5-Methyl-5-methoxy-1,1,1-trifluoroundec-3-yn-2-one (2c). Obtained from 16.8 g (0.1 mole) of 3-methyl-3-methoxynon-1-yne, yield 15.8 (59.8%), bp 61°C (1 mm), n_D^{21} 1.4120. Found: C 59.17, H 7.24, F 21.73%. $C_{13}H_{19}F_3O_2$. Calculated: C 59.08, H 7.24, F 21.56%.

1,1,1,2,2,3,3-Heptafluoro-7-methyl-7-methoxytridec-5-yn-4-one (2d). Obtained from 16.8 g (0.1 mole) of (1c) and 25.5 g (0.11 mole) of heptafluorobutyryl chloride, yield 18.9 g (51.9%), bp 93°C (5 mm) n_D^{21} 1.3920. Found: C 49.80, H 5.22, F 37.00%. $C_{15}H_{19}F_7O_2$. Calculated : C 49.45, H 5.25, F 36.5%.

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METAL COMPLEX-CATALYZED SYNTHESIS OF DIHYDROTHIAPYRANS FROM DIALKYL SULFOXIDES AND 1,3-DIENES

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A preparative method has been developed for the synthesis of dihydrothiapyrans from dialkyl sulfoxides and 1,3-dienes, catalyzed by palladium and nickel complexes. The scope of this reaction has been assessed, and a mechanism proposed, using 1,3-dienes and sulfoxides of varying structure.

Keywords: synthesis, dihydrothiapyrans, catalysts, mechanism, sulfides, 1,3-dienes.

A frequently used method of synthesis of dihydrothiapyrans is by [2π + 4π]-cycloaddition of thioketones or thioaldehydes to 1,3-dienes [1, 2]. This method is of limited practical value since there are no convenient and efficient methods of preparation of the required thioaldehydes.

We have previously reported the one-step synthesis of dihydrothiapyrans by reacting dialkyl sulfoxides with 1,3-dienes in the presence of Pd and Ni complexes [3]. Under the reaction conditions, the sulfoxides break down to thioaldehydes which react with 1,3-dienes to give dihydrothiapyrans (DHTP). In order to obtain DHTP of varying structure, and to assess the range of applicability of this catalytic reaction of thioaldehydes generated in situ, we have examined the reactions of dialkyl and alkyl aryl sulfoxides with 1- and 2-substituted 1,3-dienes in the presence of catalytic complexes of Pd, Ni, Co, Cu, and Al which are effective catalysts for the reactions of conjugated dienes with sulfur-containing reagents [4].

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TABLE 1. Effects of Structure of Dialkyl Sulfoxides in Their Reactions with Butadiene on the Yields of Dihydrothiapyrans*

Dialkyl sulfoxide	Yield of (1), %	Dialkyl sulfoxide	Yield of (1), %
$(n\text{-}C_7H_{15})_2SO$	82(c)	$(n\text{-}C_8H_{17})_2SO$	31(d)
$(n\text{-}C_6H_{13})_2SO$	79(b)	$(n\text{-}C_4H_9)_2SO$	19(a)
$(n\text{-}C_{10}H_{21})_2SO$	57(e)	$(C_6H_5CH_2SOC_6H_{13}$	20† (b+f)
		$(C_6H_5CH_2)_2SO$	10(f)

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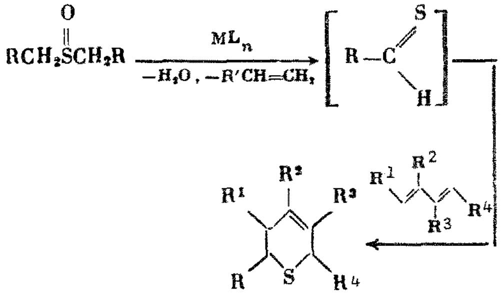
*Reaction conditions: molar ratio of sulfoxide to diene; 1:20, sulfoxide to Ni, 1:50; $[Ni(Aacac)_2]$:$[Ph_3P]$:$[AlEt_3]$ = 1:1:4, toluene, 150°C, 12 h.

