesized from the reaction of sodium arenesulfinates with 1,3-dienes in the presence of an equimolar amount of $PdCl_2$ [2,3]. The reaction proceeds via the formation of intermediate π-allyl Pd complexes according to Schemes 1 and 2.

Catalytic telomerization of butadiene with benzene- or toluene-sulfinic acids, assisted by a complex catalyst

such as $Pd(acad)_2$–PPh_3–$AlEt_3$ leads usually to a mixture of butenyl- and octadienylsulfones in reasonably good yields [1].
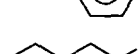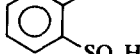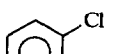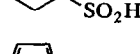
The selectivity of reaction is strongly affected by the ratio of starting reagents. Thus, at the molar ratio acid:diene = 1:1.5–2, the reaction results preferentially in butenylsulfones, while further increasing of the diene portion leads to octadienylsulfones. High yields of unsaturated sulfones are obtained in water-organic media that avoid disproportionation of sulfinic acids [1].

Further reports concern detailed studies of the effects of the nature, structure, and ratio of the catalyst on the course and the yield in telomerization of butadiene with sulfinic acids [4–13].

Many electron-donor and electron-acceptor ligands were tested as catalyst components. Only Pd catalysts containing either PPh_3, pyridine, diethylamine, or nitrobenzene showed high activity and selectivity in butadiene telomerization with sulfinic acids. The selectivity for butenylsulfone (5) increased with lower ligand concentration in the catalyst (Pd:4 = 1:2–6). With a higher concentration of Pd-catalyst, the total yield of unsaturated sulfones 5–8 increased [4,5,12].

Like benzene- and toluenesulfinic acids, para- and

$$ArSO_2X + \text{⌇⌇}$$

$ArSO_2$—⌇ (1,5)

$ArSO_2$⌇⌇ (2,6)

$ArSO_2$—⌇⌇ (3,7)

$ArSO_2$⌇⌇⌇ (4,8)

Ar = Ph (1–4); p-Tol (5–8); X = H; Na; K

Scheme 2.

TABLE 1. Effect of structure of substituted aromatic and heterocyclic sulfinic acids on product yield and structure in telomerization with butadiene

Sulfinic acid	Total yield, %	Ratio of sulfones, %		
		ArSO$_2$-⟨	ArSO$_2$⌒⌒	ArSO$_2$⌒⌒⌒⌒
⟨O⟩-SO$_2$H	97	53	39	8
Me-⟨O⟩-SO$_2$H	95	60	27	13
^{t}Bu-⟨O⟩-SO$_2$H	93	50	45	5
F-⟨O⟩-SO$_2$H	87	51	20	29
Cl-⟨O⟩-SO$_2$H	85	52	26	22
Br-⟨O⟩-SO$_2$H	81	53	28	19
^{t}Bu-⟨O⟩-SO$_2$H	93	50	45	5
F-⟨O⟩-SO$_2$H	87	51	20	29
Cl-⟨O⟩-SO$_2$H	85	52	26	22
Br-⟨O⟩-SO$_2$H	81	53	28	19
I-⟨O⟩-SO$_2$H	80	55	30	15
NC-⟨O⟩-SO$_2$H	82	54	27	19
PhO-⟨O⟩-SO$_2$H	80	46	36	18
⟨O⟩⟨O⟩-SO$_2$H (naphthalene)	91	40	37	23
⟨O⟩ OMe / SO$_2$H	98	61	13	26
⟨O⟩ Cl / SO$_2$H	85	–	70	30
⟨S⟩-SO$_2$H (thiophene)	70	70	20	10
⟨O⟩-SO$_2$H (furan)	76	75	20	5

Reaction conditions: catalyst Pd(acac)$_2$–PPh$_3$–AlEt$_3$ (1:3:4 molar ratio); Pd:sulfinic acid = 1:80; acid:butadiene = 1:3 (molar ratio); toluene:water = 4:1; 80°C, 6 h.

TABLE 2. Effects of butanesulfinic acid structures and reagent ratios on product yield and structure in telomerization assisted by Pd-catalyst

RSO_2H	Molar ratio of monomers	Yield, %	Ratio of products, %			
			RSO_2⌁	RSO_2⌁	RSO_2⌁	RSO_2⌁
$^nBuSO_2H$	1:1	56	44	54	–	2
$^nBuSO_2H$	1:4	87	48	9	9	34
$^nBuSO_2H$	1:10	82	21	4	28	47
$^iBuSO_2H$	1:4	95	52	14	5	29
$^iBuSO_2H$	1:10	81	14	1	19	66
$^sBuSO_2H$	1:4	92	–	26	–	74
$^tBuSO_2H$	1:4	90	–	23	–	77

Reaction conditions: catalyst $Pd(acac)_2$–PPh_3–$AlEt_3$ (1:3:4); Pd:acid = 1:100; toluene:water = 4:1; 40°C, 4 h.

TABLE 3. Effect of length of alkylradical in sulfinic acids on product yield and structure in telomerization with butadiene

RSO_2H	Molar ratio of monomers	Yield, %	Ratio of sulfones, %		
			RSO_2⌁	RSO_2⌁	RSO_2⌁
$^nC_8H_{17}SO_2H$	1:1	60	60	27	13
$^nC_8H_{17}SO_2H$	1:3	85	16	55	29
$^nC_8H_{17}SO_2H$	$1:3^a$	75	56	24	20
$^nC_{10}H_{21}SO_2H$	$1:3^b$	96	–	62	38
$^nC_{12}H_{25}SO_2H$	$1:3^b$	74	–	42	58

Reaction conditions: catalyst $Pd(acac)_2$–PPh_3–$AlEt_3$ (1:3:4); toluene:water = 4:1.
[a] 60°C, 10 h, Pd:acid = 1:80.
[b] 100°C, 10 h, Pd:acid = 1:30.

TABLE 4. Reactions of sulfinic acids with conjugated dienes

Sulfinic acid	Diene	Total product yield, %	Reaction products
TSA *		94	RSO_2⌁ (76%) RSO_2⌁ (24%)
TSA		85	RSO_2⌁
TSA		87	RSO_2⌁
BSA **		90	RSO_2⌁SO_2R (9)
TSA		80	RSO_2⌁
TSA		85	RSO_2⌁
BSA		90	RSO_2⌁SO_2R (10)
$^nBuSO_2H$	═·═	82	RSO_2⌁ (23%) RSO_2⌁ (77%)
$^nBuSO_2H$		98	RSO_2⌁

Reaction conditions: catalyst $Pd(acac)_2$-PPh_3-$AlEt_3$ (1:3:4); Pd:acid = 1:100; toluene:water = 4:1; 80°C, 6 h; *-toluenesulfinic acid; **-benzenesulfinic acid.
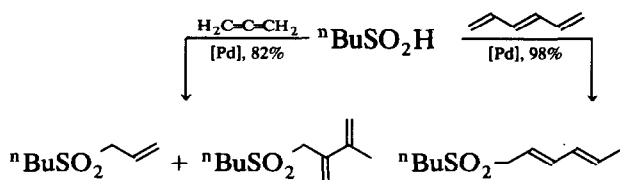
Scheme 3.

ortho-substituted arenesulfinic acids react with butadiene in the presence of the catalysts to give mixtures of butenyl- and octadienyl-sulfones in 80–98% yields. The nature of the substituents in the arenesulfinic acids has only a slight effect on the direction of telomerization with butadiene (Table 1) [6].

Lower alkanesulfinic acids react with butadiene under milder conditions (20–40°C, 4 h) than do the arenesulfinic acids (Table 2). The reactivity of the starting acids decreases with growing length of the alkyl group. The telomerization of higher sulfinic acids with 1,3-dienes requires higher temperatures and more time to give good yields of unsaturated sulfones (Table 3).

It is obvious that the reactivity of aliphatic sulfinic acids is superior to that of aromatic ones in the Pd-complex catalyzed reaction with 1,3-dienes [7].

Under similar conditions, the reaction of butadiene with sodium salts of arenesulfinic acids affords 98–99% yields of octadienylsulfones exclusively.

This method acquires still more importance since alkane- and arene-sulfinic acids have a low stability under normal conditions [14].

In contrast to butadiene, *trans*-piperylene, 2,3-dimethylbutadiene, cyclopentadiene, and cyclohexadiene undergo Pd-catalyzed reaction with toluenesulfinic acid to yield only 1:1 adducts [5,9] (Table 4).

Like the substituted dienes, allene and 1,3,5-*trans*-hexatriene react with n-butanesulfinic acid to give high yields of vinyl- and butadienylsulfones [10–13] (Scheme 3).

Disulfinic acids give unsaturated disulfones. Thus, reactions of butane-1,4-disulfinic acid with butadiene,
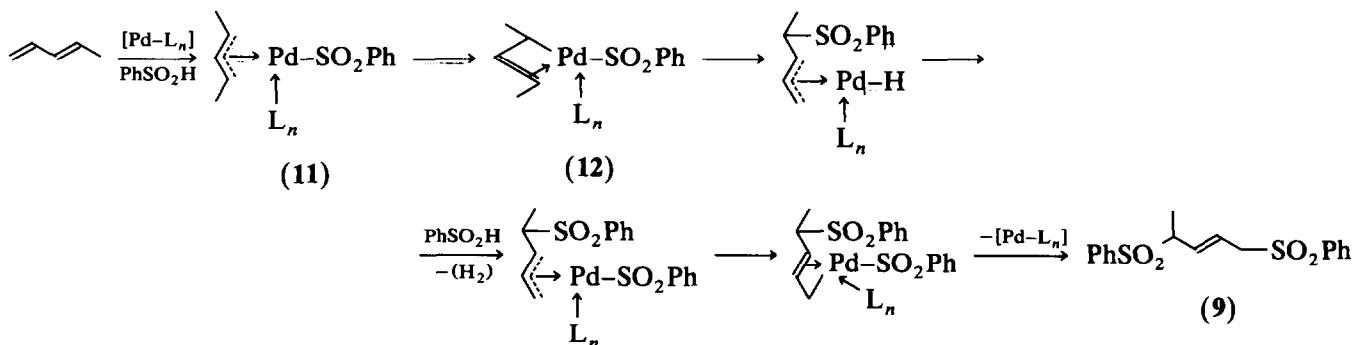
Scheme 4.

isoprene, or cyclopentadiene gave the corresponding disulfones (Scheme 4).

Disulfones (9, 10) were obtained in up to 90% yield in the telomerization of benzoylsulfinic acid with *trans*-piperylene or 1,3-cyclohexadiene (Table 4).

The formation of disulfone 9 was rationalized by assuming that two molecules of benzoylsulfinic acid add to the diene without preliminary removal of the monosulfone from the metal coordination sphere [10]. In the presence of low valent Pd-complexes, benzoylsulfinic acid most probably forms a π-allylic complex (11) that is subsequently attacked by the forms a π-allylic complex (11) that is subsequently attached by the second molecule of benzoylsulfinic acid giving a σ,π-complex (12). Further intramolecular reductive elimination leads to disulfone 9 [15–17] (Scheme 5).

The disulfone 10 may be formed in the same way.

In contrast to palladium catalysts, low-valent complexes of nickel act very selectively in the telomerization of butadiene with sulfinic acids to give allylic sulfones, each consisting of one diene molecule and the acid [18,19]. The effects of the activating ligands and of the concentration and ratio of the catalyst components on the yield of telomers 5, 6 was studied in detail in the telomerization of butadiene with toluene-

Scheme 5.
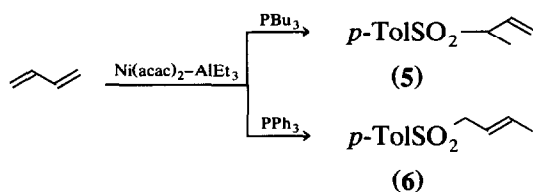
Scheme 6.

Scheme 7.

sulfinic acid [12,18]. High yields of 5, 6 were obtained with $Ni(acac)_2-Et_2NH-AlEt_3$ catalyst, and the highest selectivity for 5 and 6 was attained with the catalysts incorporating PPh_3 and PBu_3 as activating ligands (Scheme 6).

Bimetallic complex catalysts based on Pd, Ni, and Co compounds [10,12,13] were more effective (Table 5). As shown in Table 5, three-component catalytic systems based on $Ni(acac)_2$ or $Co(acac)_3$ are inactive in the telomerization, whereas these systems coupled with $Pd(acac)_2$ have a high activity, greater than that on $Pd(acac)_2$ alone.

We conducted detailed research into the mechanism of telomerization of arenesulfinic acids with 1,3-dienes in the reaction of isoprene with toluenesulfinic acid, assisted by the catalyst $Pd(acac)_2-PPh_3-AlEt_3$, and in the stoichiometric reaction of Pd^0-PPh_3 with octa-2,7-dienyl acetate and toluenesulfinic acid [20] (Scheme 7). The reaction route and the structures of intermediate complexes formed were monitored by IR- and NMR-spectroscopies [21-23].

We concluded that the active catalysts are formed by the oxidative addition of sulfinic acid to low-valent palladium complexes [12,13,20].

Thus, the mechanism of telomerization of sulfinic acids with 1,3-dienes can be outlined by Scheme 8.

In 1979 and 1982, our French colleagues reported on the reactions of 1,3-dienes with benzene- and *p*-toluenesulfinic acids, catalyzed by bis-π-allylpalladium chloride complex (Scheme 8). The reactions yielded 15-96% of related isomeric arylbutenylsulfones [24,25]. However, all attempts to obtain octadienylsulfones failed even with sufficiently excessive amounts of the starting diene (Table 6).
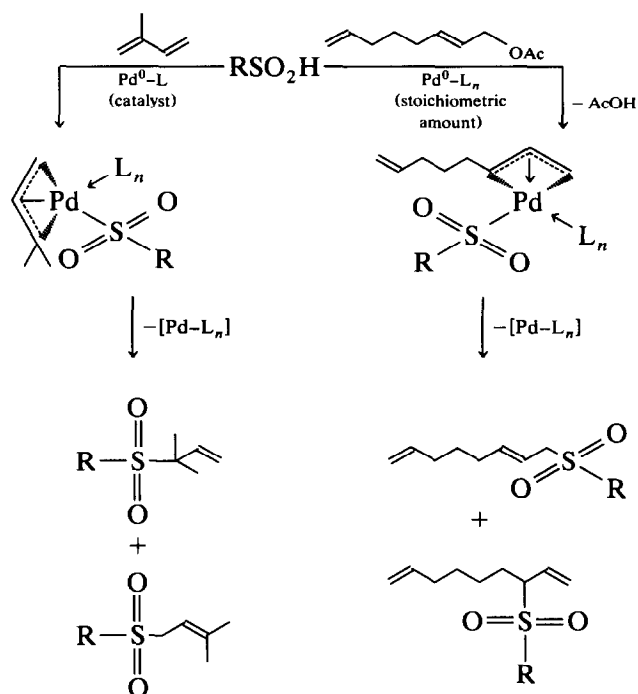
In 1986, Inoue and Hashimoto demonstrated the possibility of synthesizing allylsulfones via telomerization of sodium benzenesulfinate $PhSO_2Na \cdot 2H_2O$ with 1,2- and 1,3-dienes, using the complex catalyst $Pd(PPh_3)_4$ under CO_2 conditions (Table 7) [26]. Allylsulfones were not formed in the absence of CO_2.

