SYNTHESIS OF HIGHER UNSATURATED SULFIDES USING PALLADIUM COMPLEXES

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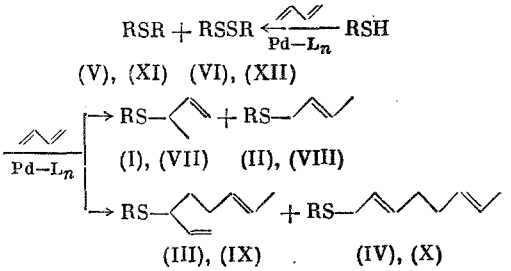
The $Pd(acac)_2$–Ph_3P–Et_3Al-catalyzed reaction of n-butanethiol with butadiene gives butenyl sulfides exclusively [1]. Attempts to change the direction of this reaction to give octadienyl sulfides have been unsuccessful. Reaction of n-octanethiol with allyl alcohol in the presence of a $[Bu_3P]_2NiBr_2$–t-BuOH catalyst has been shown to give allyl octyl sulfide in ~10% yield [2].

Conspicuosly absent from the studies discussed above are experiments using homogeneous organometallic complexes as catalysts for the synthesis of unsaturated sulfides. It was therefore of interest to us to explore the range of thiols capable of undergoing telomerization reactions with butadiene, and also to develop catalysts and reaction conditions suitable for the preparation of higher-molecular-weight sulfides in high yields.

Our preliminary experiments were based on the use of low-valence palladium complexes, obtained via the reduction of $Pd(acac)_2$ with triethylaluminum in the presence of Ph_3P, as the catalyst.

It was found that reaction of α-toluenethiol with butadiene in a 1:6 ratio in the presence of a $Pd(acac)_2$–Ph_3P–Et_3Al catalyst (1:2:4) in toluene (100°C, 6 h) gives a 90% yield of the following product mixture: butenyl (I), (II) and octadienyl sulfides (III), (IV), and di-α-tolyl sulfide (V).

The (I):(II):(III):(IV):(V) product ratio is 6:58:7:19:4, respectively.



$R = PhCH_2$ (I)—(VI); Ph (VII)—(XII).

The structures of sulfides (I)-(V), which were isolated in pure form using preparative GLC, were assigned based on their spectral data. For instance, the IR spectrum of (IV) contains absorption bands at 975, 1645, and 3030 cm^{-1}, which are characteristic of a trans-disubstituted double bond, and does not contain any bands corresponding to a vinyl group. The ^1H NMR spectrum contains a doublet at δ1.52 ppm, and the ^{13}C NMR spectrum contains a quartet at 17.92 ppm; both of these are characteristic of a Me group attached to a double bond. These data have allowed us to identify (IV) as 2,6-octadienyl α-tolyl sulfide. It should be noted that all of the known examples of telomerization reactions of 1,3-dienes with compounds containing active hydrogen atoms [3-6] involve the formation of 1,7- and 2,7-octadienyl sulfides, whereas our reactions lead to the 1,6- and 2,6-isomers exclusively. The hydrosilylation of butadiene with trimethylsilane in the presence of palladium complexes proceeds in an analogous manner [7].

Based on a comparison of our experimental results and literature data, the formation of the unsaturated sulfides (I)-(IV) and (VII)-(X) can be rationalized according to a scheme involving initial coordination of the diene and thiol to the central atom of the catalyst to generate π-allyl complexes (XIII) and (XIV) in the first stage of the reaction. Subsequent