†Ratio of (b) to (f), 40:60.

The sulfoxides examined were di-n-butyl, di-n-hexyl, di-n-heptyl, di-n-octyl, di-n-decyl, dibenzyl, and hexyl benzyl sulfoxides, and the dienes – butadiene, isoprene, trans-piperylene, 2,3-dimethylbutadiene, methyl sorbate, and 1,4-diphenyl-1,3-butadiene. The catalysts were obtained by reducing compounds of the appropriate transition metals with triethylaluminum in the presence of the ligand activators.



(1a-f — 8)

	R	R¹	R²	R³	R⁴
1a	C_3H_7	H	H	H	H
1b	C_5H_{11}	H	H	H	H
1c	C_6H_{13}	H	H	H	H
1d	C_7H_{15}	H	H	H	H
1e	C_9H_{19}	H	H	H	H
1f	Ph	H	H	H	H
2	C_7H_{15}	CH_3	H	H	H
3	C_7H_{15}	H	H	H	CH_3
4	C_7H_{15}	H	CH_3	H	H
5	C_7H_{15}	H	H	CH_3	H
6	C_7H_{15}	H	CH_3	CH_3	H
7	C_7H_{15}	CO_2CH_3	H	H	H
8	C_7H_{15}	H	H	H	CO_2CH_3

The values of dihydrothiapyrans were higher when an excess of the diene was used, so that the reactions involved the use of sulfoxide:diene ratios of 1:20.

Under the conditions used (150°C, 12 h), dibutyl sulfoxide reacted with butadiene in toluene in the presence of $Ni(Acac)_2$–Ph_3P–$AlEt_3$ (1:1:4) as catalyst to give 2-n-propyl-3,6-dihydro-2H-thiapyran (1a) in ∿19% yield. DHTP (1b, c) were obtained in high yields (∿79 and 82% respectively) from butadiene and dihexyl or diheptyl sulfoxide (Table 1). With increasing length of the alkyl chain in the dialkyl sulfoxides (C_8 and C_{10}) however, their reactivity decreased considerably, the yields of (1d) and (1e) being 30 and 57%. Under similar conditions, dibenzyl sulfoxide and butadiene gave ∿10% of (1f), while benzyl hexyl sulfoxide gave a mixture of (1b) and (1f) in a ratio of 40:60, overall yield ∿20%.

TABLE 2. Effects of Type and Structure of Catalyst Components on Yields of (1e) in the Reaction of Dibenzyl Sulfoxide with Butadiene*

$M(acac)_2$	Yield of (1e), %	Ligand† (L)	Yield of (1e), %
$Ni(acac)_2$	57	Dibenzo-18-crown-6	48
$Al(acac)_2$	44	Ph_3P	35
$Cu(acac)_2$	36	α,α'-Dipyridyl	30
$Pd(acac)_2$	35		
$Co(acac)_2$	24	$Ph_2PCH_2CH_2PPh_2$	24

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*Reaction conditions: Molar ratio $[M(acac)_2]$: [L]: $[AlEt_3]$ = 1:1:4; $[M(acac)_2]$:[sulfoxide] = 1:50; [sulfoxide]:[diene] = 1:20, toluene, 150°C, 20 h.

†Catalyst $Pd(acac)_2$:L:$AlEt_3$ (1:1:4).

With symmetrical dialkyl sulfoxides, equivalent amounts of water and the 1-alkene corresponding to the hydrocarbon radical present in the original sulfoxide were obtained. The water content of the mixture was determined by Fischer titration [5], while the olefins were identified by comparison with authentic samples. When dibenyzl sulfoxide was used, in addition to (1f), benzyl alcohol, stilbene, dibenzyl sulfide, and dibenzyl disulfide were formed in a ratio of 15:12:3:10:3.

