CONCLUSIONS

1. A paramagnetic model of mescaline, viz., 1-oxyl-2,2,6,6-tetramethyl-4-(β-aminoethyl)piperidine, has been synthesized by two methods: with the use of a trifluoroacetyl protective group or reduction of 1-oxyl-2,2,6,6-tetramethyl-4-carbamidomethylenepiperidine.

2. The methylation of the amino group in this radical resulted in a decrease in toxicity and the loss of the psychotomimetic properties.

3. The methylated iodide of 1-oxyl-2,2,6,6-tetramethyl-4-(β-dimethylaminoethyl)piperidine, which can be used to study the permeability of biological membranes, has been synthesized.

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2,6-BISORGANYLSULFONYL-1,4-DITHIAFULVENES

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UDC 542.91:547.379.53:547.738

The geminal dichloroethylenes $CCl_2=CH-XR$, where X is $C=O$ or SO_2, are characterized by high reactivity of the chlorine atoms, which are activated by electron-acceptor substituents. For example, they readily react with various nucleophiles, forming acyl and sulfonyl derivatives [1-4], as well as nitrogen- or sulfur-containing heterocyclic compounds [3, 5, 6]. We have previously found [5] that the reactions of organyl β, β-dichlorovinyl ketones with sodium sulfide and salts of thioacetic, alkylxanthic, and dialkyldithiocarbamic acids yield 2,4-diacyl-1,3-dithiethanes and 2,6-diacyl-1,4-dithiafulvenes.

In the present work we carried out the first study of the reactions of the organyl β,β-dichlorovinyl sulfones $CCl_2=CHSO_2R$ (R = alkyl, aryl) with sodium sulfide, potassium ethylxanthate, and potassium butylxanthate in an ethanolic medium at 20-30°C with sulfone–nucleophile ratios from 1 : 1 to 1 : 2. The reaction products, as in the case of organyl β,β-dichlorovinyl ketones, correspond in composition to the dimers of organylsulfonylthioketenes $(RSO_2CH=C=S)_2$. An analysis of the IR and PMR spectra of the synthesized compounds shows that, regardless of the nature of the sulfur-containing nucleophile, the reactions yield 2,6-bisorganylsulfonyl-1,4-dithiafulvenes I-VI:

Irkutsk Institute of Organic Chemistry, Siberian Branch of the Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 368-372, February, 1980. Original article submitted December 13, 1978.

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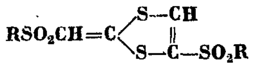
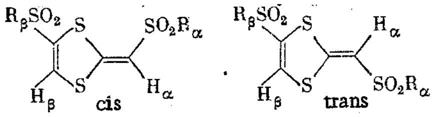
TABLE 1. Constants of the Compounds Synthesized 

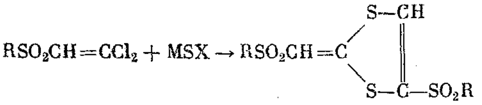
Compound	R	Yield, % in reaction with		Isomeric comp., %		mp, °C	Found, %			Empirical formula	Calc., %		
		Na_2S	KSC(=S)OR¹ *	cis	trans		C	H	S		C	H	S
(I)	Et	–	35	90 60	10 40	112–115 125–125,5	31,83 31,30	3,99 4,28	42,31 41,99	$C_8H_8O_4S_4$ $C_8H_8O_4S_4$	31,98 31,98	4,02 4,02	42,65 42,65
(II)	*n*-Pr	87	40	65 20	35 80	100–101 127–128	36,25 36,51	4,91 4,45	39,24 38,53	$C_{10}H_{16}O_4S_4$ $C_{10}H_{16}O_4S_4$	36,55 36,55	4,91 4,91	39,04 39,04
(III)	*n*-Bu	51	34	35 –	65 100	102–104 125–126	40,13 40,93	5,44 5,35	35,85 36,19	$C_{12}H_{20}O_4S_4$ $C_{12}H_{20}O_4S_4$	40,42 40,42	5,64 5,64	35,97 35,97
(IV)	*n*-C_6H_{13}	–	42	–	–	128–129	46,55	6,79	30,98	$C_{16}H_{28}O_4S_4$	46,57	6,84	31,08
(V)	Ph	–	39	–	–	168–170	48,52	3,46	32,68	$C_{16}H_{12}O_4S_4$	48,46	3.05	32,34
(VI)	$PhCH_2$	45	45	100 55	– 45	107–108 223–224	49,44 49,38	3,76 3,59	29,66 29,22	$C_{18}H_{16}O_4S_4$ $C_{18}H_{16}O_4S_4$	50,87 50,87	3,79 3,79	30,21 30,21

* R^1 = Et, n-Bu.

