SYNTHESIS OF CYCLIC 1,4-DISULFIDES AND ALKYLTHIOPHENES BY CATALYTIC THIACYCLIZATION OF ACETYLENES WITH SULFUR

U. M. Dzhemilev, N. Z. Baibulatova,
T. K. Tkachenko, R. V. Kunakova,
L. M. Khalilov, and A. A. Berg

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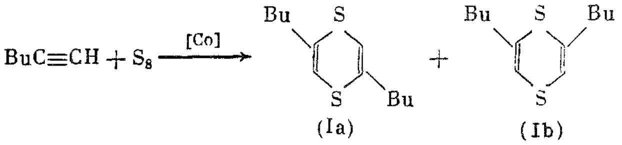
In continuation of the study of the reaction of 1,3-dienes with sulfur and also to develop new methods of synthesis of practically useful thia- and dithiacyclanes, we studied the reaction of mono- and disubstituted acetylenes with cyclooctasulfane, S_8, with two- and three-component cobalt- and palladium-containing complex catalysts having high catalytic activity in the condensation reaction of dienes with small molecules and atoms [1-3].

Thus, reaction of 1-hexyne and sulfur (S_8) (mole ratio 1-hexyne:S_8 = 1:1) in toluene solution in the presence of the catalyst $Co(acac)_2$—Ph_3P—Et_3Al (1:2:4) produces a mixture of thiacyclanes with ~7% yield, which is consistent with chromatography—mass spectrometry (GC-MS) data for compounds (Ia) and (Ib) at a 45:55 ratio. The isomers (Ia) and (Ib) were separated by HPLC and their structure was established using ^1H and ^{13}C NMR and UV spectroscopy.



The ^{13}C NMR of sulfides (Ia) and (Ib) differ little; for example, the carbon signals in the butyl radical are located at 13.78-36.11 ppm. The singlets at 140.00 and 140.61 ppm and the intense doublet at 115.12 and 115.64 ppm are related to the carbon atoms in the double bonds. Besides this, the values of the direct spin—spin coupling constants of the methine carbon were found using high resolution spectra in both isomers (Ia) and (Ib) to be the same, ($^1J_{^{13}C^1H}$ = 176 Hz). The values of the vicinal coupling constants for C^2 and C^5 or C^2 and C^6 with the methylene proton of the carbon atoms also were similar at 5-6 Hz. The presence of additional vicinal constants ($^3J_{^{13}C^1H}$ = 2 Hz) for the methine carbon ($C^{3,5}$) in structure (Ib) unambiguously indicates the 2,6 location of the butyl radicals in this isomer. The final choice of structures (Ia) and (Ib) were based on analysis of the UV spectra of the disulfides obtained. In particular, the presence of an absorption maximum in the UV spectra of (Ia) and (Ib) at 263 and 264 nm (log ε = 3.64 and 3.75), respectively, shows the presence of conjugated double bonds (see [4]).

Considering that the activating ligand has a strong effect on the direction of the catalytic conversion of 1,3-dienes [5], we used a number of nitrogen- and phosphorus-containing electron-donor ligands (Table 1) in the thiacyclization reaction. Only dibenzo-18-crown-6 of all the ligand-activators allowed the production of the sulfides (Ia, b) with exceptionally high selectivity; however, the yield did not exceed 5%. With introduction of ligands like Et_2NH, Et_3N, and Bu_3P into the catalyst, the thiacyclization of 1-hexyne with sulfur produced 3-methyl-2-propyl-5-butyl-(IIa) and 3-methyl-2-propyl-6-butyl-1,4-dithiacyclohexa-2,5-diene (IIb), the concentration of which comprised 2-18% in the reaction mixture, along with 1,4-dithiacyclanes (Ia) and (Ib). The ratio of (IIa) and (IIb) was 40:60 by GC-MS. When $(PhO)_3P$ and Py were used, the formation of disulfides (Ia) + (Ib) and isomeric methylpropylbutylthiophene (IIIa) + (IIId) in the ratio (IIIa):(IIIb):(IIIc):(IIId) = 18:53:24:5 was observed.