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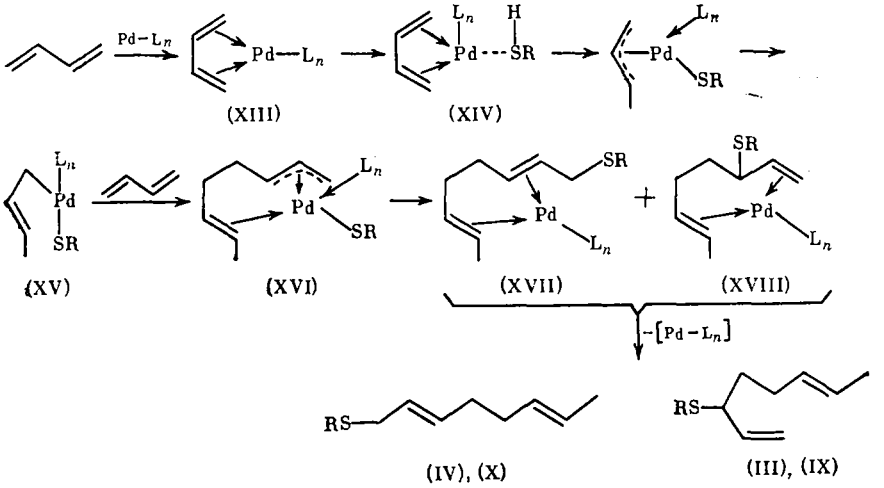
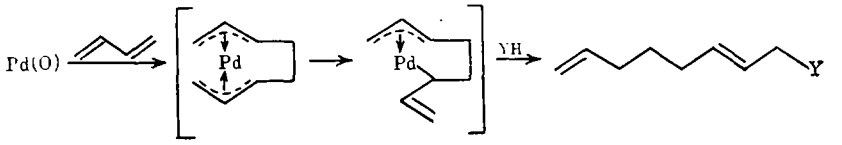
oxidative addition of the thiol leads to a σ-allyl complex (XV). Insertion of another molecule of diene into (XV) gives intermediate (XVI). Combination of the activated fragments in the latter complex leads to the formation of (XVII) and (XVIII), respectively. In the presence of excess butadiene the unsaturated sulfides are displaced from the coordination sphere of the metal and (III) and (IV) are formed. In addition to the telomerization products (I)-(IV) and (VII)-(X), the reaction conditions also induce conversion of the thiols to sulfides (V) and (XI), and disulfides (VI) and (XII), respectively.



In contrast to the reactions of thiols with butadiene, the formation of 1,7- and 2,7-telomeric addition products of 1,3-dienes and compounds containing active (acidic) hydrogen atoms may be attributed to the intermediate formation of a bis π-allyl complex:



The initial encouraging results concerning the synthesis of octadienyl sulfides upon reaction of thiols with butadiene prompted us to search for more active and selective telomerization catalysts.

This was accomplished by examining the effect of the nature and structure of the activating ligands on both the total yield and relative product composition for the telomerization of α-toluenethiol with butadiene.

It was found that ligands such as Ph_3P, $(PhO)_3B$, $(BuO)_3B$, and α,α'-dipyridyl (DPD) led to the formation of high yields of the unsaturated sulfides (I)-(IV) (94-98%). In contrast, introduction of phosphites or diethylamine to the catalyst composition decreased the total yield of products (Table 1). As can be seen in Table 1, telomerization of α-toluenethiol with butadiene in the presence of a $Pd(acac)_2$ DPD–Et_3Al (1:2:4) catalyst system leads to the maximum amount of the unsaturated sulfides (III) and (IV) in the reaction mixture (36.3%) and the minimum amount of di-α-tolyl sulfide (V) and di-α-tolyl disulfide, which makes this a valuable method for the synthesis of sulfides (III) and (IV).

The telomerization of α-toluenethiol with butadiene was then studied in some detail using the $Pd(acac)_2$ DPD–Et_3Al catalyst system. It was found that a change in the Pd:DPD ratio from 1:1 to 1:10 did not affect the total yield of telomers, but had a dramatic effect on the composition of the product mixture. For instance, at a $Pd(acac)_2$–DPD–Et_3Al ratio of 1:4:4, the concentration of 2,6-octadienyl sulfide (IV) is 77% at a total product yield of 88%. The unsaturated sulfides having a branched structure, namely, (I) and (III), are almost totally absent under these reaction conditions (Table 2).

