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E. G. KATAEV and F. R. TANTASHEVA

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Abstract

Full Text

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DIVINYL SULFOXIDE AND DIVINYL SULFONE IN THE DIENE-SYNTHESIS REACTION WITH SYMMETRICAL DIENES

(Presented by Academician B. A. Arbuzov, July 15, 1961)

It is known that vinyl alkyl-, vinyl aryl sulfones and thiovinyl ethers contain an active double bond and are capable of entering into diene condensation with a number of dienes ([1–4]). Unsaturated sulfoxides, as a rule, in nucleophilic-addition reactions are less active than unsaturated sulfones, but more active than sulfides ([5]). However, the ability of unsaturated sulfoxides to undergo diene-synthesis reactions has not been studied up to now.

It seemed of interest to us to consider diene-synthesis reactions with divinyl sulfoxide (I), which is also of interest because it contains two equivalent vinyl groups and, thus, by varying the ratio of the addends, one may expect the formation of both mono- and bis-adducts. For this purpose we studied diene-synthesis reactions of (I) with divinyl (II), 2,3-dimethylbutadiene-1,3 (III), and cyclopentadiene (IV) under different temperature conditions (100–185°) and at different ratios of diene and dienophile (see Table 1).

Table 1

No.	Ratio of dienophile : diene, mol	Reaction temp., °C	Reaction duration, h	Yield, %
1	I : II = 0.078 : 0.29	140–145	20	27
2	I : III = 0.078 : 0.158	135–140	8	36
3	I : IV = 0.051 : 0.045	95–100	1.5	90
4	I : IV = 0.078 : 0.157	140–145	7	72

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No.	Ratio of dienophile : diene, mol	Reaction temp., °C	Reaction duration, h	Yield, %
5	V : II = 0.051 : 0.047	100–110	8	78
6	V : III = 0.034 : 0.024	70–75	3	72
7	V : IV = 0.051 : 0.045	70–75	2	45
8	V : II = 0.038 : 0.184	130–135	9	100
9	V : III = 0.034 : 0.072	130–132	5	98
10	V : IV = 0.019 : 0.045	170–185	9	60

It turned out that I enters into diene synthesis with the listed dienes with varying ease, depending on the position of the diene in the usual activity series II < III < IV. However, while with cyclopentadiene divinyl sulfoxide gives both mono- and bis-adducts, depending on the ratio of the starting components and the temperature conditions, with divinyl and 2,3-dimethylbutadiene-1,3 we were able to obtain only products of addition at one vinyl group of the sulfoxide (see Table 2). Raising the reaction temperature, increasing the duration of its course, and using a solvent with an excess of diene did not lead to formation of the bis-adduct. In this connection, it was undoubtedly of interest to study the reactivity of divinyl sulfone (V) in analogous reactions. It turned out that, in contrast to I, divinyl sulfone gives two series of adducts not only with IV, but also with II and III (see Table 2). Thus, the reason for the absence of dienophilic activity of the vinyl group in mono-adducts of divinyl sulfoxide remains unclear for the time being and requires further study. To characterize I, V, their mono- and bis-adducts, and also to establish the presence of a free vinyl group in the mono-adducts, we studied their infrared spectra (see Table 3).

E. N. Prilezhaeva et al. ([6]) give the values of the frequencies of stretching vibrations of the C=C bond for a series of vinyl alkyl sulfoxides and sulfones and note that these frequencies are appreciably lowered relative to the frequencies of stretching

Table 2

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No.	R_1	R_2	R_3	R_4	R	Name of adduct	b.p., °C at $1.5–2 \cdot 10^{-2}$ mm	m.p., °C	n_D^{20}	d_4^{20}	MR_D, found	MR_D, calc.	C, % found	C, % calc.	H, % found	H, % calc.	S, % found	S, % calc.	Empirical formula
						Adducts of the diene synthesis of divinyl sulfoxide													
1	H	H	H	H	$-CH=CH_2$	Cyclohexen-3-yl vinyl sulfoxide	76–78		1.5449	1.1746	46.20	44.86	61.28	61.53	7.70	7.69	19.83	20.51	$C_8H_{12}OS$
2	H	H	CH_3	CH_3	$-CH=CH_2$	4,4-Dimethylcyclohexen-3-yl vinyl sulfoxide	78–80		1.5358	1.0584	54.22	53.96	65.96	65.16	8.90	8.75	16.57	17.39	$C_{10}H_{16}OS$
3	H	CH$_3$	H	H	$-CH=CH_2$	Bicycloheptenen-3-yl vinyl sulfoxide	85–87		1.5451	1.1246	47.34	47.13	—	—	—	—	19.10	19.05	$C_9H_{12}OS$