In order to find novel, efficient catalysts capable of converting butadiene and dialkyl sulfoxides into DHTP, taking the reaction of di-n-decyl sulfoxide with butadiene as an example we tested a number of catalytic systems based on Pd, Ni, Co, Cu, and Al, activated by electron-donor and electron-acceptor ligands. It will be seen from Table 2 that low-valent phosphine complexes of Pd, Co, Cu, and Al catalyze the heterocyclization of butadiene with di-n-decyl sulfoxide, but the yields of (1e) under these conditions did not exceed 44%. Of all the oxygen, nitrogen, phosphorus-containing mono- and bidentate ligands tested, only dibenzo-18-crown-6 ether gave (1e) in a yield of ∿48%.

These findings show that the highest yields of (1e) were obtained using the three-component catalyst $Ni(acac)_2$–PPh_3–$AlEt_3$ (1:1:4) (150°C, 20 h, solvent – toluene). In all subsequent work, therefore, this catalyst was used under the conditions chosen.

It was subsequently found that isprene, trans-piperylene, 2,3-dimethylbutadiene, and methyl sorbate react with dialkyl sulfoxides to give DHTP. Attempts to carry out this reaction with trans-1,4-diphenyl-1,3-butadiene were unsuccessful.

The heterocyclization of unsymmetrical 1,3-dienes invariably gave mixtures of the regioisomers in a ratio of 1:1.

During studies of the heterocyclization of 1- and 2-substituted dienes with dialkyl sulfoxides, it was found that in order to obtain high yields of DHTP it was essential to carry out the reaction in glass ampuls. In these experiments, in contrast to butadiene trans-piperylene reacted with dioctyl sulfoxide to give a mixture of 3- and 6-methyldihydrothiapyrans (2) and (3) in 98% yield and a ratio of 1:1 when using much lower concentrations of the catalyst and diene ([Ni $(acac)_2$]:$[R_2SO]$ = 1:400 and [dine]:$[R_2SO]$ = 6:1) (Table 3).

Experiments carried out in a glass ampul in the absence of a catalyst gave (2) and (3) in yields of less than 2%.

Under these conditions, isoprene and dioctyl sulfoxide afforded the isomeric DHTP (4) and (5) in 55% yield. 2,3-Dimethylbutadiene reacted similarly with dioctyl sulfoxide to give (6) only, in 63% yield. Least reactive towards dioctyl sulfoxide was methyl sorbate, which gave a mixture of 3- (7) and 6-methoxycarbonyl-2-n-heptyl-3,6-dihydro-2H-thiapyran (8) in ∿18% overall yield.

Attempts to carry out the [4π + 2π]-cycloaddition of alkylthioaldehydes, generated in situ from dialkyl sulfoxides, with cyclic 1,3-dienes were unsuccessful. For example, cyclopentadiene (CPD) gave the diene oligomers (trimers and tetramers) only. It is however possible that an adduct of CPD with the thioaldehyde (9) was formed, which under the

TABLE 3. Effects of Catalyst Concentration on Yields of Dihydrothiapyrans (2) and (3) Obtained from trans-Piperylene and Dioctyl Sulfoxide

Molar ratio [Ni]: [sulfoxide]	Yield of (2) and (3),* %	Yield of (2) and (3),† %
1 : 50	29	35
1 : 200	31	58
1 : 400	42	98
		2

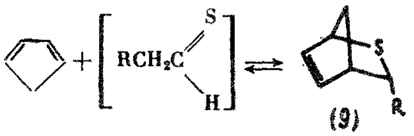
Reaction conditions: molar ratio [Ni(acac)$_2$]:[Ph$_3$P]:[AlEt$_3$] = 1:3:4, [diene]:[sulfoxide] = 6:1.
*Experiments carried out in a steel autoclave.
†Experiments carried out in a glass ampul.

TABLE 4. Composition of Products of the Reaction of CHD with Dihexyl Sulfoxide

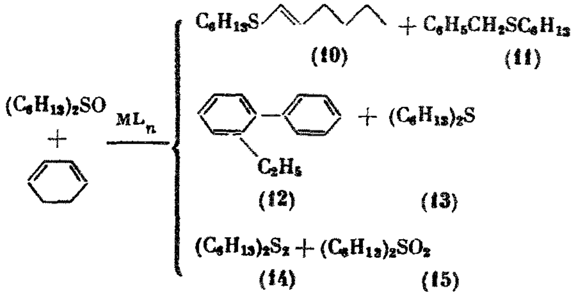
Molar ratio [CHD]: [sulfoxide]	Reaction products, %					
	10	11	12	13	14	15
6 : 1	–	27	30	30	10	3
3 : 1	–	46	–	46	8	–
1 : 6	–	20	6	7	4	12
1 : 1*	55	25	2	12	6	–
1 : 3‡	34	34	5	17	4	6
1 : 6†	–	–	–	64	20	16