This was followed by a survey of other organometallic complexes as catalysts for the telomerization of thiols with butadiene. Of the Cu, Co, Fe, Ni, and Mn complexes studied, only Ni- and Fe-containing catalysts led to the formation of unsaturated sulfides (I)-(IV) in high yields (Table 3). Although similar results were obtained using Co-, Cu-, and Mn-containing catalysts, the percent conversions in these experiments were less than 50%.

TABLE 1. Effect of Structure of the Activating Ligands on the Yield and Product Composition in the Reaction of α-Toluenethiol with Butadiene [$Pd(acac)_2$:L_n:Et_3Al = 1:2:4:$Pd(acac)_2$:α-toluenethiol = 1:50 molar ratio, 100°, 8 h, DME

Activating Ligand	Conversion of mercaptan, %	Product composition, %					
		(I)	(II)	(III)	(IV)	(V)	(VI)
$(BuO)_3B$	98	10,7	26,7	8,1	11,2	32,9	9,3
Ph_3P	97	1,8	22,1	5,0	21,0	12,5	37,6
Ph_3B	96	54,4	18,3	1,8	6,6	13,6	5,2
α, α'-Dipyridyl	94	14,1	42,8	6,2	30,1	5,1	1,7
$[Me_2N]_2C{=}O$	80	52,3	20,3	2,1	4,8	16,9	3,6
Dibenzo-18-crown-6	73	2,7	46,4	7,2	27,0	10,6	5,6
$(i\text{-}PrO)_3P$	70	8,2	48,1	5,3	21,5	15,5	1,4
Et_2NH	47	10,3	32,9	5,1	17,1	30,9	3,6
$(PhO)_3P$	40	3,8	44,6	4,7	11,4	28,5	6,9

TABLE 2. $Pd(acac)_2$—DPD—Et_3Al-Catalyzed Telomerization of α-Toluenethiol with Butadiene (100°, 8 h, solvent DMF

Pd(acac)2: DPD mole ratio	Conversion of mercaptan, %	Product composition, %					
		(I)	(II)	(III)	(IV)	(V)	(VI)
1:1	84	3,7	6,8	–	72	–	17,4
1:2	87	–	14,8	–	66,7	–	18,5
1:4	88	–	9,0	–	77,2	–	13,8
1:10	80	–	31,7	–	58,3	–	10
1:3*	20	18,6	9,0	–	57,3	–	10,1

*The reaction was carried out at 20°C for 2 days.

TABLE 3. Telomerization of α-Toluenethiol with Butadiene in the Presence of Complex Metal Catalysts (M:Ph_3P:Et_3Al = 1:2:4; α-toluenethiol butadiene = 1:6, molar ratio, 100°, 7 h, toluene solvent

Catalyst	Mercaptan conversion, %	Product composition, %					
		(I)	(II)	(III)	(IV)	(V)	(VI)
$Ni(acac)_2$	100	0,5	53.2	10,7	35,6	–	–
$Fe(acac)_2$	100	3,0	60,0	6,7	21,6	8,7	–
$Co(acac)_2$	50	10,1	45.2	7,9	26,8	3,4	6.3
$Cu(acac)_2$	49	–	55,2	10,7	32,0	–	2,1
$Mn(acac)_2$	36	–	12,0	8,5	43,2	27,3	9,0

The nature of the solvent as well as the temperature and duration of the reaction also affected both the yield and product composition in the telomerization reactions. As can be seen in Table 4, the maximum concentration of octadienyl sulfides (III) and (IV) occurred when the telomerization was carried out in DMF as solvent; the concentration of disulfide (VI) under these conditions was minimal (3%). In contrast to the results obtained with DMF, use of DMSO as solvent increased the amount of (VI) in the reaction mixture to 38%. The concentration of octadienyl sulfides also increases as the length of the reaction is increased to 19 h (Table 5). When the telomerization reaction of α-toluenethiol with butadiene was carried out under mild conditions (20°C, 19 h), the unsaturated sulfides (III) and (IV) were obtained with ∿80% selectivity, although the thiol conversion in these cases was only 25%. Thiophenol reacts in an analogous manner with butadiene. In the presence of a $Pd(acac)_2$—PPh_3—Et_3Al catalyst in DMF as solvent a mixture of butenyl (VII), (VIII), and octadienyl sulfides (IX) and (X), as well as diphenyl sulfide was obtained in a 60:24:16 ratio and in 85% total yield (Table 6). The concentration of octadienyl sulfides (IX) and (X) in the reaction mixture was less than 23%, however.