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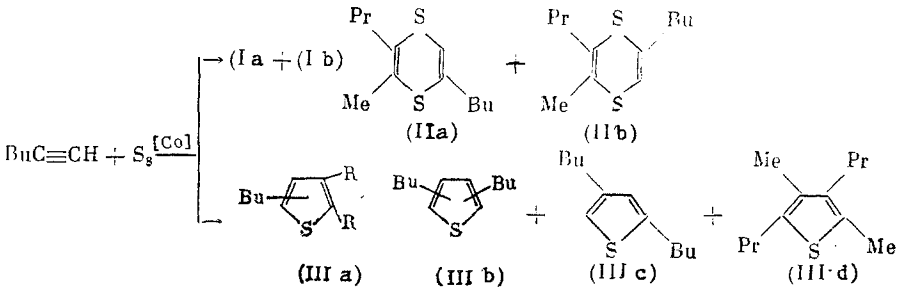

R = Pr, Me.

It follows from the composition of the products obtained that the formation of the trisubstituted disulfides (IIa) and (IIb) and thiophene (IIIa) occurs by mixed thiacyclization of sulfur with 1- and 2-hexynes which are formed as a result of isomerization of 1-hexene by low valent cobalt complexes.

In the thiacyclization of 1-hexyne with S_8, the increase in the concentration of sulfur leads to an increase in the total yield of (I) and (III) and the concentration of disulfides (Ia, b); however, with a large excess of sulfur, as well as in deficiency, the selectivity of sulfide (Ia, b) formation decreases because of formation of thiophenes (IIIa-d) (Table 2).

The solvent has a significant effect on the direction and structural selectivity of the reaction of 1-hexene with sulfur (Table 3). Upon reaction in toluene, dioxane, or DMSO, the formation of primarily 1,4-dithienes (Ia, b) is observed, while in HMPA, trisubstituted 1,4-dithienes (IIa, b) and thiophenes (IIIa-d) dominate.

We also studied the thiacyclization of sulfur with 1-pentyne, 1-heptyne, 4-decyne, and phenylacetylene. From 1-pentyne and S_8 under the conditions chosen (130°C, 6 h [alkene]:[S_8] = 1:2), 2,5-(IVa) and 2,6-dipropyl-1,4-dithiacyclohexa-2,5-diene (IVb) [(IVa):(IVb) = 40:60] and alkylsubstituted thiophene (V) in the ratio (IV):(V) = 83:17 with total yield ~95% were produced. Analysis of sulfide (V) using high resolution chromatography–mass spectrometry showed that the alkylsubstituted thiophene (V) is a difficultly separated mixture of three structural isomers in the ratio 40:50:10. 1-Heptyne reacts with S_8 giving isomeric 2,5-(VIa) and 2,6-diamyl-1,4-dithiacyclohexa-2,5-diene (VIb) [(VIa):(VIb) = 40:60] and alkylthiophenes (three isomers in the ratio 18:61:21) with total yield of ~49%. The ratio of disulfides (VIa, b) to thiophenes (VII) was 34:66.

It can be seen that formation in all the experiments of isomeric 2,5- and 2,6-dialkyl-1,4-dithiacyclohexa-2,5-dienes, the ratio of which depends both on the conditions of the reaction and on the structure of the starting acetylenes, is observed upon thiacyclization of terminal acetylenes with sulfur.

TABLE 1. Effect of Ligand-Activator, L, on the Product Yield in the Thiacyclization of 1-Hexyne with Sulfur*

L	Total yield (I)—(III), %	Composition of reaction products, %		
		(Ia, b)	(IIa, b)	(IIIa-d)
$(PhO)_3P$	25	88	–	12
Py	11	73	–	27
α,α'-Dipyridyl**	11	52	10	24
Et_2NH	10	80	2	–
Et_3N	8	82	18	–
Bu_3P	8	95	5	–
Dibenzo-18-crown-6***	5	99	–	–

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*Reaction conditions: [Co(acac)$_2$]:[L]:[Et_3Al] = 1:2:4; [1-hexyne]:[S_8] = 1:1, [Co(acac)$_2$]:[1-hexyne] = 1:100, solvent = toluene, 130°C, 6 h.