It was concluded by Inoue and Hashimoto that the contribution of CO_2 consisted in the formation of carbonic acid that subsequently converted sodium sulfinate into benzenesulfinic acid and $NaHCO_3$ [26]. We disagree with this conclusion since their earlier attempts to conduct similar reactions of sodium toluenesulfinate in water-toluene media, catalyzed by a three-component palladium complex were successful without CO_2.

Apparently, CO_2 is a "mild" ligand that is incorporated into the coordination sphere of the catalyst cen-

TABLE 5. Effect of catalyst nature and concentration on product yield in the telomerization of toluenesulfinic acid with butadiene

Catalyst	Total yield, %	Telomer ratio, %	
		$ArSO_2$—	$ArSO_2$
$Pd(acac)_2-PPh_3-AlEt_3$	29	90	10
$Pd(acac)_2-Ni(acac)_2-PPh_3-AlEt_3$	78	64	36
$Pd(acac)_2-Co(acac)_3-PPh_3-AlEt_3$	27	51	23
$Ni(acac)_2-PPh_3-AlEt_3$	20	5	9*

Experimental conditions: acid : $Ni(acac)_2 = 160:1$, 60°C; toluene : water = 4:1; * the remainder is $ArSO_2Ar$ produced by disproportionation of toluenesulfinic acid.
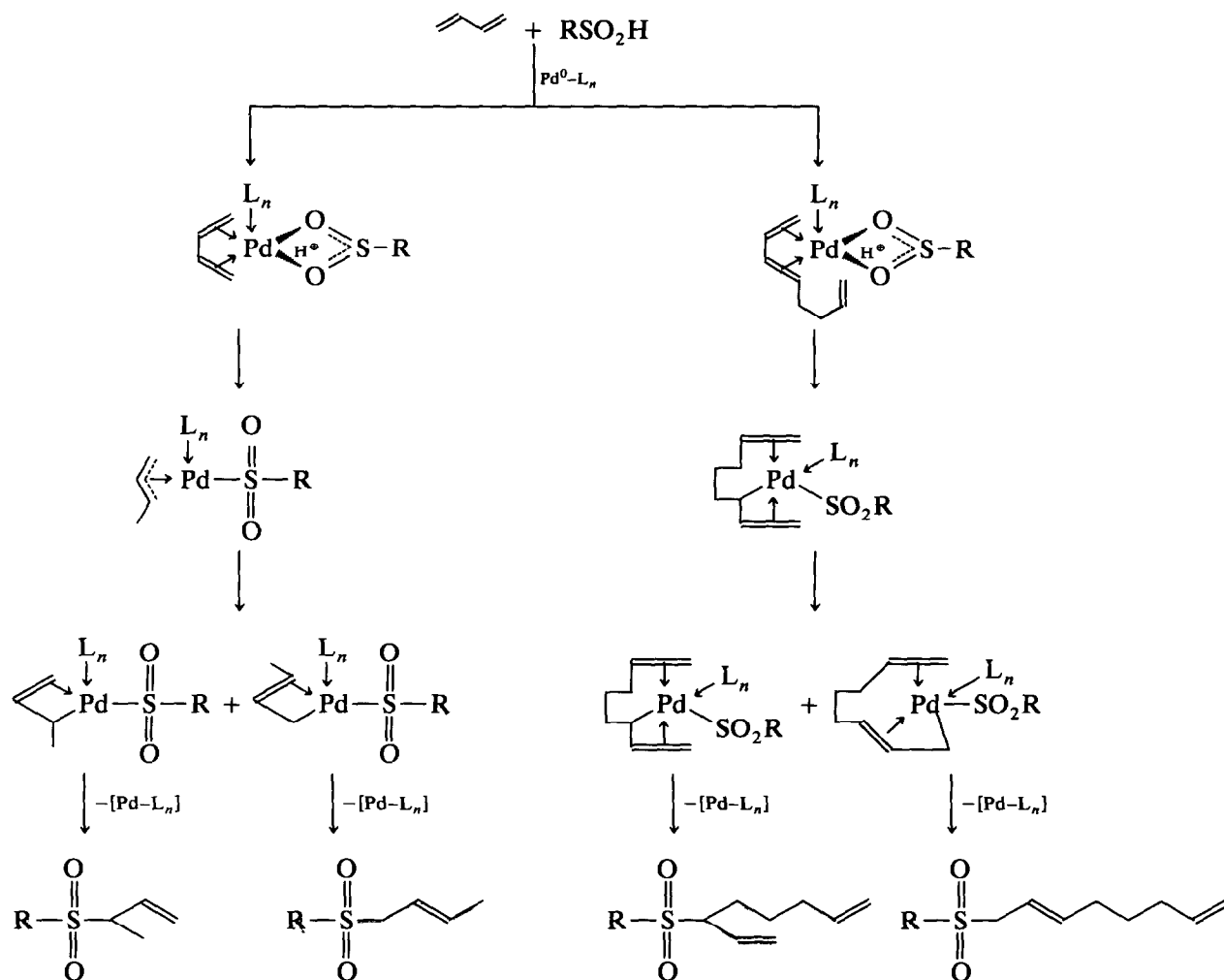
Scheme 8.

tral atom, thereby activating the latter in the course of telomerization [27].

This was supported by the results reported by Audell et al. [28], on the telomerization of benzenesulfinic acid or its sodium salt with 1,3-cyclohexadiene in the absence of CO_2. The reaction was catalyzed by Pd complexes activated with $P(OPh)_3$, Ni compounds being inactive in the reaction.

TABLE 6. Reactions of arenesulfinic acids and 1,3-dienes

Diene	ArSO$_2$H	ArSO$_2$R^1	Yield, (%)	ArSO$_2$R^2	Yield, (%)
⌇⌇	PhSO$_2$H	PhSO$_2$—⌇	76	PhSO$_2$⌇⌇	19
⌇⌇	p-TolSO$_2$H	p-TolSO$_2$—⌇	30	p-TolSO$_2$⌇⌇	
⌇⌇	PhSO$_2$H	PhSO$_2$—⌇	96	–	–
⌇⌇	p-TolSO$_2$H	p-TolSO$_2$—⌇	93	p-TolSO$_2$⌇⌇	5
⌇⌇	p-TolSO$_2$H	p-TolSO$_2$—⌇	65	p-TolSO$_2$⌇⌇	3
⌇⌇	p-TolSO$_2$H	p-TolSO$_2$—⌇	15	p-TolSO$_2$⌇⌇	10
				p-TolSO$_2$⌇⌇	70

Catalyst: bis-π-allylic PdCl$_2$ (0.1 mmol), PPh$_3$ (1.0 mmol); ArSO$_2$H (10.0 mmol), ArSO$_2$Na (0.5 mmol), diene (10.0 mmol), THP, 45°C, 18 h
[a] 60°C, 18 h. [b] The reaction with ArSO$_2$Na retains the acid unchanged. [c] The reaction with ArSO$_2$Na gives similar results.

$$M-L_n + Nu-H \longrightarrow H-M-Nu \xrightarrow{\;\;} \qquad \longrightarrow \qquad \xrightarrow{-(M-L_n)}$$
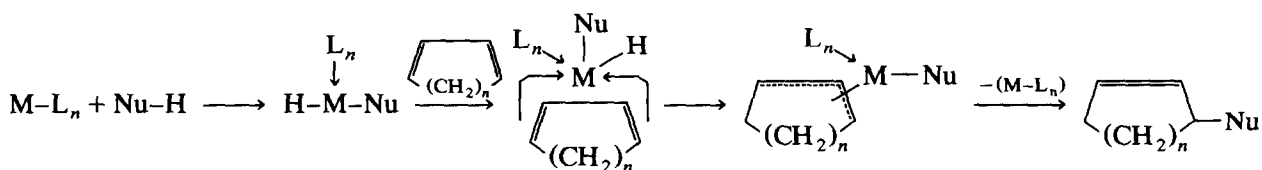
Scheme 9.

As far as the stereochemistry of the telomerization of sulfinic acids with 1,3-cyclodienes is concerned, the addition of an S-nucleophile to the dienes was found to occur via a *trans*-attack of a Pd π-allylic complex formed according to Scheme 9.

It would not be an exaggeration to say that at present the telomerization of sulfinic acids and their salts with 1,2- and 1,3-dienes and 1,3,5-trienes is one of the most promising and effective approaches to the synthesis of unsaturated sulfones.

2.2. Telomerization of 1,3-dienes with arene- and alkanesulfamides

Proceeding from the previous experience acquired with telomerization of conjugated dienes with sulfinic acids, we succeeded in conducting reactions of arene- and alkanesulfamides with 1,3-dienes, catalyzed by the Pd phosphine complexes [29] that were earlier proven useful in the synthesis of sulfones from sulfinic acids and dienes [1,4–8].

Sulfamides showed much higher selectivity than sulfinic acids in reactions with 1,3-dienes, to lead preferentially to octadienylsulfamides [29–31]. Thus, telomerization of butadiene with *para*-toluenesulfamide, assisted by the catalyst $Pd(acac)_2-PPh_3-AlEt_3$ (1:3:4) gave mono- and bis-2,7-octadienylsulfamides 13–15 in *ca.* 96% total yield (Scheme 10). At higher butadiene

concentrations, *e.g.* butadiene:sulfamide = 1:6, or with NH_4OH and $^{t}BuOH$ added to the catalytic mixture, the telomerization can be directed exclusively towards the formation of bis-adducts 14, 15 in *ca.* 97% yield. Besides 2,7-octadienyl derivatives (13, 14), the latter case gives 2,6-isomers (15) too. This is ascribed to positional isomerization of 2,7-adducts to thermodynamically more stable 2,6-isomers under the effect of Pd hydride complexes [29].

Similar results were obtained with butanesulfamide [29].

We observed also an exclusive formation of bis-octadienylsulfamides 14, 17 after such ligands as PPh_3 or $P(OPh)_3$ had been added to the Pd catalyst, whereas Et_2NH and α,α'-dipyridyl additions result in monooctadienylsulfamides (13, 16) irrespective of the structures of the starting arene- and alkanesulfamides [29,30].

The reactions conducted in toluene, dimethylformamide, or pyridine led to the highest yields of telomers.

The reaction of butadiene with n-substituted arylsulfamides was also easy to perform [30] (Scheme 11).

Replacement of the CH_3 group by allyl, amyl, or phenyl in N-methyl-*p*-toluenesulfamide exerts practically no influence upon the yields of related telomers, though it promotes higher selectivity of the reaction to result exclusively in 2,7-octadienylsulfamides.

On the contrary, the direction and product yields in reactions of butadiene with a series of N-substituted alkylsulfamides depend appreciably on the structure of

TABLE 7. Effect of starting diene structures on product yield and composition in reactions of 1,3-dienes with sulfinic acid

Diene	Reaction temp., °C	Reaction time, h	Sulfones	Yield, (%)
	80	2	PhO_2S—	20 ($E:Z = 2:1$)
			$PhSO_2$—	78 ($E:Z = 6:1$)
	80	2	$PhSO_2$—	94
	110	4	$PhSO_2$—	31 ($E:Z = 19:1$)
=·=	80	2	$PhSO_2$—	44

Reaction conditions: $PhSO_2Na \cdot 2H_2O$ (9.1 mmole); 1,3-diene (10–34 mmole); $[Pd(PPh_3)_4]$ (0.2 mmole); DMFA (10 ml); CO_2 (15 kg/cm^2).

$$RSO_2NH_2 + \qquad \Big\downarrow \qquad$$

$$\sim 96\% \;\; [Pd]$$

$$RSO_2N\underset{H}{\overset{|}{-}}\!\!\!\!\sim\!\!\!\sim\!\!\!\sim\!\!\!\sim + RSO_2N\big(\!\!\sim\!\!\!\sim\!\!\!\sim\big)_2$$

(13,16)   (14,17)

$$+ \; RSO_2N\big(\!\!\sim\!\!\!\sim\!\!\!\sim\big)_2$$

(15,18)

$R = C_6H_4CH_3$ (13–15)   R = ^{n}Bu (16–18)

Scheme 10.

$$RSO_2\underset{R^1}{N}H + \diagup\!\!\diagdown\!\!\diagup \xrightarrow[\sim 99\%]{[Pd]}$$

$$RSO_2\underset{R^1}{N}\!\!-\!\!\diagup\!\!\diagdown\!\!\diagup\!\!\diagdown\!\!\diagup + RSO_2\underset{R^1}{N}\!\!-\!\!\diagdown\!\!\diagup\!\!\diagdown$$

$$\sim 95\% \qquad\qquad \sim 5\%$$
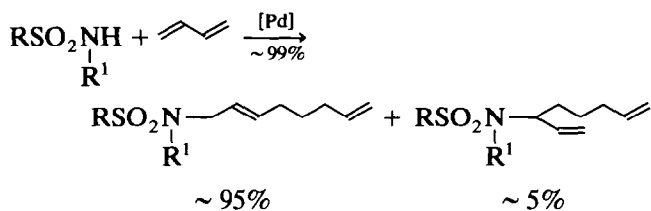
$R = p\text{-Tol}, R^1 = Me; R = R^1 = Me; R = {}^nBu,$

$R^1 = Me; R = {}^nBu, R^1 = C_5H_{11};$

$R = {}^nBu, R^1 = (CH_2=CH-CH_2).$

Scheme 11.

the N-substituent. With the N-amyl or N-allyl moiety in n-butanesulfamide, the yields of octadienylsulfamides decrease from 97 to 32%. The content of 1,7-octadienyl isomers in the reaction product increases to 12% with a lower concentration of Pd-catalyst.

In contrast to the unsubstituted sulfamides, monosubstituted sulfamides react with butadiene in the presence of Ni, Fe, Cu, Mn, or Co complexes as catalysts, the yields of telomers being below 30%.

The sulfamides show the following sequence of reactivity in telomerizations with 1,3-dienes [29–31,35]:

$$MeSO_2NHMe > p\text{-TolSO}_2NHMe > p\text{-TolSO}_2NH_2$$

$$> p\text{-TolSO}_2NHR^1 > {}^nBuSO_2NHMe$$

$$> {}^nBuSO_2NH_2 > {}^nBuSO_2NHR,$$
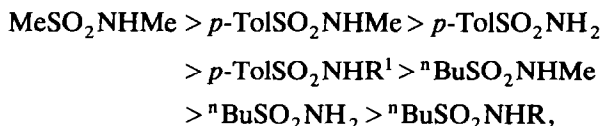
where $R = Ph, CH_2=CH-CH_2$, or C_5H_{11}.

With decreasing basicity of sulfamides, reactivity decreases in the telomerization with butadiene.

Similar reactions with alkane- and arene-sulfamides were observed for isoprene, piperylene, 2,3-dimethylbutadiene, 1,3,5-hexatriene, cyclopentadiene, and cyclohexadiene [30].