We have demonstrated that the synthesis of higher homolog unsaturated sulfides can be accomplished via the telomerization of either α-toluenethiol or thiophenol with butadiene in the presence of low-valence palladium complex catalysts. The most selective catalyst

TABLE 4. Effect of Solvent Nature on the Yield and Composition of Products in the Telomerization of α-Toluenethiol with Butadiene [$Pd(acac)_2$:Ph_3P:Et_3Al = 1:2:4; [$Pd(acac)_2$]:[α-toluene] = 1:100; [α-toluene]:[butadiene] = 1:6 (molar ratio); 100°C, 6 h]

Solvent	Mercaptan conversion, %	Product composition,%					
		(I)	(II)	(III)	(IV)	(V)	(VI)
DMF	85	4,2	39,2	9,9	32,3	10,9	3,4
DMSO	97	1,8	22,1	5,0	21,0	12,5	37,6
Toluene	90	5,6	58,4	6,9	19,1	4,4	–
Pyridine	85	2,8	35,3	8,0	30,0	14,2	9,7
HMPA	84	–	31,8	7,3	26,4	20,6	13,8
tert-Butyl alcohol	70	–	40,0	5,7	19,8	8,9	–
THF	40	–	38,8	16,1	24,6	20,4	–
Dioxane	40	9,4	50,6	4,8	11,4	10,4	13,4
Toluene + H_2O (4:1)	60	4,5	48,7	5,8	21,2	19,7	13,0

TABLE 5. Effect of Temperature and Reaction Time on the Yield and Product Composition for the Telomerization of α-Toluenethiol with Butadiene [$Pd(acac)_2$:Ph_3P:Et_3Al = 1:3:4; [$Pd(acac)_2$]:[α-toluenethiol] = 1:100 (molar ratio) DMF]

Rection time and temperature	Mercaptan conversion, %	Product composition, %					
		(I)	(II)	(III)	(IV)	(V)	(VI)
2 h (100°)	25	3,4	44	3,4	14,4	34,8	–
6 h	85	–	47,5	7,8	32,3	12,4	–
19h	87	3,2	41,4	9,6	34,4	18,4	4,2
20° (8 h)	25	4,2	6,8	17,6	56,3	–	15,0
60°	80	2,8	71,5	7,8	17,8	–	–
100°	97	1,8	22,1	5,0	21,0	12,5	37,6
140°	98	3,8	33,9	9,3	38,7	12,7	2,3

TABLE 6. Telomerization of Thiophenol with Butadiene in the Presence of a Pd Catalyst [$Pd(acac)_2$:Ph_3P:Et_3Al = 1:3:4, 100°, 8 h, [PhSH]:[butadiene] = 1:3 (molar)]

Solvent	[Pd]:[PhSH] ratio	Thiol conversion, %	Product composition, %					
			(VII)	(VIII)	(IX)	(X)	(XI)	(XII)
Toluene	1:60	96	10	70,3	2,1	7,5	2,5	7,5
DMF	1:25	90	10	61,9	3,0	10,8	6,1	8,1
DMF *	1:25	96	5,4	60,8	6,7	17,3	9,1	–
DMF **	1:50	96	3,4	64,2	4,0	18,7	3,0	6,7
$CHCl_3$	1:100	98	0,9	83,0	2,9	10,3	2,9	–
DMF ***	1:50	90	–	77	–	5	–	18

*Ratio [PhSH]:[⩘] = 1:6.
†Reaction temperature 140°C.
Catalyst $Pd(acac)_2$—DPD—Et_3Al (1:3:4).

system was obtained using $Pd(Acac)_2$, DPD, and Et_3Al in a 1:4:4 ratio. These reactions lead to the exclusive formation of 2,6- and 1,6-octadienyl sulfides.