Reaction conditions: molar ratio [Ni (acac)$_2$]:[sulfoxide] = 1:500, solvent toluene, 150°C, 12 h.
*200°C
†Catalyst Al$_2$O$_3$, 5% by weight on sulfoxide.
‡100°C, no catalyst.

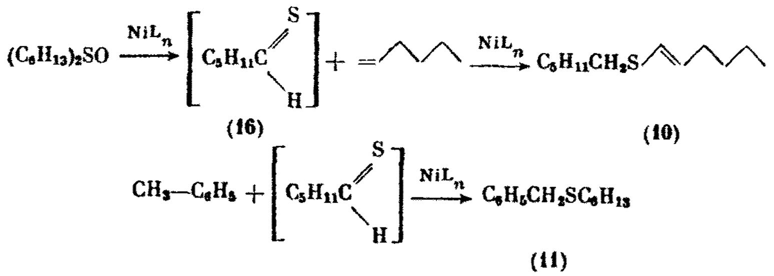
reactions conditions (150°C, 20 h) decomposed to the starting thioaldehyde and CPD [1, 2]:



Reaction of dihexyl sulfoxide with 1,3-cyclohexadiene (CHD) in toluene in the presence of a Ni catalyst likewise failed to afford heterocyclization products, a complex mixture of compounds (10-15) being obtained, the composition of which was dependent on the concentrations of the reactants (Table 4):

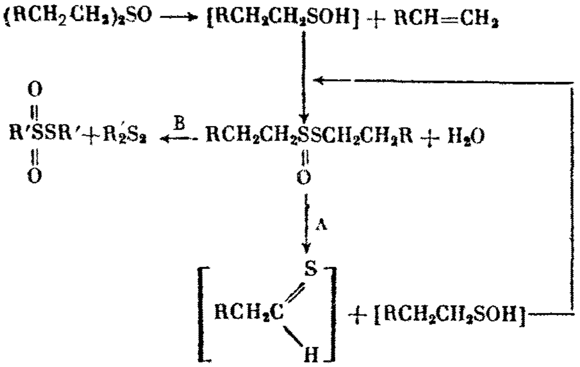


Sulfides (10) and (11) could be formed by addition of the alkylthioaldehyde (16) to hexene or toluene under these conditions in the presence of Ni complexes, as follows:


(16) (10) (11)

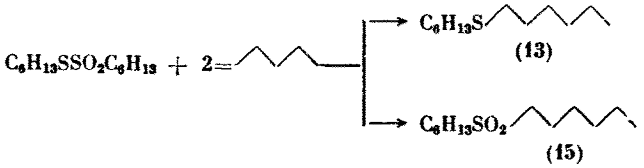
The mechanism of formation of 2-ethyldibenzyl (12), however, is unclear.

Compounds (13), (14), and (15) are probably formed from dihexyl sulfoxide, especially in view of the fact that the sulfoxide undergoes thermal decomposition to give the olefin and the unstable sulfenic acid which apparently disproportionates to the disulfide and thiosulfonate [5]:



Two competing reactions could be involved in these experiments, namely reactions A and B. If the reactivity of the diene towards the thioaldehyde is low, route B is the preferred one. In practice, with linear dienes (butadiene, isoprene, and piperylene) no disproportionation products of the original sulfoxide were formed. If, on the other hand, the diene does not undergo cycloaddition to the thioaldehyde, the disproportionation products predominate, as for example when CHD was used.