In all experiments with isoprene, 2,7-octadienylsulfamides were preferentially formed irrespective of the reaction conditions and the ratio of starting monomers (Scheme 12).

$$RSO_2\underset{Me}{N}H + \diagup\!\!\diagdown\!\!\diagup$$

$$\xrightarrow{\sim 65-98\%}$$

$$RSO_2\underset{Me}{N}\!\!-\!\!\diagup\!\!\diagdown\!\!\diagup\!\!\diagdown\!\!\diagup$$

$$RSO_2\underset{Me}{N}\!\!-\!\!\diagdown\!\!\diagup + RSO_2\underset{Me}{N}\!\!-\!\!\diagup\!\!\diagdown\!\!\diagup$$

$$R = p\text{-Tol}, {}^nBu$$
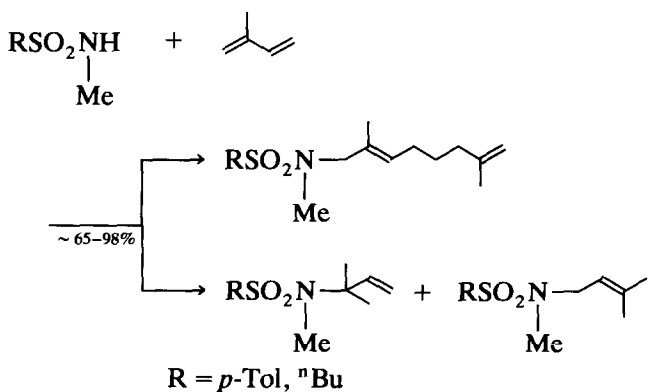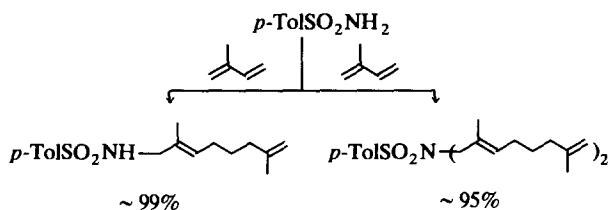
Scheme 12.

Unsubstituted *p*-toluenesulfamide reacted with two moles of isoprene to give a quantitative yield of mono-2,7-octadienylsulfamide, while a six-fold excess of the diene led to a bis-adduct (Scheme 13).

$$p\text{-TolSO}_2NH_2$$

$$p\text{-TolSO}_2NH\!\!-\!\!\diagup\!\!\diagdown\!\!\diagup\!\!\diagdown\!\!\diagup \qquad p\text{-TolSO}_2N\!\!-\!\!(\diagup\!\!\diagdown\!\!\diagup\!\!\diagdown\!\!\diagup)_2$$

$$\sim 99\% \qquad\qquad \sim 95\%$$

Scheme 13.

The reaction is less smooth with *trans-* or *cis-*piperylene, 2,3-dimethylbutadiene, or cyclodienes. N-Methyl-2,4-hexadienyl-*p*-toluene-sulfamide gave only a 25% yield in the reaction of *trans*-1,3,5-hexatriene with N-methyl-*p*-toluenesulfamide at 80°C for 10 h (Scheme 14).

However, these dienes do not react with N-methyl-n-butanesulfamide under the conditions described here.

Therefore, the interactions of unsubstituted and N-substituted alkyl- and arylsulfamides with conjugated dienes and trienes, catalyzed by transition metal complexes, can be regarded as effective single-stage syntheses of higher unsaturated linear and cyclic sulfamides that are otherwise hardly available.

2.3. Interactions of sulfinic acids and sulfamides with allylic compounds

One of the principal disadvantages of the synthetic methods described in Section 2 is that a mixture of structural telomers is usually formed. Besides, the re-

$$RSO_2N\!-\!(CH_2)_n \qquad\qquad RSO_2N\!-\!\diagup\!\!\diagdown\!\!\diagup$$
$$\underset{Me}{} \qquad\qquad\qquad \underset{Me}{}$$

$$n = 2, 19\%$$
$$n = 1, 12\% \quad [Pd] \quad 30\%$$

$$(CH_2)_n \qquad\qquad (CH_2)_n$$

$$RSO_2\underset{Me}{N}H$$

$$25\% \qquad\qquad 23\% \quad [Pd]$$

$$RSO_2\underset{Me}{N}\!\!-\!\!\diagup\!\!\diagdown\!\!\diagup \qquad RSO_2\underset{Me}{N}\!\!-\!\!\diagup\!\!\diagdown$$

Scheme 14.

R—⟋—X

$\downarrow$ [Pd]

R—⟋

.Pd.
L$_n$ X

R'SO$_2$H ⟋   ⟍ R'SO$_2$NR''-H
      ⟋ —HX   —HX ⟍

R—⟋   R—⟋

.Pd.   .Pd.
L$_n$ SO$_2$R'   L$_n$ N—SO$_2$R'
                               |
                               R''

$\downarrow$ —[Pd-L$_n$]   —[Pd-L$_n$] $\downarrow$

R—⟋—SO$_2$R'   R—⟋—SO$_2$NR'R''
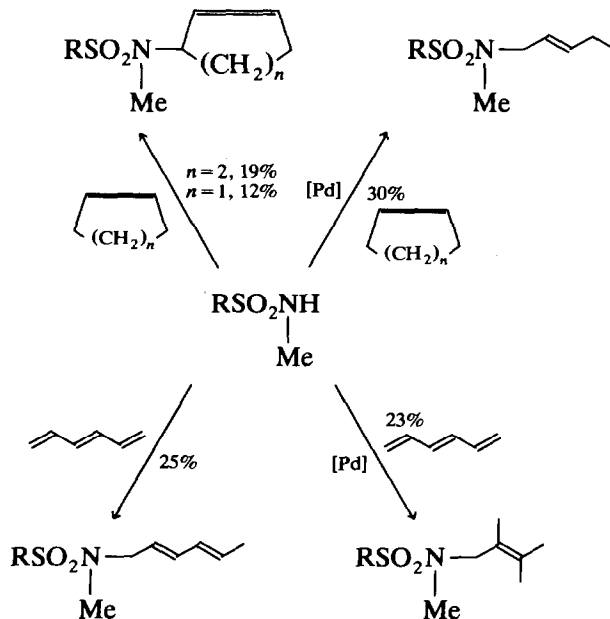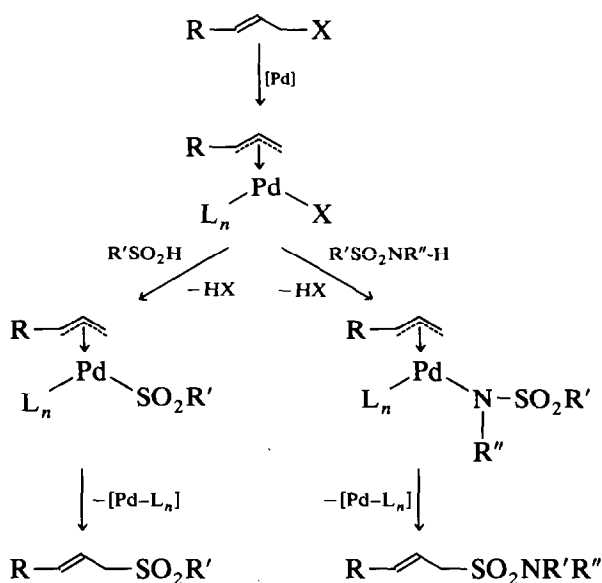
Scheme 15.

action direction, selectivity, and product yields are strongly affected by the structures of the initial monomers, and highly active and selective catalysts must be developed for each experiment.

This served as an incentive to further research in our laboratory and we suggested a new region- and stereoselective synthetic method for higher unsaturated sulfones and sulfamides [32–35]. The method is based of reactions of sulfinic acids or sulfamides with allylic electrophiles generated *in situ* from O-, S-, and N-containing allylic compounds, assisted by Pd complex catalysts according to the overall scheme depicted in Scheme 15 [36–37].

Proceeding from Scheme 15, we developed an effective synthesis of individual unsaturated sulfones from arene- and alkane-sulfinic acids and allylic alcohols, ethers, esters, and amines and their quaternized derivatives, particularly from allylic compounds having

AcO—⟋═⟍—OAc + PhSO$_2$H $\xrightarrow[50\%]{\text{[Pd]}}$

PhSO$_2$—⟋═⟍—SO$_2$Ph

(19)
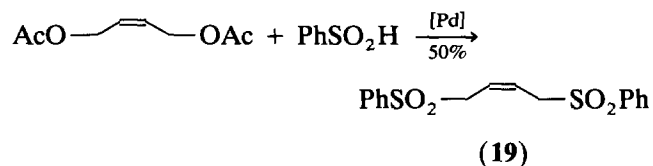
Scheme 17.

complex structures that contain several double bonds and various functional substituents (Scheme 16).

This provides a stereoselective synthesis of the disulfone (19) [33] (Scheme 17).

The structure of the unsaturated substituent in the resultant sulfones is the same as that of the hydrocarbon moiety in the starting allylic compounds: the stereochemistry of the allyl compound remains unchanged under re-allylation assisted by Pd complexes.

However, it was very difficult to extend the reaction to allylic compounds of more complicated structures. In particular, the molecules of unsaturated sulfones are formed smoothly with simple allylic or 2,7-octadienyl derivatives, but it is much less selective with more complicated allylic compounds.

Thus, reactions of alkali metal arenesulfinates with linalyl or geranyl acetates in the presence of catalytic amounts of Pd(PPh$_3$)$_4$ were not selective and gave, in each case, a mixture of linalyl-, geranyl-, and neryl-sulfones in 10, 60, and 20% yields, respectively.

Gulia et al. explained the formation of Z-sulfone in terms of isomerization of allylsulfones that are formed due to the presence of a starting arenesulfinic acid and Pd catalyst [25] (Scheme 18).

The difficulties were resolved by Tamura et al. [36,37] who used NaNO$_2$ as a promoting additive to increase activity of the Pd catalyst. Thus, the reaction of linalyl acetate with PhSO$_2$Na, catalyzed by Pd(PPh$_3$)$_4$ led exclusively to primary sulfones, i.e. a mixture of geranyl- and neryl-sulfones, whilst only a tertiary allylsulfone resulted from the reaction with NaNO$_2$ (Scheme 19).

RSO$_2$H

|Pd(acac)$_2$–PPh$_3$–AlEt$_3$

R'—⟋—X   R'X—⟍⟋⟍⟋═⟍

R'—⟋—SO$_2$R   ⟋⟍⟋⟍⟋⟍—SO$_2$R
R' = H, CH$_3$;   R' = Me; Ph
X = PhO;   X = O, NR'', S

⟋—O;
ClC$_6$H$_4$;
HO;
R''R'N
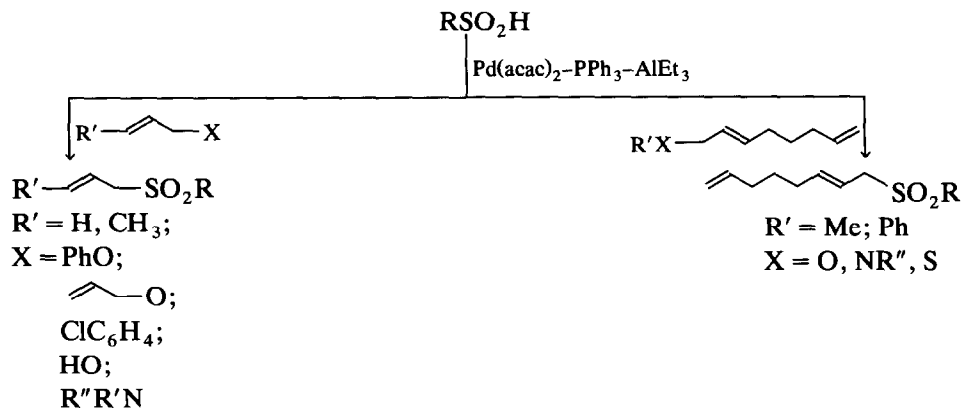
Scheme 16.

Scheme 18.

Scheme 19.

Scheme 21.

$$PhSO_2H + (\diagdown\!\!\diagup)_2S \xrightarrow{[Pd]}$$

$$PhSO_2\diagdown + PhSO_2\diagup\diagdown\diagup$$

$$PhSO_2H + (\diagup\diagdown)_2S \xrightarrow{[Pd]}$$

$$PhSO_2\diagdown + PhSO_2\diagup\diagdown\diagup$$
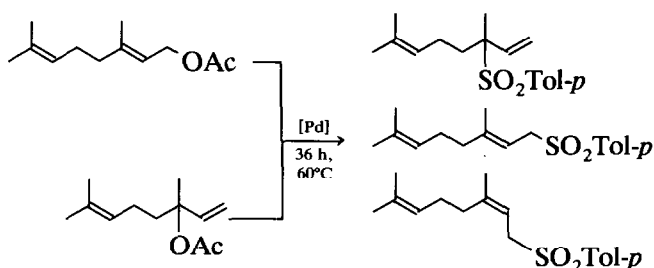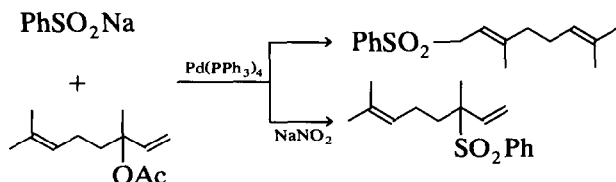
Scheme 22.

They concluded that $NaNO_2$ worked as an effective co-catalyst for $Pd(PPh_3)_4$ to suppress completely the isomerization of linalyl sulfone into thermodynamically more stable geranyl- and nerylsulfones [36,37].

Tamura et al. established a new regioselective method to synthesize allylsulfones from allylnitro-compounds and sulfinic sodium salts with the use of $Pd(PPh_3)_4$ as a catalyst. High yields of 1-phenyl-sulfonylmethylcycloalkenes were obtained from 1-nitromethylcycloalkenes and $PhSO_2Na \cdot 2H_2O$ in the presence of $Pd(PPh_3)_4$ (Scheme 20).

Therefore, regiocontrolled interactions of allylacetates or allylnitro-compounds with $PhSO_2Na$ in the presence of catalyst $Pd(acac)_2$-$NaNO_2$ result preferably in secondary or tertiary allylsulfones, whilst only primary allylsulfones are formed with $Pd(PPh_3)_4$ alone.