EXPERIMENTAL

Monomer purity was greater than 99% in all of the experiments. The sulfide mixtures were analyzed on a Khrom-41B chromatograph equipped with a flame-ionization detector and a 1.2-m-long column filled with SE-30, using helium as the carrier gas. The isomeric sulfides were isolated by preparative GLC on an LKhP-7I chromatograph using a column 0.84 m long and 18 mm in diameter filled with 15% PEG-6000 on Chromatone N-AW.

^{1}H NMR spectra were recorded on a Tesla BS-487B spectrometer, using CCl_4 solutions and HMDS as internal standard. ^{13}C NMR spectra were obtained on a Jeol FX-90Q spectrometer (22.5 MHz), using both broadband and partial proton decoupling. The solvent used was $CDCl_3$, the standard, TMS. The frequency sweep width was 4000 Hz, the ACP resolution 0.48 Hz. IR spectra were recorded on a UR-20 spectrophotometer for thin films, whereas mass spectra were obtained on an MX-13-06 spectrometer at an electron-ionization energy of 70 eV and an ionization temperature of 200°C.

General Method for the Telomerization of Thiols with Butadiene. A solution of 0.16 mmole of $Pd(acac)_2$ and 0.32 mmole Ph_3P in 2 ml of absolute toluene was cooled to −10 to −15°C under a stream of argon, and 0.48 mmole of Et_3Al was added with stirring and maintaining at this temperature for 5-10 min. The solution was transferred to a cooled autoclave (V = 17 ml) in which 8.5 mmoles thiol and 49 mmoles butadiene had been mixed beforehand, and the mixture was heated with stirring for 8 h at 100°C. The reaction mixture was worked up by treatment with 5% HCl and dried over Na_2SO_4.

After removal of solvent the residue was distilled under vacuum to separate the fractions of butenyl and octadienyl sulfides.