Dihexyl sulfone (15) and dihexyl sulfide (13) are probably formed by reaction of dihexyl thiosulfonate with 1-hexene:


(13) (15)

An alternative route to the sulfone (15) is by disproportionation of the sulfoxide to the sulfide (13) and the sulfone (15) in the presence of Ni complexes:

$$2RSOR \xrightarrow{NiL_n} RSR + RSO_2R.$$

We have therefore been able to show that it is possible to generate alkylthioaldehydes in situ from dialkyl sulfoxides in the presence of metal complex catalysts.

This has enabled new catalytic syntheses of substituted dihydrothiapyrans from linear conjugated dienes and dialkyl sulfoxides to be developed. Cyclic dienes have been found not to undergo this reaction.

EXPERIMENTAL

The reactants used were ≥98% pure. Reaction mixtures were analyzed on a Chrom-47 chomatograph with a flame ionization detector, 1.2 m column with SE-30 5%,Inerton-Super carrier, carrier gas helium. PMR spectra were obtained on a Tesla-567 (100 MHz) instrument in $CDCl_3$ relative to TMS. ^{13}C NMR spectra were obtained on a JEOL-90 Q spectrometer with full proton suppression. IR spectra were obtained on a UR-20 spectrophotometer, and mass spectra on an MX-13-06, ionizing electron energy 70 eV, ionization chamber temperature 200°C.

General Method of Preparation of Dihydrothiapyrans. To a solution of 0.05 mmole of $M(acac)_2$ and 0.05 mmole of the activator ligand in 2 ml of dry toluene was added under argon at −10 to −15°C with stirring 0.2 mmole of $AlEt_3$, and the mixture kept for 5-10 min. The solution was then transferred to a cooled ampul in which had previously been placed 10 mmoles of the sulfoxide, 60 mmoles of the diene, and 30 ml of solvent. The ampul was sealed, and heated for 20 h at 150°C. The reaction mixture was treated with 5% hydrochloric acid, passed through a layer of neutral alumina, dried over Na_2SO_4, the solvent removed, and the residue distilled under reduced pressure.

2-Propyl-3,6-dihydro-2H-thiapyran (1a). bp 48-50°C (1 mm), n_D^{20} 1.4930. IR spectrum (cm^{-1}): 980, 1655, 3030 (CH=CH), 1385, 1465, (CH_3). ^1H NMR spectrum (δ, ppm., J, Hz): 0.98 t (CH_3, J = 8.0), 1.37-1.53 m (4H, CH_2), 1.95-2.13 m (2H, CH_2C=C), 2.53-3.23 m (3H, CHS, SCH_2C=C), 5.68-5.75 m (2H, CH=CH). Found: C 67.3, H 10.0, S 22.7%, M^+ 142. $C_8H_{14}S$. Calculated: C 67.6, H 9.9, S 22.5%. M 142.28.

2-n-Pentyl-3,6-dihydro-2H-thiapyran (1b). bp 48-60°C (1 mm), n_D^{20} 1.4950. IR spectrum (cm^{-1}): 980, 1650, 3030 (CH=CH), 1380, 1460 (CH_3). ^1H NMR spectrum (δ, ppm, J, Hz): 0.85 t (CH_3, J = 8.0), 1.23-1.45 m (8H, CH_2), 1.96-2.18 m (2H, CH_2C=C), 2.56-2.76 m (1H, CHS), 2.86-3.38 m (2H, SCH_2C=C), 5.56-5.58 m (2H, CH=CH). Found: C 71.0, H 10.5, S 18.5%. M^+ 170. $C_{10}H_{13}S$. Calculated: C 70.6, H 10.6, S 18.8%. M 170.34.

2-n-Hexyl-3,6-dihydro-2H-thiapyran (1c). bp 85-87°C (1 mm), IR spectrum (cm^{-1}): 980, 1650, 3030 (CH=CH), 1380, 1460 (CH_3). ^1H NMR spectrum (δ, ppm, J, Hz): 0.85 t (CH_3, J = 7.5), 1.24-1.46 m (10H, CH_2), 1.90-2.23 m (2H, CH_2C=C), 2.53-2.76 m (1H, CHS), 2.93-3.33 m (2H, SCH_2C=C), 5.66-5.76 m (2H, CH=CH). Found: C 72.0, H 10.4, S 17.6%. M^+ 184. $C_{11}H_{20}S$. Calculated: C 71.7, H 10.9, S 17.4%. M 184.34.