The identity of the products of C-alkylation of alkali metal arylsulfinates with allyl acetates to those ob-

tained from the reaction of conjugated dienes with arylsulfinic acids suggested that Pd π-allyl complexes (20-22, see Scheme 21) contributed in both cases and that the complexes were key intermediates responsible for the formation of related allylsulfones [25].
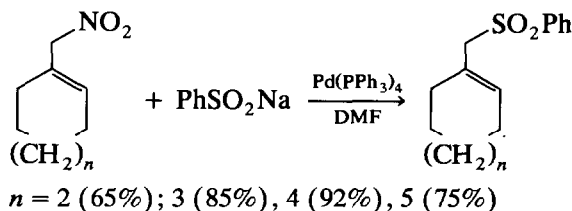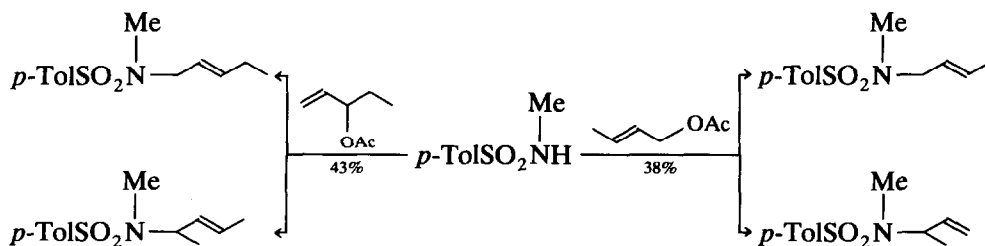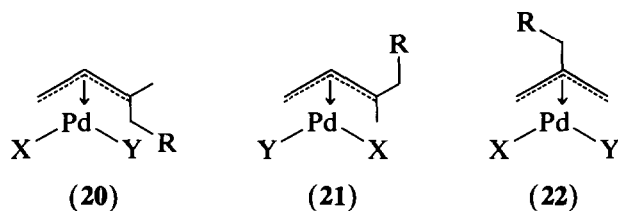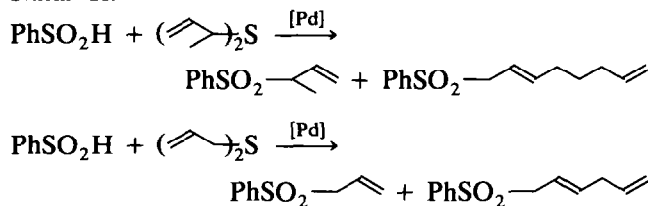
The selectivity of the reaction of sulfinic acids with allylic compounds is strongly affected by the nature of a heteroatom in the allylic structure. In particular, the reaction of benzenesulfinic acid with S-containing allylic compounds was not selective, giving a mixture of allylsulfones [33] (Scheme 22).

Similarly to sulfinic acids, sulfamides of various structures react with allylic compounds. Heating of equimolar amounts of N-methyl-p-toluenesulfamide with either allylic alcohol, diallyl or phenylallyl ester, allyl or cinnamyl acetate, or diethylallylamine with the catalytic complex $Pd(acac)_2$-PPh_3-$AlEt_3$ gave N-methyl-N-allyl-toluene-sulfamide in ca. 98% yield [38] (Scheme 23).

Allylphenylsulfone, diallylsulfide, and N-allylmorpholine do not give a satisfactory yield of the said allylsulfamide.

$$\xrightarrow{NO_2} + PhSO_2Na \xrightarrow[DMF]{Pd(PPh_3)_4} \xrightarrow{SO_2Ph}$$

$(CH_2)_n$ $(CH_2)_n$

n = 2 (65%); 3 (85%), 4 (92%), 5 (75%)

Scheme 20.

$$p\text{-TolSO}_2\text{NH} + \diagup\!\!\diagdown\!\!-R \xrightarrow[70-98\%]{[Pd]} p\text{-TolSO}_2\text{N}\diagup\!\!\diagdown$$

Scheme 23.

Scheme 24.

$$\text{Me}$$
$$p\text{-TolSO}_2\text{NH} + \ \ \text{X} \ \xrightarrow[40-86\%]{[\text{Pd}]}$$

$$\text{Me}$$
$$p\text{-TolSO}_2\text{N}$$

X = OH, OR, OCOR, NR$_2$

Scheme 25.

$$p\text{-TolSO}_2\text{NH}_2$$

$$p\text{-TolSO}_2\text{N} \!\!-\!\!\big(\quad \big)_2 \qquad p\text{-TolSO}_2\text{N} \!\!-\!\!\big(\quad \big)_2$$

+   +

$$\text{H}$$ $$\text{H}$$
$$p\text{-TolSO}_2\text{N} \qquad\qquad p\text{-TolSO}_2\text{N}$$
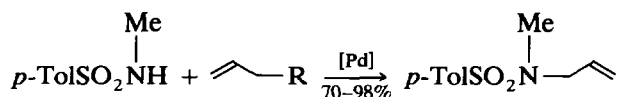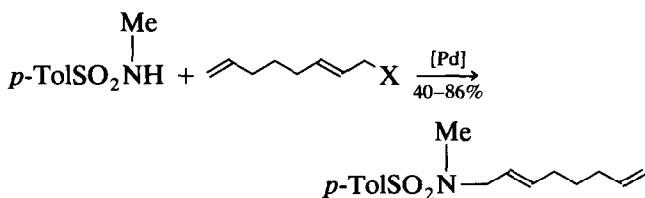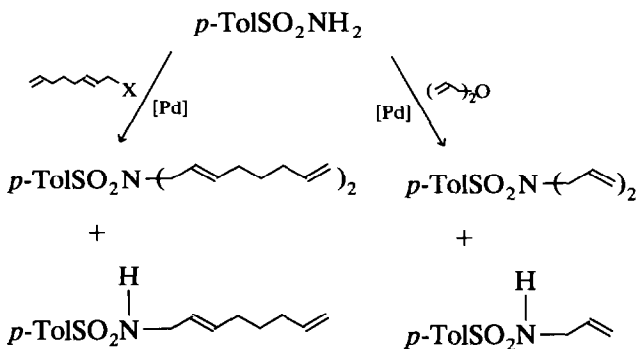
X = OH, OAc

Scheme 26.

In contrast to allyl and cinnamyl acetates, crotyl and pent-1-en-3-yl acetates react with sulfamides in the presence of Pd(acac)$_2$–PPh$_3$–AlEt$_3$ to give a mixture of isomeric allylsulfamides (Scheme 24).

Higher allylsulfamides were prepared from octadienyl alcohols, esters, ethers, amines, or N-methyl-p-toluenesulfamide by the method outlined in Scheme 25.

Unsubstituted p-toluenesulfamide reacts with allylic electrophiles to give either mono- or bis-allylsulfamides, depending on the concentration of starting allylic compound (Scheme 26).

Sulfinic acids react more readily than sulfamides with allylic compounds to give high yields of allylsulfones. Sulfamides are weaker bases than primary and secondary amines and have a less active hydrogen atom than in related sulfinic acids, hence their lower reactivity in both telomerization with 1,3-dienes and the reaction with allylic electrophiles in the presence of Pd complex catalysts.

$$\text{PhSO}_2\text{CH}_2\text{CO}_2\text{Et} \xrightarrow[[\text{Pd}]]{} \text{PhSO}_2\text{CH} \!\!-\!\!\!\!$$
$$|$$
$$\text{CO}_2\text{Et}$$

(23)

Scheme 27.

$$\text{ArSO}_2\text{CH}_2\text{CO}_2\text{Me}$$

+

$$\xrightarrow{[\text{Pd}]} \quad \text{ArSO}_2\text{CH} \!\!-\!\!\!\! \quad (24)$$
$$|$$
$$\text{CO}_2\text{Me}$$

$$\text{ArSO}_2\text{C} \!\!-\!\!\big(\qquad \big)_2$$
$$|$$
$$\text{CO}_2\text{Me} \quad (25)$$
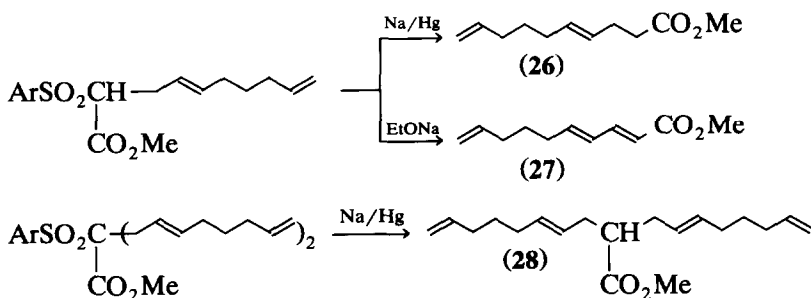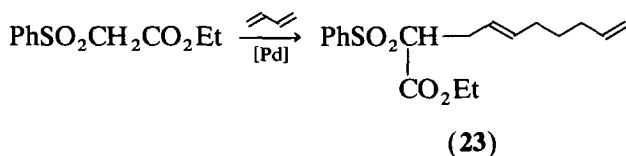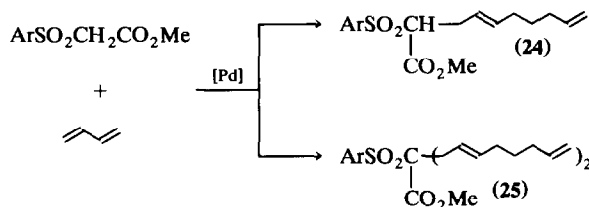
Scheme 28.

The SO$_2$NHR moiety is more bulky than SO$_2$H, increasing the steric hindrance for the formation of the intermediate Pd π-allylic complexes which are responsible for the formation of the final allylsulfamides. This steric hindrance is still more pronounced if the leaving group in the allylic electrophiles is also bulky.

In addition to 2,7-octadienylsulfamide, a yield of up to 32% of isomeric 1,7-octadienylsulfamide was obtained in the reaction of N-methyl-p-toluenesulfamide with octa-2,7-dienyl acetate. This isomer is usually not available from telomerization of butadiene with sulfamides [29]. Unreacted octa-2,7-dienyl acetate was transformed into the isomeric octa-1,7-dien-3-yl acetate in 60% yield under the reaction conditions. It was also found that Pd complexes containing arene- or alkane-sulfamides in the central metal coordination sphere promoted the isomerization [35,38].

Besides Pd complexes, the reaction can be catalyzed also by systems containing Ni, Fe, Co, Zr, Cr, or Cu [38].

Thus, we have with our colleagues developed a catalytic method to synthesize selectively allylsulfones and allylsulfamides of desired structures [32–35,38], which is an extension of the earlier approach to unsaturated sulfones and sulfamides via telomerization of 1,3-dienes with sulfinic acids and sulfamides in the presence of metal complex catalysts.

$$\xrightarrow{\text{Na/Hg}} \ \ \text{CO}_2\text{Me}$$
(26)

$$\text{ArSO}_2\text{CH} \!\!-\!\!\!\!$$
$$|$$
$$\text{CO}_2\text{Me}$$

$$\xrightarrow{\text{EtONa}} \ \ \text{CO}_2\text{Me}$$
(27)

$$\text{ArSO}_2\text{C} \!\!-\!\!\big(\qquad \big)_2 \xrightarrow{\text{Na/Hg}} \ \ \text{CH} \qquad$$
$$|$$ (28) $$|$$
$$\text{CO}_2\text{Me} \qquad\qquad\qquad\qquad\qquad \text{CO}_2\text{Me}$$

Scheme 29.

Scheme 30.

$R^1SO_2CH_2R^2$

$+$ $\xrightarrow{[Pd]}$

$R^1SO_2CH{-}\diagup\diagdown\diagup\diagdown$
            $|$
            R^2

$R^1SO_2C{-}(\diagdown\diagup\diagdown\diagup)_2$
          $|$
          R^2

$R^1 = C_2H_5$, C_6H_5, $p\text{-}MeC_6H_4$; $R^2 = CO_2CH_3$, NO_2

Scheme 31.

$R^1SO_2CHR^3 + \diagup\diagdown\diagup \xrightarrow{[Pd]} R^1SO_2C{-}\diagdown\diagup\diagdown\diagup$
      $|$ $|$
      R^2 R^2

$R^1 = p\text{-}Tol$, $R^2 = H$, $R^3 = CO_2CH_3$;

$R^1 = C_6H_5$, $R^2 = C_3H_7$, $R^3 = CO_2CH_3$
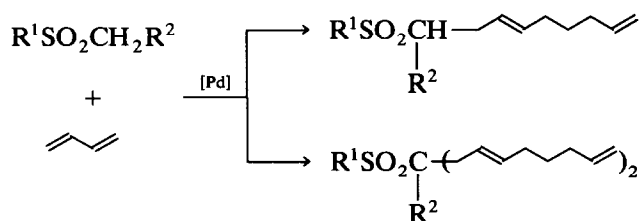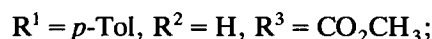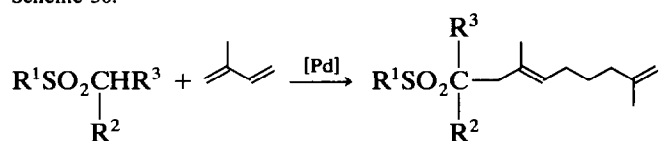
2.4. Telomerization of 1,3-dienes with sulfonyl esters, catalyzed by palladium complexes

The method based on telomerization of sulfonic esters with 1,3-dienes, catalyzed by Pd-complexes can be considered to be a very promising approach to the synthesis of unsaturated sulfones. Although this is an indirect synthetic route to organic sulfur compounds, this would be useful for the preparation of higher unsaturated sulfones.

Similarly to the known reaction of 1,3-dienes with β-diketo-esters, β-diketones, and dialkylmalonates [39–42], sulfonyl esters react with 1,3-dienes in the presence of Pd complex catalysts to sulfone (23) can be prepared from ethyl phenylsulfonylacetate and buta-diene with catalyst $PdCl_2(PPh_3)_2{-}PhONa$ [43] (Scheme 27).

With catalytic low-valent Pd phosphine complexes, phenyl- and tolyl-carbomethoxymethylsulfones react with butadiene to give both mono- and bis-octadienyl products [44]. With a higher proportion of butadiene in the reactants, the content of bis-octadienyl esters reaches ca. 40%. The activity of the catalytic system $Pd(acac)_2{-}PPh_3{-}AlEt_3$ was found to increase appreciably with added CF_3COOH ($Pd : CF_3COOH = 1 : 10$), giving satisfactory yields of higher unsaturated sulfones (Scheme 28).

This reaction is important also from the preparative

Scheme 32.

$p\text{-}TolSO_2CH_2R$

$+$ $\xrightarrow[60\text{-}70\%]{[Pd]}$

$p\text{-}TolSO_2CH{-}\diagup\diagdown\diagup\diagdown$ (with R substituent)

$+$

$p\text{-}TolSO_2CH{-}\diagdown\diagup$
            $|$
            R

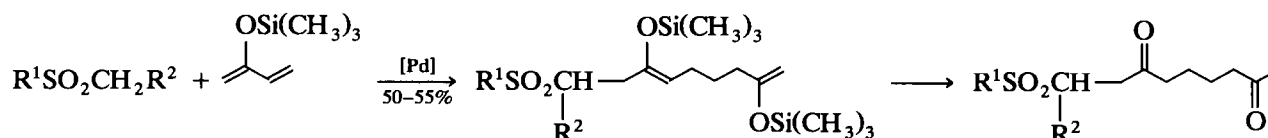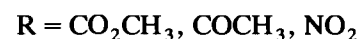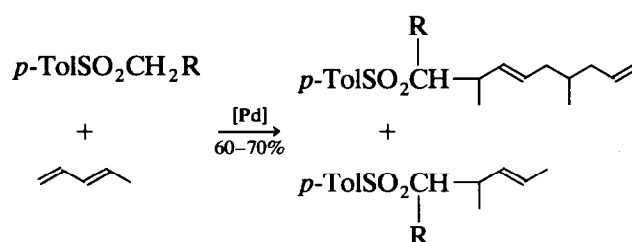$R = CO_2CH_3$, $COCH_3$, NO_2

Scheme 33.