3-(1-Butenyl)α-Tolyl Sulfide (I), 1-(2-Butenyl)-α-Tolyl Sulfide (II), 3-(1,6-Octadienyl)-α-Tolyl Sulfide (III), and 1(2,6-Octadienyl)-α-Tolyl Sulfide (IV). Reaction of 1.05 g α-toluenethiol and 2.6 g butadiene in DMF at 100°C for 8 h gave 1.49 g (85.7%) of a mixture of the unsaturated sulfides (I)-(IV) in a 46:5:38:11 ratio, respectively, along with 0.23 g (14.3%) of sulfide (V) and disulfide (VI) in a 76:24 ratio. Isomers (I) and (II), as well as (III)-(V), were separated by preparative GLC, (I) + (II), bp 70-76°C (2 mm). (III) + (IV) + (V), bp 115-120°C (1 mm). (I), IR spectrum (ν, cm^{-1}): 920, 1000, 3080 ($CH{=}CH_2$), 720, 775, 1600, 3030 (Ar), 1380, 1460 (CH_3). PMR spectrum (δ, ppm): 1.1 d (3H, CH_3), 2.9 m (1H, $SCHC{=}$), 3.4 s (2H, $ArCH_2S$), 4.8 m (2H, $C{=}CH_2$), 5.3 (1H, $CH{=}C$), 7.1 m (5H, Ar), M^+ 178. (II), IR spectrum (ν, cm^{-1}): 970, 1640, 3010 (trans$CH{=}CH$), 720, 775, 1600, 3030 (Ar), 1380, 1460 (CH_3). PMR spectrum (δ, ppm): 1.6 d (3H, $CH_3C{=}$), 2.78 m (2H, $SCH_2C{=}$), 3.44 s (2H, $ArCH_2S$), 5.3 m (2H, $CH{=}CH$), 7.1 s (5H, Ar), M^+ 178. (III), IR spectrum (ν, cm^{-1}): 920, 1000, 3080 ($CH{=}CH_2$), 975, 1650, 3010 (trans-$CH{=}CH$), 720, 775, 1600, 3030 (Ar). PMR spectrum (δ, ppm): 1.53 d (3H, $CH_3C{=}$), 1.44 m (2H, CH_2), 2.0 m (2H, $CH_2C{=}$), 2.9 m (1H, $SCHC{=}$), 3.4 s (2H, $ArCH_2S$), 4.88 m (2H, $C{=}CH_2$), 5.5 m (3H, $CH{=}CH$, $CH{=}C$), 7.1 m (5H, Ar), M^+ 232. ^{13}C NMR spectrum (δ, ppm): 43.4 d (C^1), 36.73 t (C^2), 35.78 t (C^3), 128.30 d (C^4), 127.00 d (C^5), 17.92 q (C^6), 140.96 s (C^7), 115.14 t (C^8), 37.06 t (C^9), 138.50 s (C^{10}), 128.36 d (C^{11}), 128.86 d (C^{12}), 126.84 d (C^{13}). (IV), IR spectrum (ν, cm^{-1}): 975, 1645, 3010 (trans-$CH{=}CH$), 720, 775, 1600, 3030 (Ar), 1380, 1460 (CH_3). PMR spectrum (δ, ppm): 1.52 d (3H, $CH_3C{=}$), 2.00 m (4H, $CH_2C{=}$), 3.4 s ($ArCH_2S$), 2.83 m (2H, $SCH_2C{=}$), 7.1 s (5H, Ar), M^+ 232. ^{13}C NMR spectrum (δ, ppm): 33.16 t (C^1), 125.24 d (C^2), 133.30 d (C^3), 32.27 t (C^4), 32.47 t (C^5), 130.55 d (C^6) 126.02 d (C^7), 17.92 q (C^8), 34.68 t (C^9), 138.53 s (C^{10}), 128.32 d (C^{11}), 128.68 d (C^{12}), 126.71 d (C^{13}). (V), mp 50-51°C [8]. Found: C 77.57; H 6.45; S 14.63%. $C_{14}H_{14}S$. Calculated: C 78.5; H 6.5; S 15%. (VI), mp 69-70°C [8]. Found: C 69.50: H 5.67; S 26.29%. $C_{14}H_{14}S_2$. Calculated: C 68.3; H 5.7: S 26%.

3-(1-Butenyl Phenyl Sulfide (VII). 1-(2-Butenyl) Phenyl Sulfide (VIII), 3-(1,6-Octadienyl) Phenyl Sulfide (IX), and 1-(2,6-Octadienyl) Phenyl Sulfide (X). Reaction of 0.94 g thiophenol and 2.6 g butadiene in DMS at 140°C for 10 h gave 1.31 g (90.3%) of a mixture of unsaturated sulfides (VII)-(X) in a 71:4:21:4 ratio. and 0.15 g (9.7%) of sulfide (XI) and disulfide (XII) in a 31:69 ratio. Isomers (VII) and (VIII), as well as sulfides (IX)-(XI), were separated by preparative GLC. (VII) + (VIII), bp 53-63°C (2 mm). (IX) + (X) + (XI), bp 130-133°C (2 mm). (VII), IR spectrum (ν, cm^{-1}): 920, 1000, 3010 ($CH{=}CH_2$), 695, 745, 1580, 3030 (Ar), 1380, 1460 (CH_3). PMR spectrum (δ, ppm): 1.1 d (3H, CH_3), 3.4 m (1H, $SCHC{=}$), 5.3 m (1H, $CH{=}C$), 4.8 m (2H$C{=}CH_2$), 7.1 m (5H, Ar), M^+ 164. (VIII), IR spectrum (ν, cm^{-1}): 695, 745. 1580, 3030 (Ar), 970, 1640, 3010 (trans-$CH{=}CH$), 1380, 1460 (CH_3). PMR spectrum (δ, ppm): 1.53 d (3H, $CH_3C{=}$), 3.37 m (2H, $SCH_2C{=}$), 5.42 m (2H, $CH{=}CH$), 7.12 m (5H, Ar). (IX), IR spectrum (ν, cm^{-1}): 920, 1000, 3080 ($CH{=}CH_2$), 975, 1650, 3010 (trans-$CH{=}CH$), 695, 750, 1580, 3030 (Ar), 1380, 1460 (CH_3). PMR spectrum (δ, ppm): 1.5 d (3H, $CH_3C{=}$), 2.0 m (2H, $CH_2C{=}$), 3.3 m (1H, $SCHC{=}$), 1.44 m (2H, CH_2), 4.8 m (2H, $C{=}CH_2$) 5.3 m (3H, $CH{=}CH$), 7.1 m (5H, Ar), M^+ 218. (X), IR spectrum (ν, cm^{-1}): 695, 750, 1580, 3030 (Ar), 970, 1650, 3010 (trans-$CH{=}CH$), 1380, 1460 (CH_3). PMR spectrum (δ, ppm): 1.5 d (3H, $CH_3C{=}$), 2.0 m (4H, $CH_2C{=}$), 3.3 m (2H, $SCH_2C{=}$), 5.3 m (4H, $CH{=}CH$), 7.1 m (5H, Ar), M^+ 218. (XI), bp 115°C (1 mm) or 295°C [8]. Found: C 76.7; H 6.6; S 16.7%. $C_{12}H_{10}S$. Calculated: C 77.4; H 5.4; S 17.2%. (XII), mp 60°C [8]. Found: C 67.13; H 4.72; S 29.11%. $C_{12}H_{10}S_2$. Calculated: C 66; H 4.6; S 29.4%.