TABLE 2. Parameters of the PMR Spectra of 2,6-Bisorganylsulfonyl-1,4-dithiafulvenes



Compound	R	Isomer	Solvent	Chemical shifts, δ, ppm						
				H_α	H_β	R				
						$(CH_2)_\alpha$	$(CH_2)_\beta$	Me_α	Me_β	Ph
(I)	Et	cis	$CDCl_3$	6,21	7,38	3,05	3,20	1,35	1,38	
		trans		6,22	7,36	3,05	3,20	1,35	1,38	
(II)	*n*-Pr	cis	$CDCl_3$	6,21	7,38	3,03 1,80	3,11 1,90	1,05	1,09	
		trans		6,22	7,36	3,01 1,80	3,11 1,90	1,05	1,09	
(III)	*n*-Bu	cis	$CDCl_3$	6,20	7,38	3,03 1,58	3,13	0,97		
		trans		6,22	7,36	3,03 1,58	3,13	0,97		
(III)	*n*-Bu	cis	MeOH	6,49	7,59	–		–		
		trans		6,49	7,53	–		–		
(III)	*n*-Bu	cis	Me_2SO	6,96	7,95	–		–		
		trans		6,97	7,93					
(III)	*n*-Bu	–	CF_3COOH	5,87	7,41	3,03 1,30		0,90		
(IV)	C_6H_{13}	cis	$CDCl_3$	6,20	7,36	3,00 1,36	3,13	0,95		
		trans		6.21	7,37	3,00 1,36	3,13	0.95		
(V)	Ph	–	$(CD_3)_2SO$	6.65	7.85	–		–		7,3–8,0
(VI)	$PhCH_2$	cis	Me_2SO	6.80	7,58	4.51	4.77	–		
		trans		6,79	7.54	4,51	4,84	–		

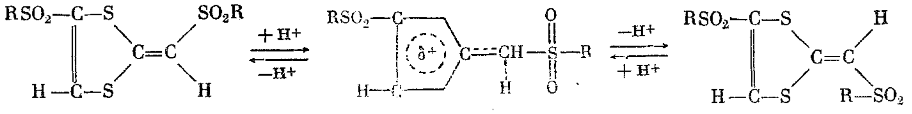


$$RSO_2CH{=}CCl_2 + MSX \rightarrow RSO_2CH{=}C\begin{cases} S{-}CH \\ S{-}C{-}SO_2R \end{cases}$$

M = Na, K; X = Na, C(= S)OEt, C(= S)OBu; R = Et (I), Pr (II), Bu (III), C_6H_{13} (IV), Ph (V), $PhCH_2$ (VI)

The constants of the products are given in Table 1.

The parameters of the PMR spectra of compounds I-VI (Table 2) are consistent with the literature data for 2,6-diacyl-1,4-dithiafulvenes [5], as well as alkyl- and aryl-substituted 1,4-dithiafulvenes, which were obtained by photolysis or thermolysis of 1,2,3-thiadiazoles [7]. Compounds I-VI, like the 2,6-diacyl-1,4-dithiafulvenes, exist in the form of cis and trans isomers (see Table 2). The PMR spectra of one of them shows spin–spin coupling of the olefinic protons (in $CDCl_3$, $J^5_{H_3H_6} \cong 1.4$ Hz), just as in the case of 2,6-diacyl-1,4-dithiafulvenes [5]. According to [8], J^5 is realized in the trans isomer. The ratio between the isomers, according to the data in the PMR spectra, depends on the conditions for the synthesis and isolation of the reaction products. For example, under the action of a catalytic amount of acid, solutions of I-VI display displacement of the isomeric equilibrium toward the trans isomer, which is apparently due to the easy isomerization in the protonated form:



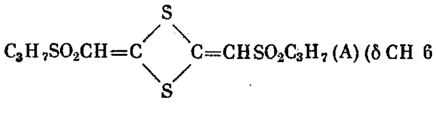
In the PMR spectra of I-VI in CF_3COOH the signals of the olefinic protons are strongly broadened, but unlike the acyl analogs [5], there is no significant downfield shift. This is due to the protonation of the double bond, rather than a chemical change in the original sulfonyldithiafulvene, since the PMR spectrum of III regenerated from a solution in CF_3COOH is characterized by the original parameters.

The IR spectra of compounds I-VI contain intense absorption bands of the SO_2 (1120-1140 and 1300-1320 cm^{-1}), C = C (1510, 1565 cm^{-1}), and =CH (3060, 3070, 3100 cm^{-1}) groups.

Thanks to the different solubilities of the cis and trans isomers of I-VI in organic solvents, upon recrystallization it was possible to obtain fractions enriched with one of the isomers with melting points different by 10–30°C (see Table 1), but identical elemental compositions and IR spectra. The isomeric composition was determined from the PMR data.

Compounds I-VI are white crystalline odorless substances, which are insoluble in water and soluble in DMSO, $CHCl_3$, ethanol, and CCl_4. They are stable during storage in the dark, but in the light or under UV irradiation they rapidly change color to orange and bright red. Unlike the acyl analogs [5], they are not paramagnetic.

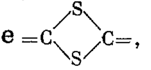
The yield of products I-VI depends on the nature of the sulfur-containing nucleophile: With $Na_2S \cdot 9H_2O$ in EtOH it reaches 87%, and with alkyl xanthate it decreases to 35-40%. In order to understand the latter finding, we recorded the PMR spectrum of a reaction mixture of propyl β,β-dichlorovinyl sulfone with potassium butylxanthate in EtOH. Along with the signals of the olefinic protons and the C_3H_7 group in dithiafulvene II, this spectrum shows signals with shifts equal to 8.56, 8.21, 6.78, and 6.10 ppm with an overall integral intensity equal to 10% of the main product. A comparison with the spectrum of 2,4-diacetyl-1,3-dithiethane [5] [δ(CH) = 6.50 ppm] allows us to postulate the presence of the corresponding symmetric sulfonyl compound,


(A) (δ CH 6,78 ppm)

along with the products of unknown structure in the reaction mixture. Similar symmetric compounds were obtained, for example, as a result of the dimerization of individual bistrifluoromethyl- and di-tert-butylthioketenes [7], and the formation of asymmetric compounds like I-VI is associated with the conversion of intermediate acetylene thiols [7, 9, 10]. The formation of acetylene intermediates was detected during the synthesis of 2,6-dialkyl(aryl)-1,4-dithiafulvenes by the decomposition of thiadiazoles in [9, 10].

We carried out the reaction of butyl β,β-dichlorovinyl sulfone with potassium ethylxanthate in absolute dioxane. The IR spectrum of the precipitate formed from the reaction medium did not contain absorption bands of a triple bond, attesting to the absence of salts with the general formula $RSO_2C \equiv C-SK$. At the same time, the PMR spectrum of this reaction mixture showed the characteristic signals of the cis and trans isomers of dithiafulvene III.

Thus, the reaction of organyl β,β-dichlorovinyl sulfones with Na_2S results in the synthesis of previously unknown 2,6-bisorganylsulfonyl-1,4-dithiafulvenes and is a one-step preparative method for their synthesis. The reaction of dichlorovinyl sulfones with potassium alkylxanthate is ambiguous, although the formation of 1,4-dithiafulvenes under the conditions investigated is also the main direction of the reaction.

It is known [5] that the yield of 2,4-diacyl-1,3-dithiethanes in the reactions of β,β-dichlorovinyl ketones with potassium alkylxanthates is ≈ 40-45%. The corresponding sulfonyl dithiethanes (A), if they form, form only in insignificant amounts. This is apparently due to the stabilization of the stressed heterocycle , by conjugation with a carbonyl group, which is weakened (or absent) in the case of the sulfonyl group.