$p\text{-}TolSO_2CH + \diagup\diagdown \xrightarrow[45\text{-}60\%]{[Pd]}$
            $|$
            R^2

$p\text{-}TolSO_2C{-}\diagdown\diagup\diagdown\diagup$
            $|$
            R^2

$R^1 = Me$, $R^2 = CO_2CH_3$; $R^1 = Me$, $R^2 = COCH_3$;

$R^1 = H$, $R^2 = NO_2$
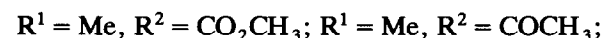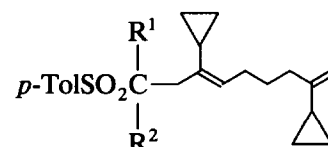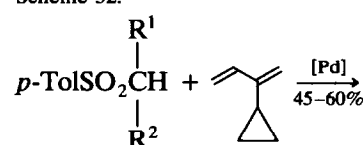
viewpoint as it paves the way to the synthesis of polyunsaturated carboxylic acids of required structures.

Thus, treatment of unsaturated sulfonyl esters (24, 25) with 6% sodium amalgam in methanol [45] gives methyl deca-E4,9-dienoate (26). Desulfonation of the sulfonyl esters with sodium ethoxide leads to methyl deca-E2,E4,9-trienoate (27). Reducing desulfonation of the bis-octa-2,7-dienylesters (25) gives the tetraunsaturated ester (28) [44] (Scheme 29).

Therefore, a convenient and simple route to polyunsaturated acids which are otherwise almost unavailable consists in the telomerization of sulfonyl esters containing active hydrogen atoms with butadiene in the presence of Pd complexes, which is followed by desulfonation of the acids.

Detailed studies of the reaction for a wider range of sulfones and 1,3-dienes were reported elsewhere [46–52]. The ratio of mono- and bis-telomers in the reaction of sulfonyl esters with butadiene was found to be determined mostly by the ratio of starting reagents, but was essentially affected by the structure of the sulfonyl

Scheme 34.

$R^1SO_2CH_2R^2 + \diagup\diagdown\diagup^{OSi(CH_3)_3} \xrightarrow[50\text{-}55\%]{[Pd]} R^1SO_2CH{-}\diagdown\diagup\diagdown\diagup^{OSi(CH_3)_3}$ ... $R^1SO_2CH{-}\diagdown\diagup\diagdown\diagup$
              $|$ $|$
              R^2 R^2

$R^1 = p\text{-}Tol$, $R^2 = NO_2$; $R^1 = C_6H_5$, $R^2 = CO_2CH_3$
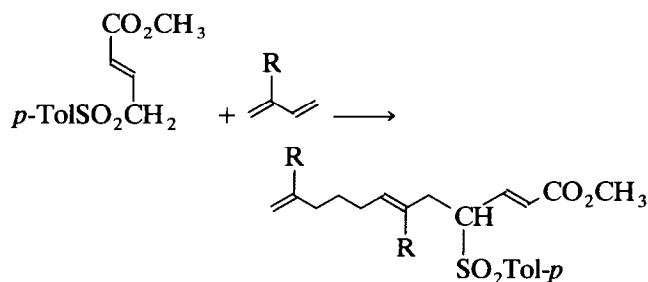
R = H, CH$_3$

Scheme 35.

moiety in the reaction of β-ketosulfones with butadiene [48]. Thus, p-tolylsulfonylacetone gives predominantly monooctadienylsulfoketone, whereas ethylsulfonylacetone reacts with four molecules of butadiene to give preferentially a dialkadienyl product irrespective of the butadiene concentration (Scheme 30). Similarly, p-tolylsulfonylnitromethane reacts with butadiene to afford a dialkyl adduct.

Isoprene reacts "tail-to-tail" with β-substituted sulfones in the presence of catalyst PdCl$_2$(PPh$_3$)$_2$–C$_6$H$_5$ONa to lead exclusively to monooctadienylsulfones [48] (Scheme 31).

Low yields (20–25%) of butenyl isomers were obtained along with alkadienyl products of β-substituted sulfones in experiments with piperylene [50] (Scheme 32).

Reactions of sulfonyl esters with 2-cyclopropyl-1,3-butadienes afforded unsaturated sulfonyl esters containing cyclopropane fragments [49] (Scheme 33).

Diketosulfones were obtained in catalytic telomerization of 2-trimethylsiloxy-1,3-butadiene with sulfones, followed by hydrolysis of the alkoxysilanes [49] (Scheme 34).

The vinylogue effect provides for a high activity of hydrogen in unsaturated sulfones, hence their interesting potential as starting reagents for telomerization (Scheme 35).

Therefore, telomerization of conjugated dienes with

(29,30)   (31)
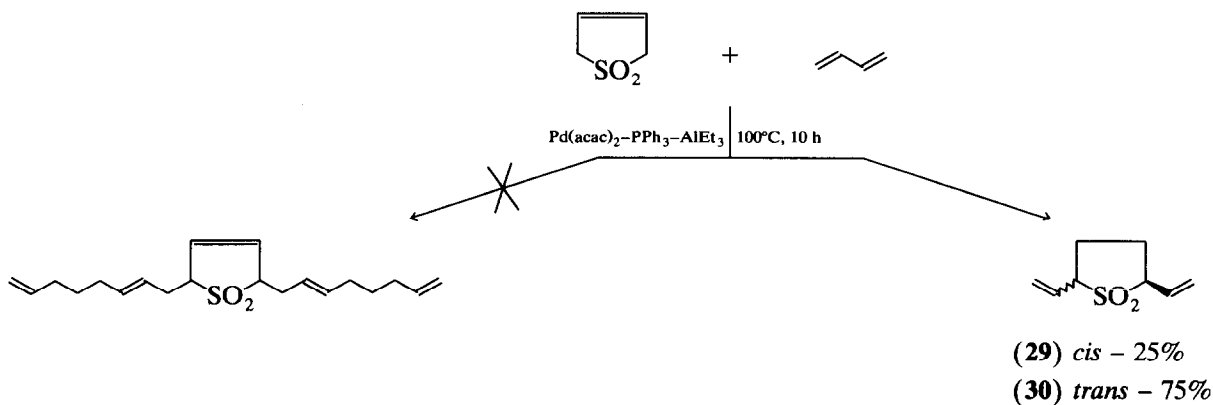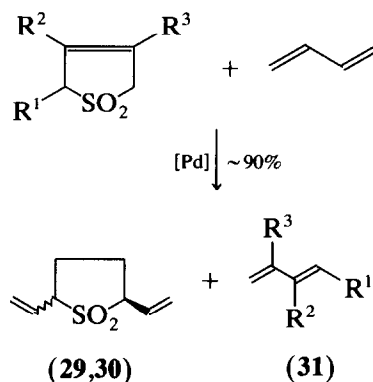
$R^1 = R^2 = R^3 = H$; $R^1 = CH_3$, $R^2 = R^3 = H$;

$R^1 = H$, $R^2 = R^3 = CH_3$
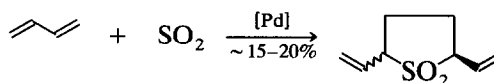
Scheme 37.
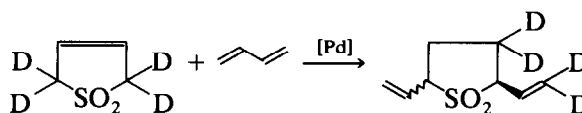
Scheme 38.

sulfones containing active methylene moieties, is an effective synthetic method for unsaturated functionally substituted sulfones that can be usefully employed as synthons to prepare biologically active compounds [48,49].

2.5. Reactions of 3-sulfolenes with 1,3-dienes, catalyzed by palladium complexes

In 1979, our research was mainly concerned with telomerization of 3-sulfolene with 1,3-dienes, catalyzed by palladium complexes Pd(acac)$_2$–PPh$_3$–AlR [53]. Quite unexpectedly, we obtained a mixture of *cis*- and *trans*-2,5-divinylsulfolanes (29, 30), and our further studies were directed towards defining the limitations of this new reaction [54–58] (Scheme 36).

Pd(acac)$_2$–PPh$_3$–AlEt$_3$ 100°C, 10 h

(29) *cis* – 25%
(30) *trans* – 75%
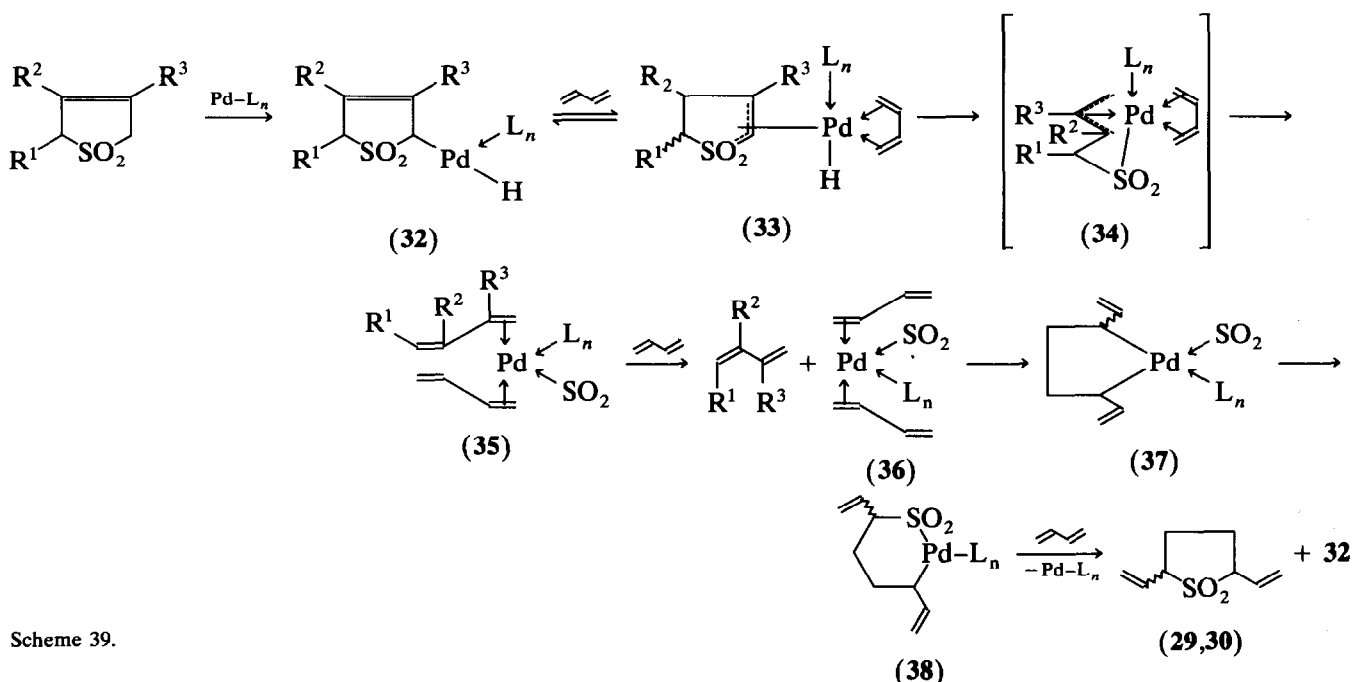
Scheme 36.

Scheme 39.

This unusual reaction was found to occur with different substituted 3-sulfolenes which give a mixture of *cis*- and *trans*-divinylsulfolanes (**29, 30**), in the constant ratio of 25:75 [53,54]. Along with **29** and **30**, there were also formed the conjugated dienes **31** (Scheme 37). The structure of **31** was similar to that of the diene included in the starting 3-sulfolenes.

The starting 3-sulfolenes dissociate into the related diene and SO_2, and the SO_2 reacts with butadiene to give the isomeric 2,5-divinylsulfolanes **29, 30**.

Under these conditions, the direct reaction of the butadiene with gaseous SO_2 yields about 15–20% of **29, 30**, probably because of deactivation of the catalyst due to the formation of coordinatively saturated complexes of Pd with SO_2. The assumed reaction mechanism was further supported by our co-worker's studies [54] of reaction of 2,2,5,5-tetradeutero-3-sulfolene with butadiene, catalyzed by $Pd(acac)_2$–PPh_3–AlR_3 (Scheme 38).

We proposed [53] that the sulfolene adds to the metal ion to give the hydride complex **32**. Complex **33** is formed by $\sigma \rightarrow \pi$ isomerization of the allylic ligand and subsequent coordination of the butadiene. Cleavage of the C–S bond and hydride transfer give intermediate **34**; this liberates a diene molecule that is then substituted in complex **35**. Coupling of activated butadiene ligands transforms **36** into complex **36**. The reaction is completed by insertion of SO_2 and cyclization of **37** and **38** to the final *cis*, and *trans*-2,5-divinylsulfolanes **29, 30** (Scheme 39).

The reaction is general; it works well with isoprene, *trans*-piperylene, and 2,3-dimethylbutadiene to lead to

mixtures of related *cis*- and *trans*-2,5-dialkenylsulfolanes **39–48, 49–54**, and **55**, respectively [55] (Scheme 40, 41, and 42). Individual isomers were isolated by
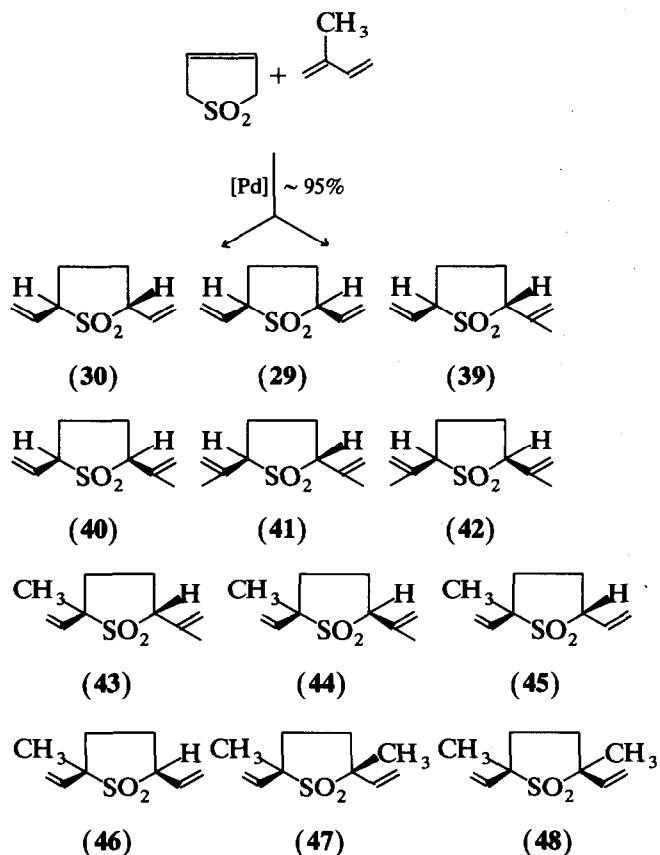
Scheme 40.

preparative GLC and, following the data of spectral analysis, the sulfolanes were unambiguously identified as *cis*- or *trans*-isomers [55,56]. Thus, chemical shifts of geminal protons at C^3 and C^4 were larger for the *trans*-isomer than for the *cis*-isomer in the sulfolanes **29**, **30** [59]. According to the rule of shielding of β-substituents. Anteums *et al.* interpreted the signals of all the ring protons in the ^{1}H NMR spectra of isomers of **29** and **30** [60].

trans-Piperylene reacts with 3-sulfolene to give a mixture of four pairs of isomeric 2,5-disubstituted sulfolanes **29**, **30**, **49–54** (Scheme 41).