**Solvent = THF.

***Solvent = dioxane.

TABLE 2. Effect of Starting Reagent Ratio on the Product Yield for Reaction of 1-Hexyne with Sulfur*

[1-Hexyne]: [S_8]	Total yield (I) + (III), %	Composition of reaction products, %	
		(Ia, b)	(IIIa-d)
3 : 1	27	85	15
1 : 1	7	98	–
1 : 2	96	98	–
1 : 4	96	98	–
1 : 10	98	89	11

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*Reaction conditions: [$Co(acac)_2$]:[Ph_3P]:[Et_3Al] = 1:2:4, [$Co(acac)_2$]:[1-hexyne] = 1:100; solvent = toluene, 130°C, 6 h.

TABLE 3. Effect of Solvent on the Yield and Composition of Products of Reaction of 1-Hexyne with Sulfur*

Solvent	Total yield (I) + (III), %	Composition of reaction, %			
		(Ia, b)	(IIa, b)	(IIIa–d)	unidentified products
Toluene	96	100	–	–	–
HMPA	58	13	43	27	27
Sulfolane	50	–	–	45	55
Pyridine	22	64	–	–	36
Dioxane	20	100	–	–	–
DMSO	11	89	–	–	11

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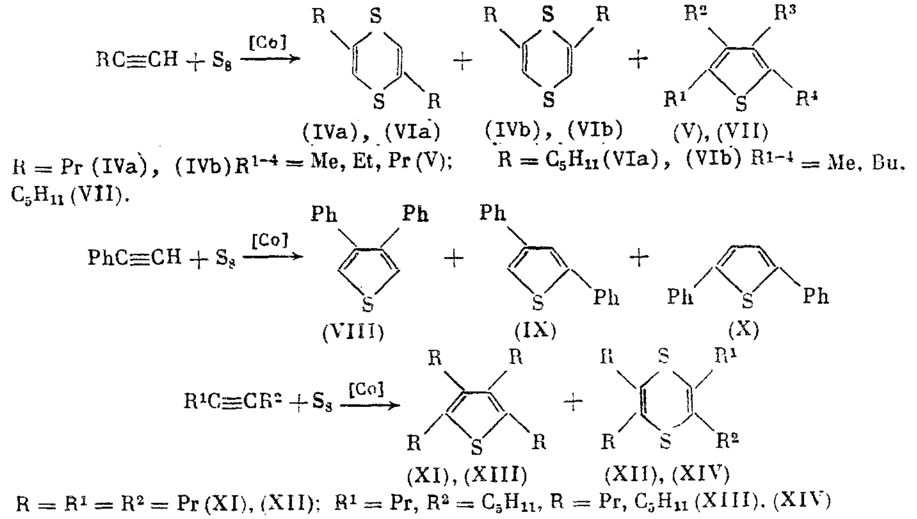
*Reaction conditions: [$Co(acac)_2$]:[Ph_3P]:[Et_3Al] = 1:2:4, [1-hexyne]:[S_8] = 1:2, [$Co(acac)_2$]:[1-hexyne] = 1:100, 130°C, 6 h.

The formation of exclusively 2,4-(VIII), 2,5-(IX), and 3,4-diphenylthiophene (X) in the ratio 30:40:30 with total yield ~50% occurs upon changing the terminal alkylacetylene to phenylacetylene in the reaction with S_8. The formation of even traces of diphenyl 1,4-dithiacyclohexa-2,5-diene was not observed in these experiments. This reaction can proceed in the absence of catalyst, but the total yield of thiophenes (VIII)-(X) does not exceed ~13%.



R = Pr (IVa), (IVb) R^{1-4} = Me, Et, Pr (V); R = C_5H_{11} (VIa), (VIb) R^{1-4} = Me, Bu, C_5H_{11} (VII).

R = R^1 = R^2 = Pr (XI), (XII); R^1 = Pr, R^2 = C_5H_{11}, R = Pr, C_5H_{11} (XIII), (XIV)

Disubstituted acetylenes were used intending to produce tetrasubstituted 1,4-dithiacyclohexadienes; however, from 4-octyne and sulfur primarily tetrapropylthiophene (XI) and a small quantity of tetrapropyl-1,4-dithiacyclohexa-2,5-diene (XII) in the ratio 95:5 with total yield ~20% were obtained. In a similar manner, the reaction of 4-diene with sulfur gave a mixture of dipropyldimethylthiophene (XIII) and dipropyldiamyl-1,4-dithiacyclohexa-2,5-diene (XIV) in the ratio 90:10 with ~10% yield.