EXPERIMENTAL

The PMR spectra were recorded on a Tesla BS-487C spectrometer (80 MHz) for 3-5% solutions of the compounds. The internal references were HMDS and TMS. The IR spectra were recorded on a UR-20 spectrophotometer in tablets with KBr.

2,6-Dipropylsulfonyl-1,4-dithiafulvene (II). a. A solution of 13 g of propyl β,β-dichlorovinyl sulfone in 100 ml of ethanol was given an addition of 18 g (20% excess) of $Na_2S \cdot 9H_2O$ in small portions so that the reaction temperature did not exceed 30°C. After 6 h the reaction mixture was poured into water, acidified with 1-2 ml of concentrated HCl, and left to stand overnight. On the next day the precipitate was filtered, washed with H_2O, and dried. This yielded 9.3 g of II (see Table 1).

b. A solution of 13 g of propyl β,β-dichlorovinyl sulfone in 100 ml of ethanol was given an addition of 20.5 g of potassium ethylxanthate in small portions. The reaction mixture was stirred for 6 h, and on the next day it was poured into H_2O and acidified with 2 ml of conc. HCl. The organic layer was separated, and the aqueous layer was extracted with ether. The combined extract and the organic layer were dried with $MgSO_4$, the ether was distilled off, and the residue was washed repeatedly with petroleum ether and then with diethyl ether. The residue yielded 4.0 g of dithiafulvene II. The decomposition product of potassium butylxanthate $(BuOCS)_2$ with bp 100-108°C (1-1.5 mm) and n_D^{20} 1.5160 was recovered from the petroleum ether by distillation. Found: C, 53.85; H, 8.44; S, 30.98%. Calculated for $C_{10}H_{18}O_2S_2$: C, 51.24; H, 7.74; S, 27.36%.

The PMR spectrum has signals for the protons of the BuO group. IR spectrum (ν, cm^{-1}): 1050-1100 (C–O–C), 1200 [C(=S)–O–], 1460 (def. C–H), 2880, 2940, 2960 (C–H). Distillation of the ether yielded a mixture of conversion products of the sulfone, which could not be separated by distillation.

Dithiafulvenes I and III-VI were obtained in a similar manner (see Table 1).

2,6-Diethylsulfonyl-1,4-dithiafulvene (I). This compound was synthesized from 3.8 g (0.02 mole) of ethyl β,β-dichlorovinyl sulfone and 6.4 g (0.04 mole) of potassium ethylxanthate. The yield was 1 g.

2,6-Dibutylsulfonyl-1,4-dithiafulvene (III). This compound was synthesized from 5.2 g of the sulfone and 6.9 g of $Na_2S \cdot 9H_2O$ or from 4 g of the sulfone and 8.8 g of potassium butylxanthate. The yields were 2.2 and 1.1 g of III, respectively.

2,6-Dihexylsulfonyl-1,4-dithiafulvene (IV). This compound was obtained from 3.2 g of hexyl β,β-dichlorovinyl sulfone and 6.4 g of potassium butylxanthate. The yield was 1.04 g of IV.

2,6-Diphenylsulfonyl-1,4-dithiafulvene (V). This compound was obtained from 2.4 g of phenyl β,β-dichlorovinyl sulfone and 3.7 g of potassium butylxanthate. The yield was 0.78 g of V.

2,6-Dibenzylsulfonyl-1,4-dithiafulvene (VI). This compound was obtained by reacting 1 g of benzyl sulfone with 1.5 g of potassium butylxanthate or with 1.2 g of $Na_2S \cdot 9H_2O$. The yield was 0.63 or 0.40 g, respectively.

CONCLUSIONS

The reactions of organyl β,β-dichlorovinyl sulfones with sulfur-containing nucleophiles, viz., sodium sulfide and salts of alkylxanthic acids, have been studied. A preparative method for synthesizing heretofore unknown 2,6-bisorganylsulfonyl-1,4-dithiafulvenes from organyl β,β-dichlorovinyl sulfones and $Na_2S \cdot 9H_2O$ in ethanol has been proposed. The isomeric composition of the compounds synthesized was studied, and their easy isomerization in an acidic medium has been established.

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