Under similar conditions, 3-sulfolene and 2,3-di-methylbutadiene lead to sulfolanes **55**, **29**, **30** (Scheme 42).

Our attempts to extend the reaction of 3-sulfolenes with 1,3-dienes over different cyclic unsaturated sulfones were successful [61]. For instance, 2,5-dihydro-thiepyn-1,1-dioxide and 1,3-dienes lead to 2-alkenyl-5-alkadienylsulfolanes **56–59** (Scheme 43). In particular, *trans*-2-vinyl-5-butadienylsulfolane (**56**) results selectively from the experiments with butadiene. Sulfolanes **29**, **30** are formed along with **56** with increasing concentration of butadiene in the catalysate.

A Diels–Alder adduct is the only final product in the reaction of thiet-1,1-dioxide with butadiene, assisted by Pd phosphine complexes (Scheme 44).

This therefore provides a single-step synthesis of 2,5-dialkenyl- and 2-alkenyl-5-alka-1,3-dienylsulfolanes.

2.6. Telomerization of butadiene with sulfur-containing alcohols, carboxylic acids and thiols

In the search of new catalytic methods of synthesizing heteroatomic compounds containing divalent sulfur, we developed an approach to unsaturated sulfides [62–65], based on the telomerization of oxyalkylsulfides or carboxyalkylsulfides with butadiene, catalyzed by Pd complexes which are activated by electron-donor and electron-acceptor ligands.

Despite the generally accepted viewpoint that sulfides poison complexed catalysts, we performed successful telomerizations of alkylthioethanols with butadiene in the presence of palladium complexes to obtain unsaturated thioesters of different structures (Scheme 45).
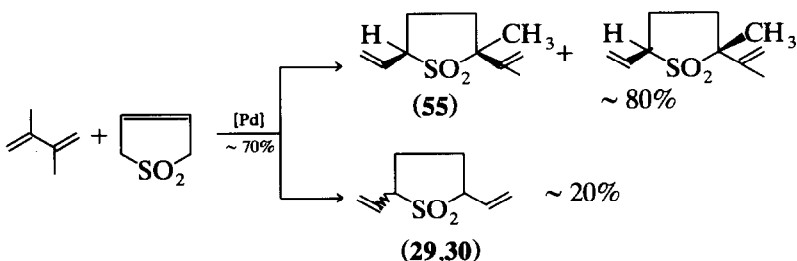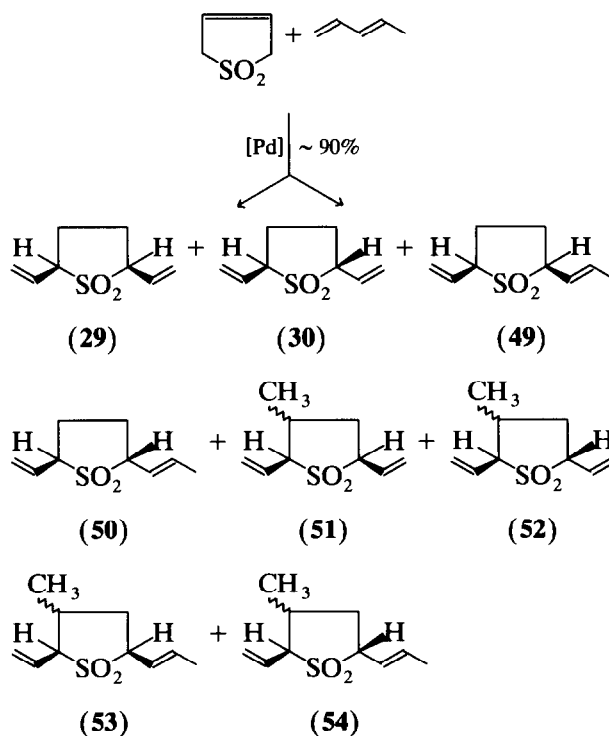
Scheme 41.

The highest yields of unsaturated thioesters were observed for reactions conducted in THF (tetrahydrofuran) or toluene and catalyzed by Pd^{2+}–[PPh_3 or $P(OPh)_3$]–AlR_3.

Alkylthioethanols are more effective than the usual aliphatic and aromatic alcohols for the telomerization with butadiene, resulting in high yields of 2,7-octadienyl esters.

In contrast to thioalcohols, carboxyalkylsulfides react less selectively in the presence of the above catalyst to give a mixture of some butenyl- and but mainly octadienylsulfides [62] (Scheme 46).

Introduction on PPh_3 into a Pd-catalyst led to about 95% yield of the octadienylsulfides **66**, **67**, while catalysts involving (^{i}PrO)$_3$P gave mainly the butenylsulfides **64**, **65** (57%).

We concluded that it would be better to synthesize unsaturated sulfides via telomerization of conjugated dienes with thiols, assisted by palladium metal-complexed catalysts [63,64].

Scheme 42.

(58)

(59)

72%

80%

(56)

(57)

Scheme 43.

SO_2 + $\diagup\!\!\!\diagdown$ $\xrightarrow{[Pd]}$ SO_2
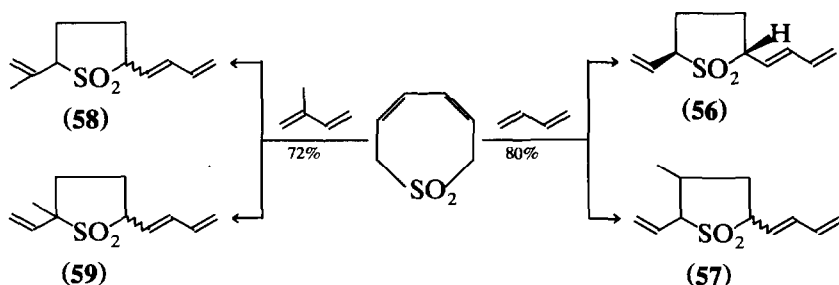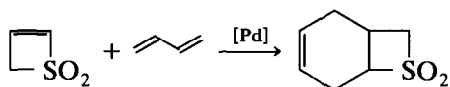
Scheme 44.

Butadiene reacts with n-butanethiol with $Pd(acac)_2$–PPh_3–$AlEt_3$ catalyst to give a mixture of butenylsulfides **72** : **73** = 7 : 3 in about 95% total yield [63]. All our attempts to divert the reaction towards octadienylsulfides failed, but butenyl- (**74, 75, 78, 79**) and octadienylsulfides (**76, 77, 80, 81**) were prepared in sufficiently good yields with aromatic thiols [64] (Scheme 47).

The use of $Pd(acac)_2$–α,α'-dipyridyl–AlR_3 as a catalyst and THF or DMF (dimethylformamide) as solvents gave a high selectivity for **76, 77, 80**, and **81**.

It is notable that 1,7- and 2,7-octadienyl derivatives are formed in almost all known telomerizations of

$RSCH_2CH_2OH$ + $\diagup\!\!\!\diagdown\!\!\!\diagup$ $\xrightarrow[70-98\%]{Pd(acac)_2-PPh_3-AlEt_3}$

$RSCH_2CH_2O\diagdown\!\!\!\diagup\!\!\!\diagdown\!\!\!\diagup\!\!\!\diagdown$
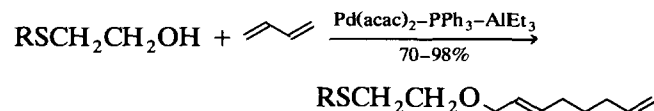
R = Et, Pr, ^iPr, ^nBu, ^iBu, ^sBu, $t-C_5H_{11}$,

C_6H_{11}, $PhCH_2$

Scheme 45.

$RSCH_2CO_2H$

+ $\diagup\!\!\!\diagdown\!\!\!\diagup$ $\xrightarrow[\sim 95\%]{[Pd]}$

$RSCH_2CO_2$— (**60,64,68**) + $RSCH_2CO_2$— (**61,65,69**) + $RSCH_2CO_2$— (**62,66,70**) + $RSCH_2CO_2$— (**63,67,71**)
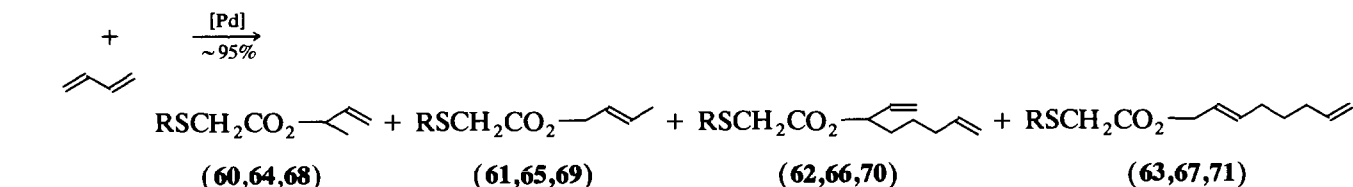
R = ^iPr (**60–63**), ^nBu (**64–67**), $PhCH_2$ (**68–71**)

Scheme 46.

RSH

+ $\diagup\!\!\!\diagdown\!\!\!\diagup$ $\xrightarrow{[Pd]}$ RS— (**72,74,78**) + RS— (**73,75,79**) + RS— (**76,80**) + RS— (**77,81**)
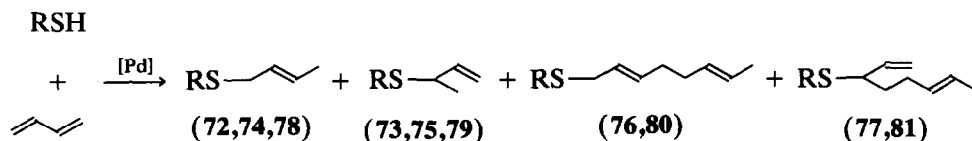
R = ^nBu (**72,74**), Ph (**74–77**), $PhCH_2$ (**78–81**)

Scheme 47.

butadiene with S-, C-, O-, and N-nucleophiles, while telomers with 1,6- and 2,6-positioned double bonds result with alkyl- and arylthiols [63,64]. Besides the Pd complexes, the reaction can be catalyzed by systems based on Ni, Fe, Co, Cu, or Mn compounds to lead to unsaturated sulfides but in yields below 46% [64].

3. Catalytic activation of SO_2, CS_2, S by transition metal complexes in reactions with conjugated dienes and acetylenes

The activation of small molecules and atoms such as SO_2, CS_2, S, assisted by homogeneous and heterogeneous metal-complexed catalysts, should occupy a prominent place among the most promising and rapidly developing directions of the synthesis of organic sulfur compounds.

These programs are of both scientific and industrial interest because small molecules and atoms represent inexpensive and important reducible raw materials that provide for unconventional approaches to chemical engineering and for utilization of hazardous gas blowouts which would otherwise pore environmental problems [27,66–68].

3.1. Reactions of SO_2 with conjugated dienes

We encountered the problem of activating SO_2 in reactions with 1,3-dienes when we were studying telomerization of 3-sulfones with conjugated dienes, catalyzed by Pd complexes [53–55]. The direct reaction of SO_2 with butadiene, catalyzed by $Pd(acac)_2$–PPh_3–$AlEt_3$ resulted in only 15–20% yields of isomeric 2,5-divinylsulfolanes [69]. The reaction direction and product yields are affected by the ratios of the catalyst's components (Pd : phosphine) and of starting monomers. Thus, the highest yield of (29,30), about 75%, was obtained with a catalytic system containing an excess of PPh_3 (Pd : PPh_3 : Al = 1 : 20 : 2). Selwyn and Harold explained the need for a high excess of the activating ligand in terms of interactions of PPh_3 and SO_2 [70]. Our results show [69] that a good deal of PPh_3 (70%) is transformed by SO_2 into a mixture of $Ph_3P=O$ and $Ph_3P=S$ that show low efficiency in the reaction of butadiene with SO_2.

$$3\ PPh_3 + SO_2 \xrightarrow{[Pd]} 2\ Ph_3P{=}O + Ph_3P{=}S$$
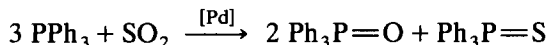
With a large excess of PPh_3, the catalyst retains its activity for a longer time, resulting in an increased yield of 2,5-divinyl-sulfolane. Our reaction scheme (Scheme 48) suggests the formation of a bis-π-allylic complexes. Further insertion of SO_2 through the metal–carbon bond leads to bis-π-complexes of two types 83 and 84 that are subsequently transformed into sulfolanes 29, 30, either thermally or assisted by the butadiene.

The direction and structural selectivity of the reaction of SO_2 with butadiene are strongly affected by the nature of the activating ligand. For example, alkyl phosphines direct the reaction towards the formation of butadiene macrocyclic cyclooligomers, in particular of cyclohexadecatetraene (85) in about 80% yield (Scheme 49).

Sulfur dioxide reacts similarly with isoprene and trans-piperylene, giving the related 2,5-dialkenylsulfolanes (39–54). Unlike isoprene and trans-piperylene, 2,3-dimethyl-1,3-butadiene led to 3,4-dimethyl-3-sulfolene [13,54] (Scheme 50).

Of particular interest is a single-step reaction of SO_2 with 1,3,5-hexatriene, affording trans-bis-2,5-butadienylsulfolane [54] which would be otherwise available only through a rather complicated multi-step process.

Cyclic co-oligomerization of SO_2 with a mixture of hexatriene and butadiene yields about 40% of trans-2-vinyl-5-butadienylsulfolane (56). In addition to sulfolanes, the reaction also gives the triene and butadiene co-oligomers (Scheme 51).

The reactions of SO_2 with 1,3,5-hexatriene does not need the large excess of PPh_3 in the Pd catalyst that is
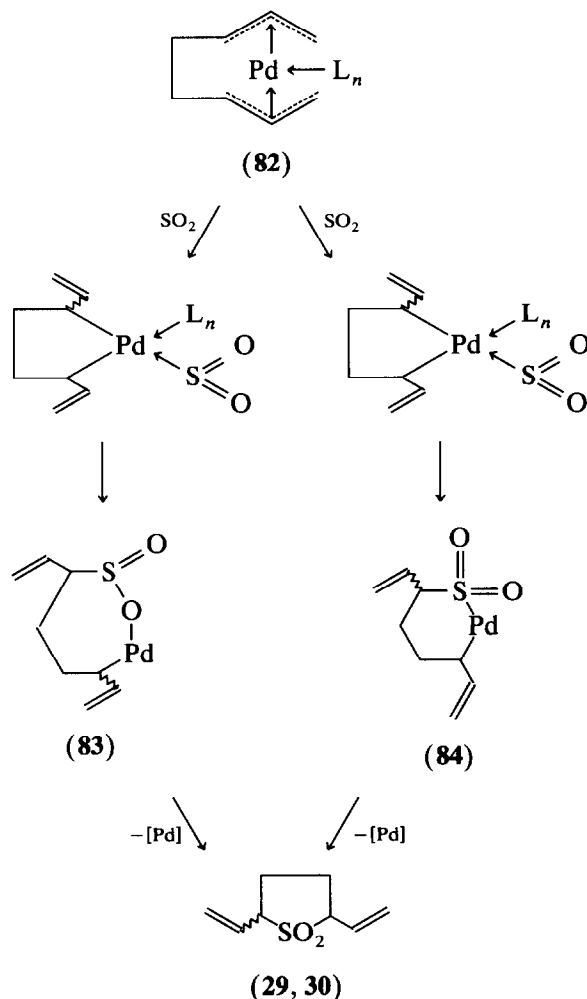
Scheme 48.

required with butadiene. A deficiency of PPh_3 in the reaction is most likely made up by an excess of hexatriene which is a sufficiently strong π-donor like PPh_3 and coordinates at the catalyst central atom, stabilizing the intermediate catalytically active species.