The reaction of 1-hexyne with S_8 in the presence of $Pd(acac)_2$–Ph_3P–Et_3Al in toluene (130°C, 6 h) was studied for comparison of the catalytic activity of cobalt complexes and palladium compounds in the thiacyclization of terminal acetylenes with sulfur. Under the conditions chosen, a mixture of 2,5- and 2,6-dibutyl-1,4-dithiacyclohexa-2,5-diene (Ia, b) and dibutylthiophene (IIIa-d) in the ratio 34:66 with total yield ~18% is produced.

The complex catalysts containing Pd are seen to be inferior to the cobalt complexes in their activity and selectivity in the thiacyclization reaction. Thus, by changing the reaction conditions, composition of the catalyst, and also the structure of the starting acetylene, methods of regulating the direction of thiacyclization in order to synthesize selectively 1,4-dithiacyclohexadienes and thiophenes were found.

EXPERIMENTAL

Reagents of ≥99% purity were used. The mixture of sulfides was analyzed on a Chrom-47 chromatograph using a flame ionization detector, SE-30 (5% on Inerton-Super) 1.2 m column, and helium carrier gas. Separation of isomeric disulfides used preparative GLC on a Perkin-Elmer F-21 chromatograph with a 0.86 × 50 m column; thiophenes, PEG-6000 (15%) on an N-AW chromaton; and 1,4-dithiacyclohexadienes (Ia, b) and (IIa, b), an SE-30 column (5% on chromaton N-AW). Isomeric disulfides (Ia) and (Ib) were separated by HPLC on a DuPont 8800 chromatograph, Zorbax NH_3 21.2 × 250 column, UV detector, and hexane eluent. NMR spectra (^1H) were recorded on a Tesla BS = 567 (100 Hz) instrument in $CDCl_3$ relative to TMS. NMR spectra (^{13}C) were taken from a Joel FX-90Q spectrometer with proton suppression and single resonance. IR spectra were recorded on a UR-20 (films) spectrophotometer and UV spectra on a Specord M-40 instrument. Mass spectra were obtained on a MX-13-06 instrument with ionization electron energy 70 eV, ionization chamber temperature 200°C. GC-MS used a Finigan-4021 instrument with a 0.25 mm × 50 m BP-1 column, inlet temperature of 250°C, and ionizing voltage of 70 eV.

General Method of Reaction of Alkynes with Sulfur. To a solution of 0.16 mmole of $M(acac)_2$ (M = Co or Pd) and 0.32 mmoles of ligand, L, in 2 ml toluene cooled to −15 to −10°C under a stream of argon with stirring was added 0.48 mmole of Et_3Al. After 5-10 min the solution was transferred to a cooled autoclave (17 ml), where 16 mmoles of alkene, 32 mmoles of sulfur, and 5 ml absolute solvent had previously been mixed, and the mixture was heated at 130°C with mixing for 6 h. The reaction mixture was passed through a layer of neutral aluminum oxide (30 g), and the residue after evaporation was distilled in vacuum and the thiophene and dithiacyclohexadiene fractions were separated.