2-n-Nonyl-3,6-dihydro-2H-thiapyran (1e). bp 130-132°C (1 mm), n_D^{20} 1.4900. IR spectrum (cm^{-1}): 980, 1660, 3030 (CH=CH), 1380, 1460 (CH_3). ^1H NMR spectrum (δ, ppm, J, Hz): 0.83 t (CH_3, J = 8.0), 1.25-1.37 m (16H, CH_2), 1.92-2.25 m (2H, CH_2C=C), 2.48-2.66 m (1H, SCH), 2.95-3.40 m (2H, SCH_2C=C), 5.72-5.73 m (2H, CH=CH). Found: C 74.5, H 11.5, S 14.0%. M^+ 226. $C_{14}H_{26}S$. Calculated: C 74.3, H 11.5, S 14.2%. M 226.46.

2-Phenyl-3,6-dihydro-2H-thiapyran (1f). bp 78-80°C (1 mm), n_D^{20} 1.4920. IR spectrum (cm^{-1}): 725,775, 1600 (Ar), 980, 1660, 3030 (CH=CH). ^1H NMR spectrum (δ, ppm.): 2.48-2.60 m (2H, CH_2C=C), 2.94-3.08 m, 3.45-3.63 m (2H, SCH_2), 3.90-4.04 m (1H, PhCHS), 5.90-5.92 m (2H, CH=CH), 7.2-7.37 m (5H, Ar), ^{13}C NMR spectrum (δ, ppm): 27.68 t (C^6), 33.16 t (C^3), 42.56 d (C^2), 123.89 d (C^{10}), 127.36 d ($C^{8,12}$), 128.20 (C^4), 128.53 d ($C^{9,11}$), 142.30 s (C^7). Found: C 75.1, H 6.6, S 18.3%. M^+ 176. $C_{11}H_{12}S$. Calculated: C 75.0, H 6.8, S 18.2%. M 176.29.

3- (2) and 6-Methyl-2-n-heptyl-3,6-dihydro-2H-thiapyran (3). bp 104-106°C (1 mm). IR spectrum (cm^{-1}): 980, 1650, 3030 (CH=CH), 1385, 1475 (CH_3). ^1H NMR spectrum (δ, ppm): 0.88 m (CH_3), 1.14-1.37 m (CH_2, CH_3), 1.92-2.23 m (CH_2C=C), 2.65-3.70 m (CHS, CH_2C=C), 5.60-5.69 m (CH=CH). ^{13}C NMR spectrum (δ, ppm): 14.14 q (CH_3, C^{13}), 21.08 q and 23.46 q (CH_3, C^{14}), 22.70 t (C^{12}), 25.87 t 27.02 t (C^8, C^6-2a) 29.26 t (C^{10}), 29.53 t (C^9), 31.86 t (C^{11}), 32.45 t, 33.05 t(C^7), 35.06 t, 35.22 t, 35.65 t (C^3-2b, C^6-2b, C^2-2a), 40.15 d (C^2-2a), 126.40 d, 127.16, 130.30 d, 131.17 d (C^4, C^5). Found: C 73.2, H 11.6, S 15.2%. M^+ 212. $C_{13}H_{24}S$. Calculated: C 73.6, H 11.3, S 15.10%. M 213.43.

4- (4) and 5-Methyl-2-n-heptyl-3,6-dihydro-2H-thiapyran (5). bp 85-90°C (1 mm). ^1H NMR (δ, ppm): 0.89 m (CH_3), 1.29-1.49 m (CH_2), 1.71 s (CH_3C=C), 2.04-2.33 m (CH_2C=C), 2.46-3.26 m (CHS, CH_2C=C), 5.56 m (1H, CH=C). ^{13}C NMR spectrum (δ, ppm): 14.09 q (C^{13}), 22.67 q (C^{12}), 24.23 q, 24.75 q (C^{14}), 26.35 t, 27.09 t, 29.52 t, 29.86 t, 33.42 t, 35.15 t, 35.41 t, 37.88 t (C^3, C^6, C^7, C^8, C^9), 29.31 t (C^{10}), 31.81 t (C^{11}), 38.19 d, 39.10 d (C^2), 117.72 d (C^4-5), 122.18 d (C^5-4), 130.64 d (C^4-4), 134.93 d (C^5-5). Found: C 73.3, H 11.7, S 15.0%. M^+ 212. $C_{13}H_{24}S$. Calculated: C 73.6, H 11.3, S 15.10%. M 213.43.