We obtained 2,5-disubstituted sulfolanes with the use of low-valent Pd complexes in catalytic reactions of SO_2 with conjugated dienes and 1,3,5-hexatriene [13,54,69]. The earlier literature contains only one reference, Klein (1968), concerning the catalytic activation of SO_2 in reactions with olefins, in particular with ethylene in the presence of $PdCl_2$ [73] (Scheme 52).

3.2. Catalytic activation of CS_2 in reactions with 1,3-dienes

Following the successful activation of SO_2 [69] and CO_2 [76,77], we attempted using Pd complexed catalysts in reactions of CS_2 with conjugated dienes, but out first attempts failed [74].
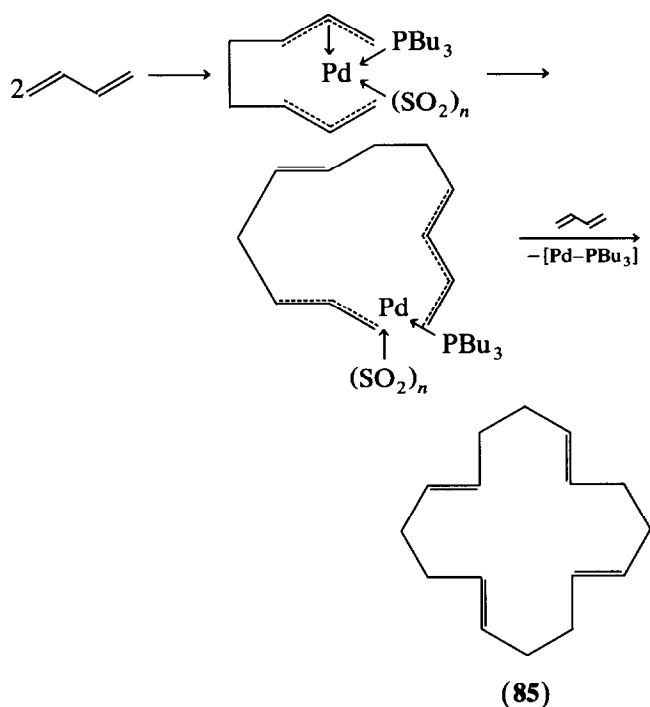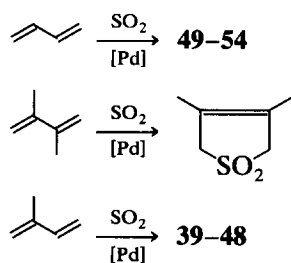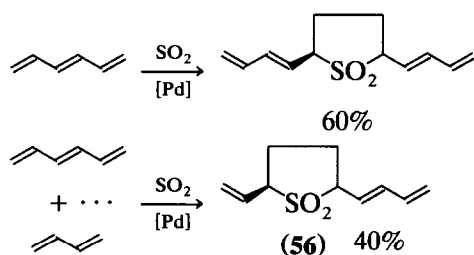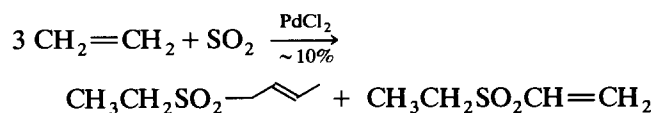
We consider carbon disulfide to be a "rigid" ligand that most probably coordinates at the catalyst central atom, thereby blocking the catalyst and making difficult the access of other substrates involved in the reaction [74–76].

The reaction of CS_2 with butadiene can be conducted in the presence of the catalytic system $Pd(acac)_2$–$(Ph_2PCH_2)_2$ (1:1), the system containing two small molecules, namely CO_2 and NH_3 [74]. 1,4-Dithianes (86–94), sulfoxides (95, 96), and sulfides (97, 98) are formed (Scheme 53).

No promoting effect of CO_2 and NH_3 is observed if these are introduced into the reaction mixture separately.

The reaction may be also catalyzed by Ni and Co complexes activated with either $(Ph_2PCH)_2$ or $(^iPrO)_3P$. Unlike palladium complexes, Ni- and Co-complexed catalysts afforded alkylsubstituted 1,4-dithianes as the main products in the reaction of CS_2 with butadiene [13,67]. Diphosphine complexes of palladium were found to show the highest catalytic efficiancy [74].

It is peculiar that saturated 1,4-dithianes, sulfides, and 1,4-bis-sulfoxides are usually formed in the reactions of CS_2 with butadiene. We believe that under heterocyclization conditions, NH_3 provides for additional hydrogen atoms. Hence, unsaturated linear and cyclic sulfides formed at the first reaction step, are then reduced to 1,4-dithianes (86–94) in the presence of Pd catalyst.

It is most likely that CO_2 assists in the oxidation of (86, 88) to sulfoxides (95, 96) in the presence of Pd complexes. High yields of 1,4-dithianes (86–94) were obtained in DMF, HMFA, and N-methylpyrrolidone with equimolar ratios of Pd^{+2} to $(Ph_2PCH_2)_2$.

Also, one should allow for the possible generation of active SO species from CO_2 and CS_2 in the presence of Pd complexes. It is these species that react very selectively with butadiene to afford 1,4-bis-sulfoxides (95) and (96) according to Scheme 54.

Thus, thiacyclization of butadiene with CS_2, catalyzed by Pd, Ni, or Co complexes in the presence of CO_2 and NH_3, represents rather a complicated process consisting of (i) generation of S or SO from CS_2, CO_2, and NH_3 (ii) cyclization of S or SO activated molecules of the diene, and (iii) reduction and oxidation of the sulfides formed. Despite this, the reaction is undoubtedly interesting for single-step preparation of 1,4-thiacyclohexanes and their sulfoxides from butadiene and CS_2.

Under similar conditions, isoprene reacts with CS_2 to lead to saturated sulfides (99–101) [13,67] (Scheme 55).

Unlike isoprene, trans-piperylene reacts with CS_2 in

(85)

Scheme 49.

Scheme 50.

Scheme 51.

$$3\ CH_2{=}CH_2 + SO_2 \xrightarrow[\sim 10\%]{PdCl_2}$$

$$CH_3CH_2SO_2{-}\!\!\diagup\!\!\diagdown\!\!\diagup + CH_3CH_2SO_2CH{=}CH_2$$

Scheme 52.

Scheme 53.

Scheme 54.

Scheme 55.

Scheme 56.

DMF at lower temperature (120°C) to give a mixture of linear unsaturated mono- and disulfides (102–107) and cyclic 1,4-disulfoxides (108, 109), in the ratio 102–105: 106–107:108–109 = 55:25:20 (Scheme 56).

With the same catalyst, 1,3-dithiolane is selectively formed in reaction of allene with CS_2 [13,79] (Scheme 57).

To conclude, the reactions of CS_2 with 1,2- and 1,3-dienes, catalyzed by Pd, Ni, Co complexes coupled with CO_2 and NH_3 molecules, can serve as a promising and useful route to saturated and unsaturated linear, cyclic, and bicyclic mono- and disulfides as well as sulfoxides.

3.3. Reactions of elemental sulfur with 1,3-dienes

Much information has been accumulated on photochemical, thermal, and chemical reactions of elemental sulfur with olefins, dienes, acetylenes, and carbonyl compounds [80,81], but until our recent research of catalytic activation of sulfur with metal complexes, there were no references concerning this aspect of the subject. We believed that catalytic activation of ele-

Scheme 57.

Scheme 58.

Scheme 59.

mental sulfur, *e.g.* cyclooctasulfane S_8, in homogeneous catalytic transformations with concomittant generation of mono- and divalent sulfur, would provide single-step synthetic methods for inaccessible unsaturated linear and cyclic sulfides [82–94].
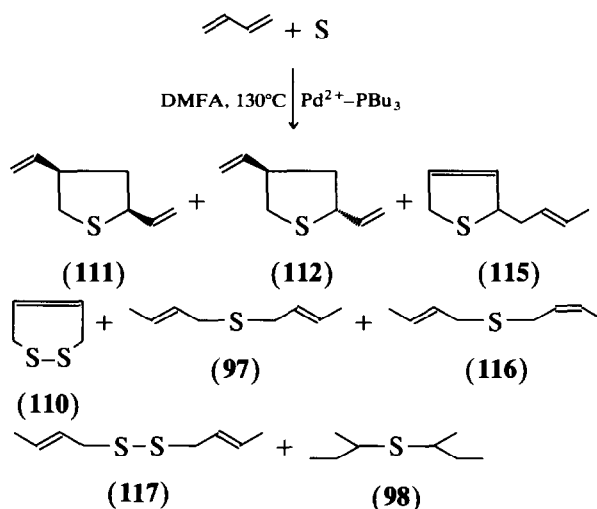
We developed methods to synthesize sulfides, in particular those of unique structures. By selection of the experimental conditions, the ratio of reagents, and the nature of the catalyst components, the direction of the reaction of butadiene with sulfur can be strictly controlled towards the formation of five-membered mono- and disulfides (110–112), and macrocyclic mono- (113) and trisulfides (114) [13,82] (Scheme 58).

A rather complex mixture of linear and cyclic mono- and disulfides was found in the reaction conducted in DMF in the presence of catalyst Pd^{2+}-PBu$_3$ [83,94] (Scheme 59).

The existence of a five-membered disulfide (110) in the mixture of mono- and disulfides was the first indication of the formation of active species S_2 from S_8, assisted by Pd complexes.

In terms of preparative organic chemistry, S_2 molecules are available from either photolysis of S_2Hg_2 or heated allotropic S_{10} [90].

Phosphine complexes of Ni, Co, or Cu can be used to catalyze the reaction, but the yields of a mixture of sulfides (97–98, 110–112, 115–117) are usually below 10%. As for CS_2 [74], the reactions show better selec-

tivity and higher yields of target sulfides (117, 87, 91) if CO_2 and/or NH_3 are introduced into the catalyst [83,94] (Scheme 60). Similar results were obtained in reactions conducted with Et_2NH and morpholine, giving saturated 1,4-dithianes in about 80% yields.

In contrast to butadiene, isoprene reacts selectively with sulfur in the presence of Pd catalyst to afford sulfides (118, 119) in a 65:35 ratio. Under these conditions, the reaction of sulfur with 1,3,7-octatriene resulted in *cis*, *trans*-2,5-disubstituted thiophanes (120, 121) [94] (Scheme 61).

3.4. Reactions of sulfur with acetylenes, catalyzed by transition metal complexes.

Bonnemann *et al.* [95,96] used cobalt complexes to catalyze the reaction of sulfur with acetylenes to obtain disubstituted thiophenes (Scheme 62).

Thiacyclization of acetylenes with elemental sulfur in the presence of transition metal complexes was later
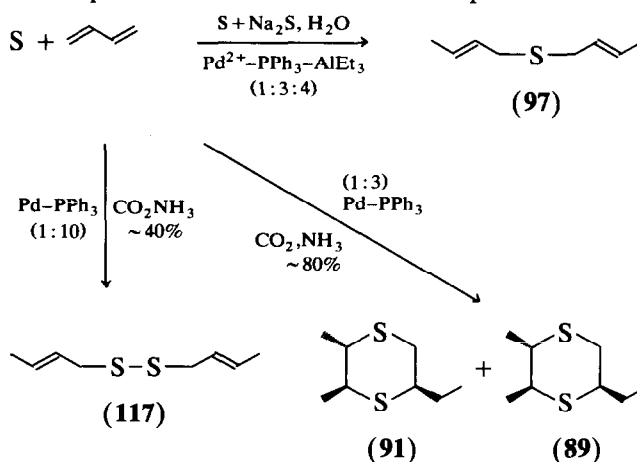
Scheme 60.

Scheme 61.

studied in detail in our laboratory [13,84–94], and some new reactions were identified. Thus, a mixture of 2,5- and 2,6-dibutyl-1,4-dithiacyclohexa-2,5-dienes (122,123) (45:55) results from equimolar amounts of 1-hexyne and sulfur heated in toluene with $Co(acac)_2$–PPh_3–$AlEt_3$.
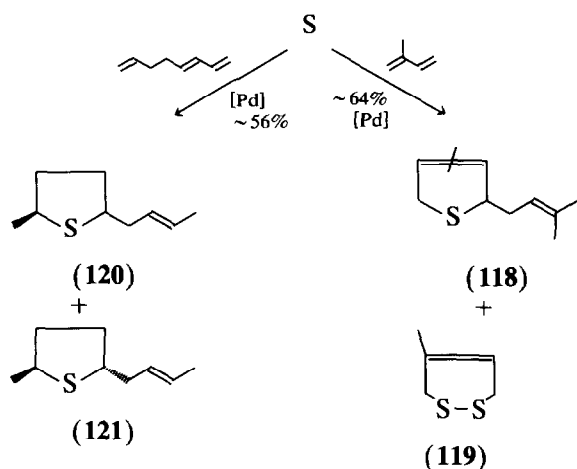
Insertion of such ligands as Et_2NH, Et_3N, or Bu_3P into the catalyst leads to trialkylsubstituted 1,4-di-thienes (124, 125) in addition to 122, 123, while di-, tri-, and tetra-alkylthiophenes (126–129) are formed with the use of $(PhO)_3P$ or C_5H_5N as ligands [84] (Scheme 63).

The compounds 123–124 and 126–129 are formed by thiacyclization of sulfur with a mixture of 1-hexyne and 2-hexyne. The tetraalkylthiophenes probably result from a shift of the triple bond of 1-hexyne to the C^2–C^3-position, which is assisted by low-valent cobalt complexes.

With higher concentrations of sulfur in the catalysate, the yield of 1,4-dithienes (122, 123) increases to reach its maximum (98%) at a molar ratio of acetylene to sulfur of 1:2.

Under these conditions 1-pentyne, 1-heptyne, 4-oc-tyne, 4-decyne, and phenylacetylene react similarly with sulfur. Terminal alkynes lead to 1,4-dithiene deriva-tives, whereas disubstituted alkynes and phenylacety-lene afford preferably alkylsubstituted thiophenes. The efficacy and selectivity of palladium catalysts are infe-rior to those of cobalt complexes.

It is clear now that the new syntheses of alkylsubsti-tuted 1,4-dithienes or thiophenes consists in simultane-ous activation of the molecules of acetylenes and ele-
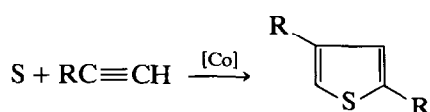
Scheme 62.
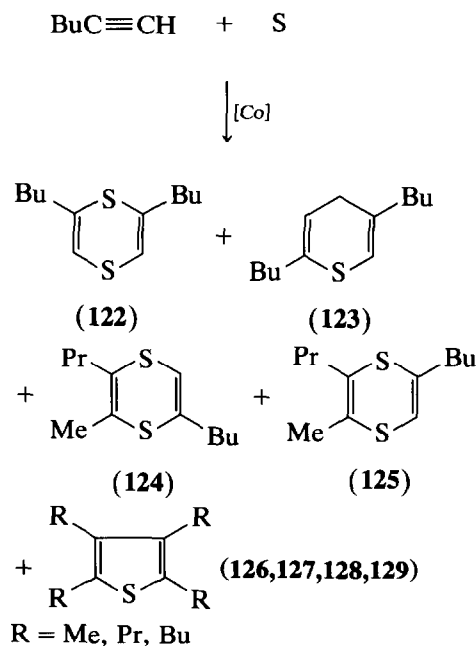
Scheme 63.

mental sulfur via coordination of the substrates at the catalyst central atom, and further heterocyclization of the activated fragments, probably through the forma-tion of dithiolate complexes, to mono- and disulfides. This is shown in Scheme 64.