2,5-(Ia), 2,6-Dibutyl-1,4-dithiacyclohexa-2,5-diene (Ib). From 0.51 g sulfur and 1.31 g 1-hexene (M = Co, L = Ph_3P), 0.1 g of a mixture of disulfides (Ia) and (Ib) was obtained. Under analogous conditions from 1.0 g sulfur and 1.31 g 1-hexyne, 1.0 g (96%) of disulfides (Ia) and (Ib) in the ratio 45:55 was obtained in agreement with GC-MS, bp 82°C (1 mm). IR spectra (ν, cm^{-1}): 780, 3010 (CH=C), 1380, 1460 (CH_3). Found: C 62.8; H 8.9; and S 28.3%; M^+ 228. $C_{12}H_{20}S_2$. Calculated: C 63.1; H 8.8; and S 28.1%; M 228.54. Isomers (Ia) and (Ib) were separated by HPLC. Disulfide (Ia). UV spectrum: λ_{max} = 263 nm, log ε = 3.64. PMR spectrum (δ, ppm; J, Hz): 0.90 t (6H, CH_3, J = 6.5), 1.40 m (8H, CH_2), 2.35 t (4H, $CH_2C{=}C$, J = 7.5), 5.91 s (2H, SCH=C). NMR ^{13}C spectrum ($CDCl_3$, δ, ppm, J, Hz): 13.78 q ($C^{10,14}$), 22.02 t ($C^{9,13}$), 30.64 t ($C^{8,12}$), 36.11 t ($C^{7,11}$), 115.12 d.t.d ($C^{3,5}$, ^1J = 176, ^3J = 6; ^3J = 2), 140.61 s ($C^{2,6}$). Disulfide (Ib). UV spectrum: λ_{max} = 264 nm, log ε = 3.75. PMR spectrum (δ, ppm, J, Hz): 0.89 t (6H, CH_3, J = 6.5), 1.4 m (8H, CH_2), 2.35 t (4H, $CH_2C{=}C$, J = 7), 5.95 s (2H, S-CH=C). NMR ^{13}C spectrum (δ, ppm, J, Hz): 13.78 q ($C^{10,14}$), 22.02 t ($C^{9,13}$), 30.77 t ($C^{8,12}$), 36.05 t ($C^{7,11}$), 115.64 d.t ($C^{3,5}$, ^1J = 176, ^3J = 5), 140.00 s ($C^{2,6}$).

2-Methyl-3-propyl-6-butyl-(IIa), 2-Methyl-3-propyl-5-butyl-1,4-dithiacyclohexa-2,5-diene (IIb). From 0.51 g sulfur and 1.31 g 1-hexyne (M = Co, L = Et_3N) were obtained 0.18 g (10%) of a reaction mixture comprised of disulfides (Ia, b) and (IIa, b) in the ratio 82:18. The mixture of disulfides (Ia, b) and (IIa, b) were separated from the mixture by distillation and preparative GLC. Disulfides (IIa, b), bp 88°C (1 mm). IR spectrum (ν, cm^{-1}): 780, 3010 (CH=C), 1380, 1460 (CH_3). PMR spectrum (δ, ppm, J, Hz): 0.88 t (6H, CH_3, J = 7), 1.44 m (6H, CH_2), 2.30 t (2H, $CH_2C{=}C$, J = 7), 2.37 t (2H, $CH_2C{=}C$, J = 7) 6.03 s and 6.04 s (2H, CH=C). Found: C 63.0; H 8.7; and S 28.3%; M^+ 228. $C_{12}H_{20}S_2$. Calculated: C 63.1; H 8.8; and S 28.1%. M 228.44. Dithiene (IIa): NMR ^{13}C spectrum (δ, ppm): 13.44 q (C^{14}), 13.78 q (C^{10}), 20.37 q (C^7), 21.96 t ($C^{9,13}$), 30.82 t (C^{11}), 36.11 t (C^{12}), 36.19 t (C^8), 116.90 d (C^5), 127.65 s (C^2), 131.72 s (C^3), 142.00 s (C^6). Dithiene (IIb). NMR ^{13}C spectrum (δ, ppm): 13.44 q (C^{14}), 13.78 q (C^{10}), 20.72 q (C^7), 21.96 q ($C^{9,13}$), 30.82 t (C^{11}), 36.11 t (C^{12}), 36.45 t (C^8), 116.64 d (C^6), 126.82 s (C^2), 130.94 s (C^3), 141.82 s (C^5).