4,5-Dimethyl-2-n-heptyl-3,6-dihydro-2H-thiapyran (6). bp 108-110°C (1 mm), n_D^{20} 1.4840. ^1H NMR spectrum (δ, ppm, J, Hz): 0.88 t (CH_3, 8.0), 1.14-2.28 m (15H, CH_2, CH_3), 1.67-2.19 m (CH_2C=C), 2.40-3.34 m (3H, CHS, SCH_2C=C). Found: C 74.0, H 12.0, S 14.0%. M^+ 226. $C_{14}H_{26}S$. Calculated: C 74.3, H 11.5, S 14.2%. M 226.46.

3- (7) and 6-Methoxycarbonyl-2-n-heptyl-3,6-dihydro-2H-thiapyran (8). bp of mixture 125-128°C (1 mm). IR spectrum (cm^{-1}): 980, 1660, 3030 (CH=CH), 1380, 1460 (CH_3), 1735, 1260 (CO_2R). ^{1}H NMR spectrum (δ, ppm): 0.90 m (CH_3), 1.18-1.68 m (CH_2, CH_3), 2.08-2.22 m (CHC=C), 2.58-2.80 m (CHS), 3.02-3.36 m (SCHC=C), 3.40-3.62 m (RO_2CH–C=C), 3.58 s, 3.63 s (CH_3O_2C), 5.72-5.75 m (CH=CH). M$^+$ 270. $C_{15}H_{26}O_2S$. M 270.47.

Compounds (10-14) were isolated by preparative GLC on a Perkin-Elmer F-2 apparatus, column 5 m × 8 mm with SE-30 (5%) on Chromaton N-AW–DMCS 0.2-0.25, carrier gas helium.

1-Hexenyl Hexyl Sulfide (10). IR spectrum (ν, cm^{-1}): 995, 1620, 3200 (trans-CH=CH), 1380, 1460 (CH_3). ^{1}H NMR spectrum (δ, ppm, J, Hz): 0.89 t ($2CH_3$, 6.5), 1.34-1.40 m (12H, CH_2), 2.0-2.74 m (2H, CH_2C=C), 2.64 t (2H SCH_2, 7.0), 5.58-5.84 m (2H, CH=CH). Found: C 71.8, H 12.1, S 16.1%. M$^+$ 200. $C_{12}H_{24}S$. Calculated: C 72.0, H 12.0, S 16.0%. M 200.42.

Benzyl Hexyl Sulfide (11). ^{1}H NMR spectrum (δ, ppm, J, Hz): 0.9 t (CH_3, 7.0), 1.25-1.40 m (6H, CH_2), 1.50-1.65 m (2H, CH_2), 2.45 t (2H, SCH_2, 7.5), 3.70 s (2H, $PhCH_2S$), 7.25-7.35 m (5H, Ar). ^{13}C NMR spectrum (δ, ppm): 14.01 q (C^1), 22.54 t (C^2), 28.58 t (C^5), 29.25 t (C^4), 31.44 t (C^3), 31.49 t (C^6), 36.38 s (C^7), 126.86 d (C^{11}), 128.45 d ($C^{9,13}$), 128.85 d ($C^{10,12}$), 138.74 (C^8). M$^+$ 208. $C_{13}H_{20}S$. M 208.39.

The physicochemical constants for dihexyl sulfide (13), dihexyl disulfide (14), dihexyl sulfone (15), and 2-n-heptyl-3,6-dihydro-2H-thiapyran (1d) were in accordance with the literature data [6] and [3]. The mass spectrum of 2-ethylbiphenyl (12) was in agreement with that reported [7].

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