CONCLUSIONS

1. The telomerization of α-toluenethiol or thiophenol with butadiene has been accomplished using low-valence palladium complex catalysts to give higher homolog 1,6- and 2,6-octadienyl sulfides.

2. The feasibility of Ni, Co, Fe, Cu, and Mn complexes as catalysts for the telomerization of butadiene with α-toluenethiol has also been demonstrated.

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STRUCTURE AND REACTIVITY OF 3- AND 4-[(4'-CHLOROPHENYL)SULFAMOYL]-1-DIAZOALKAN-2-ONES

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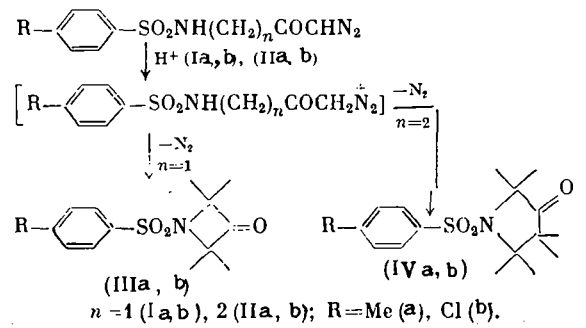
It has been shown that tosylaminoalkyl-α-diazoketones (Ia), (IIa), under acidic cleavage conditions, undergo intramolecular cyclization to form azetidine and pyrrolidine derivatives [1, 2]. We have performed similar reactions in the case of 3- and 4-[(4'-chlorophenyl)sulfamoyl]-1-diazoalkan-2-ones (Ib), (IIb):



n = 1 (Ia, b), 2 (IIa, b); R = Me (a), Cl (b).

Under the action of conc. H_2SO_4, diazoketone (Ib) undergoes a transformation to azetidin-3-one (IIIb) in a 45% yield only in a weakly nucleophilic medium. The reaction is accompanied by the formation of acyclic compounds — derivatives of α-methyl ketones. In a stronger nucleophilic medium (e.g., CH_3COOH) the latter become the main reaction products. Elongation of the alkyl chain in the diazoketone by one methylene group favors intramolecular alkylation. Thus, compound (IIb) changes into pyrrolidine (IVb) in a 30-40% yield already during decomposition in CH_3COOH, and in H_2SO_4 compound (IVb) constitutes the main product (over 80%). Consequently, the formation of the five-membered heterocyclic compound under the conditions of intramolecular cyclization reaction is more favorable as compared with the four-membered ring. The ease of the heterocyclization of compound (IIb) with the formation of the pyrrolidine system allows one to assume the presence of such a conforma-

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