Methylpropylbutyl-(IIIa), Symmetric dibutyl-(IIIb), 2,4-Dibutyl-(IIIc), 2,4-Dimethyl-3,5-dipropylthiophene (IIId). From 1.02 g sulfur and 1.31 g 1-hexene (M = Co, L = $(PhO)_3P$) was obtained 0.22 (25%) disulfide (Ia, b) and thiophene (IIIa-d) in the ratio 88:12. The ratio by GC-MS of thiophenes was (IIIa):(IIIb):(IIIc):(IIId) = 18:53:24:5, and the mass of the isomers was 196. From 1.02 g sulfur and 1.31 g 1-hexyne (M = Pd, L = Ph_3P) was obtained 0.15 g (18%) thiophenes (IIIa-d) and dithiene (Ia, b) in the ratio 66:34. Thiophenes (IIIa-d), bp 68°C (1 mm). Found: C 73.8; H 10.0; and S 16.2%; M^+ 196. $C_{12}H_{20}S$. Calculated: C 73.5; H 10.2; and S 16.3%; M 196.38. Thiophenes (IIIa-d) were separated by preparative GLC. Thiophene (IIIa). IR spectrum (ν, cm^{-1}): 845, 1045, 1090, 1360, 1445 (thiophene ring), 1390, 1470 (CH_3). PMR spectrum (δ, ppm, J, Hz): 0.91 t (6H, CH_3, J = 8), 1.13-1.59 m (6H, CH_2), 2.28 s (3H, $CH_3C=C$), 2.41 t (2H, $CH_2C=C$, J = 6) 2.70 t (2H, $CH_2C=C$, J = 6), 6.46 s (1H, $CH=C$). NMR spectrum ^{13}C (δ, ppm): 12.83 q, 13.87 q, and 14.00 q (CH_3), 22.24 t, 23.71 t, and 33.85 t (CH_2), 29.69 t and 30.38 t ($CH_2C=$), 125.83 d ($CH=$), 129.64 s, 137.53 s, 140.87 s ($C=$). Thiophene (IIIb). IR spectrum (ν, cm^{-1}): 810, 1035, 1090, 1365, 1445, 1500 (thiophene ring), 1385, 1470 (CH_3). PMR spectrum (δ, ppm, J, Hz): 0.92 t (CH, CH_3, J = 6), 1.42 m (8H, CH_2), 2.75 t (4H, $CH_2C=C$, J = 8), 6.55 s (2H, $CH=CH$). NMR ^{13}C spectrum (δ, ppm): 13.87 q ($C^{9,13}$), 22.28 t ($C^{8,12}$), 29.91 t ($C^{6,10}$), 33.89 t ($C^{7,11}$), 123.31 d ($CH=$), 143.25 s ($C=$). Thiophene (IIIc). IR spectrum (ν, cm^{-1}): 750, 850, 1445, 1565 (thiophene ring), 1390, 1475 (CH_3). PMR spectrum (δ, ppm, J, Hz): 0.93 t (6H, CH_3, J = 6), 1.55 m (8H, CH_2), 2.54 t (2H, $CH_2C=C$, J = 7), 2.69 t (2H, $CH_2C=C$, J = 7), 6.61 s (1H, $CH=C$), 6.67 s (1H, $CH=C$). NMR ^{13}C spectrum (δ, ppm): 13.83 q, 13.91 q ($C^{9,13}$), 22.24 t, 22.45 t ($C^{8,12}$), 29.86 t, 30.25 t ($C^{7,11}$), 32.60 t, 33.84 t ($C^{6,10}$), 117.07 d (C^5), 125.44 d (C^3), 142.82 s and 145.5 s ($C^{2,4}$). Thiophene (IIId). IR spectrum (ν, cm^{-1}): 740, 810, 1035, 1085, 1350, 1445, 1560 (thiophene ring), 1385, 1465 (CH_3). PMR spectrum (δ, ppm, J, Hz): 0.92 t (6H, CH_3, J = 7), 1.39 m (4H, CH_2), 1.75 s (3H, $CH_3C=C$), 1.86 s (3H, $CH_3C=C$), 1.88 t (2H, $CH_2C=C$, J = 7), 2.18 t (2H, $CH_2C=C$, J = 7).