As we reported earlier [13,94], 1,4-dithienes or thiopenes can be selectively prepared with these new

Scheme 64.

$$ZC\equiv CZ + 1/8\,S_8 \xrightarrow[130^\circ C,\ 16\ h]{CpRh\ (cod)}$$

$$Z = CO_2Me$$

Scheme 65.

methods in which the reaction selectivity can be controlled by varying the reaction conditions, and the composition and nature of catalyst components, as well as by the use of different acetylenes.

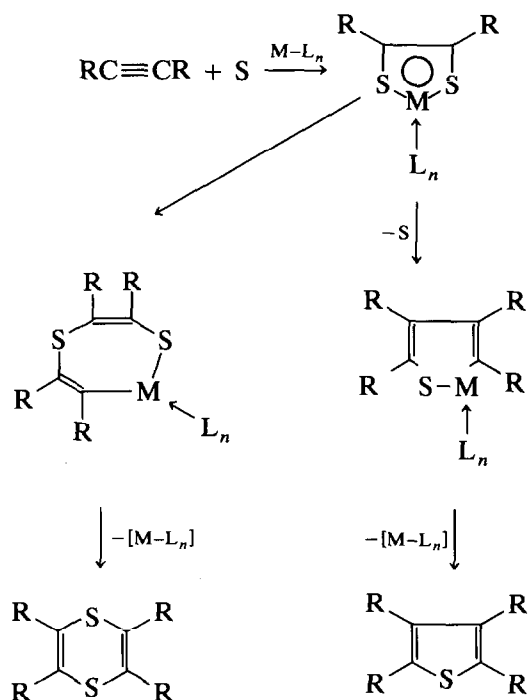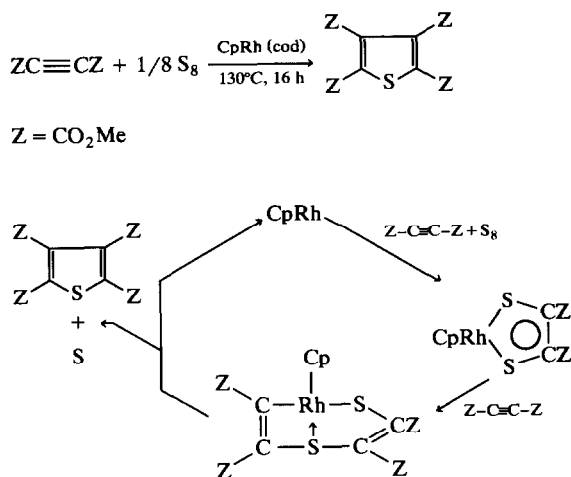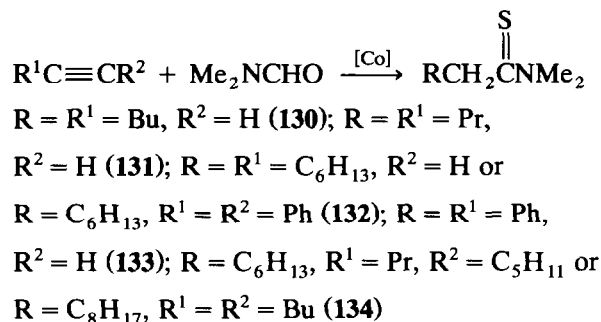Kajtani *et al.* [97] reported that rhodium complexes catalyze the reaction of sulfur with dimethyl acetylenedicarboxylate to give 2,3,4,5-tetramethoxy-carbonylthiophene, and they proposed the reaction scheme depicted in Scheme 65.

3.5. Synthesis of alkylthioamides from sulfur and alkylacetylenes, assisted by metal-complexed catalysts

Reactions of elemental sulfur with phenylacetylene or acetylene in the presence of ammonia or different amines give satisfactory yields of thioamides [14,80]. Alkylacetylenes fail to enter the Wilgerodt-Kindler reaction and are transformed exclusively to carboamides. We assumed that the use of transition metal complexes might activate the alkylacetylenes as well as other reagents by coordination at the catalyst central metal atom to give high yields of the required products.

Our first attempts at preparing alkylthioamides by this reaction route were fruitless. Thus, the reaction of 1-hexyne and diethylamine or piperidine with sulfur in the presence of Pd- or Co-containing catalyst gave a complicated mixture of amides, thioamides, and other products which were difficult to isolate and identify [88]. However, N,N'-dimethylalkanethioamides can be prepared in DMF as a solvent and with $Co(acac)_2$-PPh_3 as a catalyst, even in the absence of primary or sec-

$$R^1C\equiv CR^2 + Me_2NCHO \xrightarrow{[Co]} RCH_2\overset{\overset{\displaystyle S}{\|}}{C}NMe_2$$

R = R¹ = Bu, R² = H (130); R = R¹ = Pr,

R² = H (131); R = R¹ = C₆H₁₃, R² = H or

R = C₆H₁₃, R¹ = R² = Ph (132); R = R¹ = Ph,

R² = H (133); R = C₆H₁₃, R¹ = Pr, R² = C₅H₁₁ or

R = C₈H₁₇, R¹ = R² = Bu (134)

Scheme 66.

ondary amines. In this way 1-hexyne and sulfur afforded N,N-dimethylhexanethioamide (130) and 1,4-dithienes (122-125) in the ratio 130:120 + 123:124 + 125 = 15:62:23, in about 56% total yield. The compound 130 consists of an alkyne molecule, a sulfur atom, and an Me₂NH moiety from DMF [98].

Alkylthioamides can be synthesized in quantitative yields under optimized reaction conditions with DMF as solvent and a ratio of sulfur to alkyne of 4:1 (Scheme 66).

It is peculiar that either 1-octyne and 4-octyne with sulfur in DMF gave thioamide 132, while 4-decyne or 5-decyne resulted in thioamide 134. This indicates that disubstituted alkynes reacting with sulfur in DMF in the presence of Co complexes, undergo positional isomerization leading to terminal alkynes which are then transformed into the related thioamides 130, 134 [88,90].

Palladium complexes can also be used as catalysts, but afforded a mixture of thioamide 130 and thiophenes 126-129 in 7:3 ratio.

These alkylthioamides can usefully be prepared in reaction of thioamidation of mono- and disubstituted acetylenes with sulfur in DMF, catalyzed by Co or Pd complexes.

3.6. Reactions of sulfur with acetylenes and alkyl halides

Our previous experience gained in the synthesis of organic sulfur compounds with the use of homogeneous metal-complexed catalysts, stimulated our further work with reactions of elemental sulfur. Thus, elemental sulfur was found to react simultaneously with acetylenes and halogenated alkanes, giving Z,E-vinylalkanesulfides [13,85,91,99].

Butyl-2-hexen-(2Z)-ylsulfide (135), butyl-2-hexen-(2E)-ylsulfide (136) as well as (122, 123, 137, 138) were

$$BuC\equiv CH + S + BuBr \xrightarrow[64-98\%]{[Co]} BuS\diagup\!\!\!\diagdown\!\!\!\diagup + BuS\diagdown\!\!\!\diagup\!\!\!\diagdown\!\!\!\diagup + 122,123 + Bu_2S_2 + Bu_2S_3$$

(135)   (136)   (137)   (138)

Scheme 67.

$$PrC\equiv CPr + S + BuCl$$

Scheme 68.

$$HC\equiv C(CH_2)_6C\equiv CH + S_8 + BuCl \xrightarrow[\sim 18\%]{[Ni]}$$
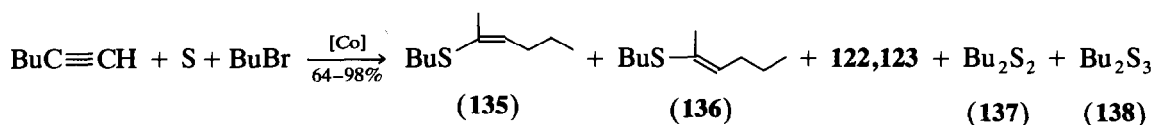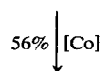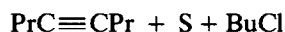
Scheme 69.

prepared from the reaction of equimolar amounts of sulfur, 1-hexyne, and BuBr in DMF, catalyzed by Co(acac)$_2$-PPh$_3$-AlEt$_3$ [99] (Scheme 67).

Catalysts like Ni(acac)$_2$-PPh$_3$-AlEt$_3$ are more selective than the cobalt complexes and give only vinylsulfides 135, 136 in yields from 76 to 98%.

The selectivity and yields of sulfides decrease in the following series: BuCl > BuBr > BuI.

The direction and product composition of the reaction are dependent on the Ni catalyst concentration. For example, the selectivity for vinylsulfides 135, 136 is decreased due to the formation of alkylthiophenes and dialkyldisulfides in the reaction with lower catalyst concentration.
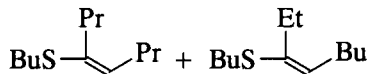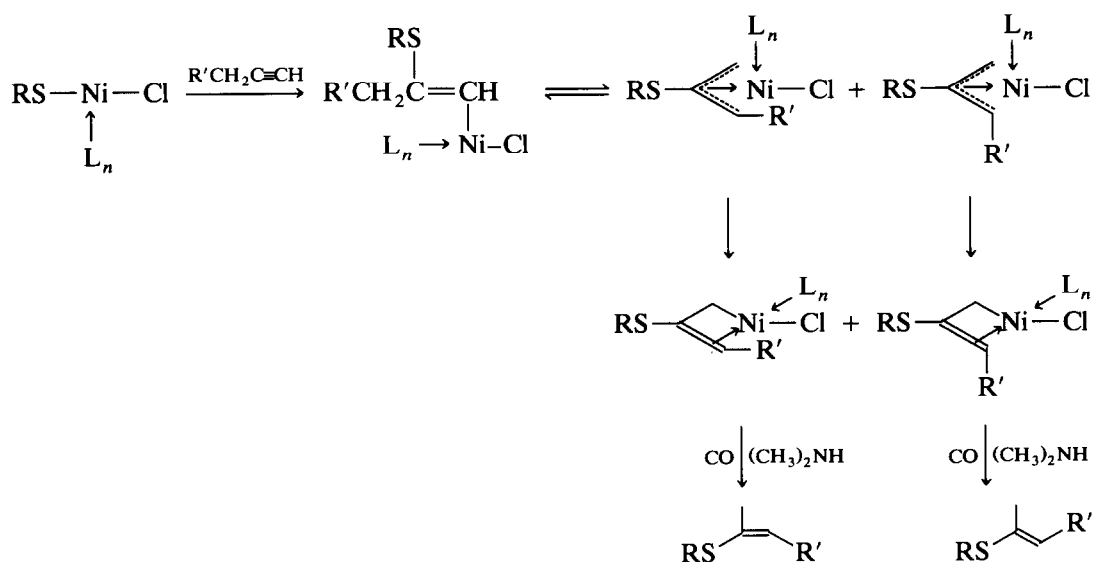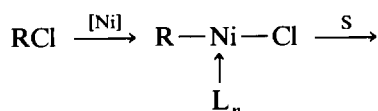
The reaction is general and may be extended to different alkyl halides and to mono- and di-substituted acetylenes. A similar reaction with disubstituted acetylenes exhibits lower selectivity; in particular, a mixture of sulfides 139–142 results from 4-octyne, sulfur, and BuCl (Scheme 68).

Under these conditions, 1,9-decadyine with sulfur and BuCl afford Z-, E-vinylsulfides in 40:60 ratio (Scheme 69).

We assumed a scheme for the reaction leading to the vinylsulfides [13,94,99], which shows intermediate complexes with M–C and M–S–C bonds that are further involved in the catalysis (Scheme 70).

Thus, DMF is decomposed into (CH$_3$)$_2$NH and CO, the dimethylamine supplies additional hydrogen atoms and then is transformed into tetramethylurea via π-complexes like > N–Ni–Cl in the presence of excessive (CH$_3$)$_2$NH and CO.

Reactions of sulfur with acetylenes in the presence of transition metal catalysts provide a convenient synthesis of various organic sulfur compounds such as alkylsubstituted dithienes, alkylvinylsulfides, thiophenes, and alkylthioamides. As opposed to 1,3-dienes, alkynes show higher selectivity in the reactions with sulfur. Hence, the reaction direction can be rigidly
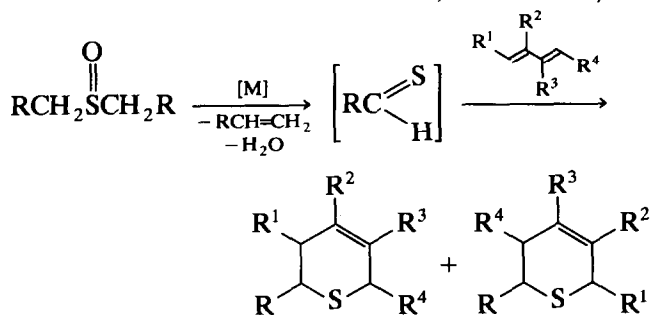
Scheme 70.

M = Pd, Ni, Co, Fe, Cu, Al

Scheme 71.

$$Ar-S-S-Ar + \diagup\!\!\!\!\diagdown \xrightarrow[CO_2, NH_3]{[M]} ArS\!\!-\!\!(\diagup\!\!\!\!\diagdown)_n\!\!-\!\!SAr$$

$$n = 1,2,3,4$$
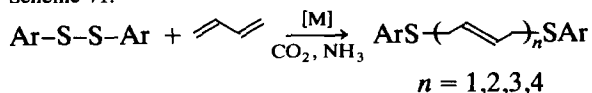
M = Pd, Ni

Scheme 72.

regulated by varying the catalyst composition, solvent, and reaction conditions.

We have recently also developed some new preparative methods: the syntheses of dihydrothiopyranes and 1,4-disulfides are considered to be of special-interest and practical importance. It is possible that alkanethials can be easily generated from dialkylsulfoxides in their reactions with 1,3-dienes, catalyzed by Pd, Ni, Co, Fe, Cu, or Al complexes modified with nitrogen- or phosphoruscontaining ligands [100–102]. Dialkylsulfoxide is split into water, olefin, and thioaldehyde. The latter reacts subsequently with 1,3-dienes to lead to 3,6-dihydro-2H-thiopyrane derivatives in high yields [100] (Scheme 71).

Polyunsaturated disulfides can be prepared from reaction of diaryldisulfides with butadiene, catalyzed by palladium and nickel complexes that are, in their turn, promoted by CO_2 and NH_3 [103–106] (Scheme 72).

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