2,5- and 2,6-Dipropyl-1,4-dithiacyclohexa-2,5-dienes (IVa, (IVb), and Alkylthiophenes (V). From 1.02 g sulfur and 1.09 g 1-heptyne (M = Co, L = Ph_3P) was obtained 0.74 g (95%) of the disulfides (IVa, b) and thiophenes (V) in the ratio 83:17. According to GC-MS, the ratio of isomers (IVa):(IVb) = 40:60, and the thiophene (V) was three structural isomers in the ratio 40:50:10. Disulfide (IVa, b), bp 66°C (1 mm), oil. IR spectrum (ν, cm^{-1}): 770, 3005 ($CH=C$), 1380, 1460 (CH_3). PMR spectrum (δ, ppm, J, Hz): 0.89 t (6H, CH_3, J = 6), 1.59 m (4H, CH_2), 2.32 t (4H, $CH_2C=C$, J = 6), 5.61 s and 5.95 s (2H, $SCH=C$). Found: C 59.8; H 7.8; and S 32.4%; M^+ 200. $C_{10}H_{16}S_2$. Calculated: C 60.0; H 8.0; and S 32.0%; M 200.38. Thiophene (V), bp 50°C (1 mm). IR spectrum (ν, cm^{-1}): 1350, 1440, (CH_3), 800, 840, 900, 1030, 1080 (thiophene ring). PMR spectrum (δ, ppm): 0.96 t (CH_3), 1.59 t (CH_2), 2.3 s ($CH_3C=C$), 2.5 t ($CH_2C=C$), 2.72 t ($CH_2C=C$), 6.44 s, 6.56 s, 6.60 s, 6.65 s ($CH=C$). Found: C 71.1; H 9.3; and S 19.6%; M^+ 168. $C_{10}H_{16}S$. Calculated C 71.4; H 9.5; and S 19.0%; M 168.32.

2,5-(VIa), 2,6-Diamyl-1,4-dithiacyclohexa-2,5-diene (VIb), Thiophene (VII). From 1.02 g sulfur and 1.54 g 1-pentyne (M = Co, L = Ph) was obtained 0.49 g (49%) of a mixture of sulfides (VIa, b) and (VII) in the ratio 34:66. According to GC-MS, the ratio of isomers (VIa):(VIb) = 40:60, and the thiophene (VII) was three isomers in the ratio 18:61:21. Disulfides (VIa, b), bp 92°C (1 mm), oil. IR spectrum (ν, cm^{-1}): 780, 3010 ($CH=C$), 1380, 1460 (CH_3). PMR spectrum (δ, ppm, J, Hz): 0.88 t (6H, CH_3, J = 7), 1.23 m (12H, CH_2), 2.3 t (4H, $CH_2C=C$, J = 7), 5.76 s and 5.80 s (2H, $CH=C$). Found: C 75.2; H 10.9; and S 13.9%; M^+ 256. $C_{14}H_{24}S_2$. Calculated C 75.0; H 11.0; and S 14.0%; M 256.50. Thiophene (VII), bp 79°C (1 mm). IR spectrum (ν, cm^{-1}): 730, 800, 1030, 1440 (thiophene ring), 1380, 1460 (CH_3). PMR spectrum (δ, ppm, J, Hz): 0.89 t (CH_3, J = 7), 1.20-1.58 m (CH_2), 2.27 s ($CH_3C=C$), 2.34-2.53 m ($CH_2C=C$), 2.60-2.80 m ($CH_2C=C$), 6.45 s, 6.54 s, 6.60 s, 6.66 s ($CH=C$). Found: C 74.9; H 10.5; and S 14.6%; M^+ 224. $C_{14}H_{24}S$. Calculated: C 75.0; H 10.7; and S 14.3%; M 224.44.

3,4-(VIII), 2,4-(IX), and 2,5-Diphenylthiophene (X). From 1.02 g sulfur and 1.63 g phenylacetylene (M = Co, L = Ph_3P) was obtained 0.94 g (50%) of thiophenes (VIII)-(X) in the ratio 40:30:30. Found: C 81.5; H 5.1; and S 13.4%; M^+ 236. $C_{16}H_{12}S$. Calculated: C 81.3; H 5.1; and S 13.6%; M 236.34. Thiophene (VIII) was separated from the mixture of sulfides by HPLC, mp 113-115°C. IR spectrum (ν, cm^{-1}): 700, 755, 1530, 3030 (Ar), 780, 910, 1030, 3080, 1380, 1460, 1530 (thiophene ring). PMR spectrum (δ, ppm): 6.54 s (2H, $CH=C$), 7.29-7.35 m (6H, HAr), 7.54-7.60 m (4H, HAr). NMR ^{13}C spectrum (δ, ppm): 117.25 d ($C^{2,5}$), 127.04 d ($C^{7;11}$), 128.51 d ($C^{7,12}$), 128.60 d ($C^{9,13}$), 136.44 s ($C^{6,10}$), 140.52 s ($C^{3,4}$). Thiopenes (IX) and (X), mp 128°C. IR spectrum (ν, cm^{-1}): 700, 750, 1600 (Ar), 740, 810, 1030, 1070, 1370, 1450 (thiopene ring). PMR spectrum (δ, ppm): 7.19-7.45 m (8H, HAr, CH=C), 7.56-7.65 m (4H, HAr). NMR ^{13}C spectrum (δ, ppm): 119.63 d, 122.27 d, 123.92 d (CH=), 125.51 d, 125.78 d, 126.26 d, 127.21 d, 127.43 d, 127.61 d, 128.86 d (CH, Ar), 134.28 s, 135.80 s (C, Ar), 143.08 s, 143.56 s, 144.99 s (C=).

Tetrapropylthiophene (XI) and Tetrapropyl-1,4-dithiacyclohexa-2,5-diene (XII). From 1.02 g sulfur and 1.76 g 4-octyne (M = Co, L = Ph_3P) was obtained 1.93 g (21%) of a mixture of sulfides (XI) and (XII) in the ratio 95:5. Thiophene (XI), bp 55°C (1 mm), oil. IR spectrum (ν, cm^{-1}): 750, 830, 915, 1060, 1355, 1420 (thiophene ring), 1390, 1470 (CH_3C). NMR ^1H spectrum (δ, ppm, J, Hz): 0.96 t (12H, CH_3, J = 6), 1.43 m (8H, CH_2), 2.34 t (8H, CH_2C=C, J = 7). Found: C 76.6; H 11.0; and S 12.4%; M^+ 252. $C_{12}H_{28}S$. Calculated: C 76.3; H 11.2; and S 12.7%; M 252.50. Disulfide (XII), bp 87°C (1 mm), oil. IR spectrum (ν, cm^{-1}): 1380, 1460 (CH_3). PMR spectrum (δ, ppm, J, Hz): 0.83 t (12H, CH_3, J = 6), 1.40 m (8H, CH_2), 2.5 t (8H, CH_2C=C, J = 7). Found: C 67.2; H 9.8; and S 23.0%; M^+ 284. $C_{16}H_{28}S_2$. Calculated C 67.6; H 10.0; and S 22.7%; M 284.56.

Symmetric Dipropyldiamylthiophene (XIII) and Symmetric Dipropyldiamyl-1,4-dithiacyclohexa-2,5-diene (XIV). From 1.02 g sulfur and 2.21 g 4-decyne (M = Co, L = Ph_3P) was obtained 0.5 g (10%) of reaction mixture comprised of thiophene (XIII) and sulfide (XIV) in the ratio 90:10, and 0.56 g of starting 4-decyne. Thiophene (XIII), bp 64°C (1 mm), oil. IR spectrum (ν, cm^{-1}): 750, 830, 915, 1060, 1355, 1420 (thiophene ring), 1390, 1470, (CH_3). PMR spectrum (δ, ppm, J, Hz): 0.92 t (12H, CH_3, J = 6), 1.13-1.63 m (16H, CH_2), 2.12 t (8H, CH_2C=C, J = 7). Found: C 77.5; H 11.3; and S 10.2%; M^+ 308. $C_{20}H_{36}S$. Calculated C 77.9; H 11.7; and S 10.4%; M 308.62. Disulfide (XIV), bp 100°C (1 mm), oil. IR spectrum (ν, cm^{-1}): 1380, 1460 (CH_3). PMR spectrum (δ, ppm): 0.83-0.96 m (12H, CH_3), 1.08-1.96 m (16H, CH_2), 2.17-2.92 m (8H, CH_2C=C). Found: C 71.0; H 10.9; and S 19.0%; M^+ 340. $C_{20}H_{36}S_2$. Calculated: C 70.6; H 10.6; and S 18.8%; M 340.68.

CONCLUSIONS

1. The thiacyclization of mono- and disubstituted acetylenes with sulfur, leading to the production of dialkyl-1,4-dithiacyclohexa-2,5-dienes and thiophenes with high yield and catalyzed by the $Co(acac)_2$–$AlEt_3$ system in the presence of various ligands, is characterized.

2. The path of thiacyclization depends on the structure of the starting acetylene and the nature of the catalyst.

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