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No.	R_1	R_2	R_3	R_4	R	Name of adduct	b.p., °C at $1.5–2 \cdot 10^{-2}$ mm	m.p., °C	n_D^{20}	d_4^{20}	MR_D found	MR_D calc.	C, % found*	C, % calc.	H, % found	H, % calc.	S, % found	S, % calc.	Empirical formula
4	H	CH	H	H	[[unde-	Di-1,2-	122–84						72.08	71.73	7.68	7.69	12.96	13.68	$C_{14}H_{18}OS$
	—	—			bi-	[2,2,1]-			—	—	—	—							
		H			cyclo-	bicyclohepten-													
					struc-	3-													
					tural	yl													
					for-	sul-													
					mula	fox-													
					with	ide													
					CH_2														
					bridge]]														
						Adducts of the diene synthesis of divinyl sulfone													
1	H	H	H	H	—CH=	Cyclo-	88–90		1.5120	1.0164	46.37	44.61					18.28	18.61	$C_8H_{12}O_2S$
						3-			—										
						yl													
						vinyl													
						sul-													
						fone													
2	H	H	H	H	[[unde-	Dicyclohexen-	141						63.45	63.68	8.13	8.02	13.65	14.81	$C_{12}H_{18}O_2S$
					cy-	3-			—	—	—	—							
					clo-	yl													
					hex-	vinyl													
					enyl-	sul-													
					stru-	fone													
					tural														
					for-														
					mula]]														

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No.	R_1	R_2	R_3	R_4	R	Name of adduct	b.p., °C at $1.5–2 \cdot 10^{-2}$ mm	m.p., °C	n_D^{20}	d_4^{20}	MR_D, found	MR_D, calc.	C, % found*	C, % calc.	H, % found	H, % calc.	S, % found	S, % calc.	Empirical formula
3	H	H	CH_3	CH_3	$-CH=CH_2$	(3,4-Dimethyl-3)-yl vinyl sulfone	103–104	—	1.5119	1.1323	53.13	53.85					15.85	16.00	$C_{10}H_{16}O_2S$

No.	Visible substituents / fragment	Compound	Formula	Visible analytical / physical data
4	H; H; CH_3; CH_3	Di-(3,4-dimethylcyclohexen-3-yl)sulfone	$C_{16}H_{26}O_2S$	11.35; 11.12
5	H; H; $-CH_2-$H; H; $-CH-CH_2$	[2,2,1]-Bicyclohepten-3-yl vinyl sulfone	$C_9H_{12}O_2S$	17.40; 17.24; —; —; —; 47.03; 46.50; 1.2136; 1.5247; 110–112; —
6	H; H; $-CH_2-$H; H; $-CH_2-$H	Di-[2,2,1]-bicyclohepten-3-yl sulfone	$C_{14}H_{18}O_2S$	12.81; 12.26; 7.25; 7.31; 67.12; 67.49; —; —; —; —; 76

* Group values are given for SO 8.70, for SO_2 8.60 (calculated from the data of the work).

** Analysis for sulfur was carried out by the method of H. V. Sokolova and V. A. Orestova ([10]), improved by NIMRP.

vibrations of the C=C bond of olefinic hydrocarbons. As follows from Table 3, in the case of divinyl sulfoxide and sulfone and their mono-adducts these frequencies are still further lowered: $\nu_{C=C}$ 1607 cm^{-1} in the sulfone and 1595 cm^{-1} in the sulfoxide. The presence of absorption bands in the region of the stretching vibrations of C=C and the out-of-plane deformation vibrations of

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the C–H bond of the methylene group in $RCH=CH_2$ (960-930 cm^{-1}) for the mono-adducts indicates the preservation of one free vinyl group.

Along with this, the appearance of a rather intense absorption band in the region of 1651 cm^{-1}, characteristic of the stretching vibrations of the C=C bond in the cyclohexene ring, and in the region of 1569 cm^{-1} in the bicycloheptene ring, indicates the formation of the corresponding rings ([7]). In the spectra of the bis-adducts, absorption bands characteristic of the free vinyl group are absent.

For taking the infrared spectra, the authors express their gratitude to E. G. Yarkova and R. M. Mamina.

Experimental Part

Divinyl sulfoxide was obtained by the method described by Ford-Moore ([5]). B.p. 61°/4 mm; n_D^{20} 1.5143; d_4^{20} 1.0800. Literature data: b.p. 67-68°/5-6 mm; n_D^{20} 1.5100; d_4^{20} 1.0810.

Divinyl sulfone was synthesized by the procedure of Overberger et al. ([8]). B.p. 104-105°/10 mm, n_D^{20} 1.4772; d_4^{20} 1.1781. Literature data for divinyl sulfone ([9]): b.p. 110°/17 mm; n_D^{20} 1.4782; d_4^{20} 1.1790.

Diene-synthesis reactions were carried out in sealed tubes, in an atmosphere of CO_2, in the presence of hydroquinone, under the conditions given in Table 1. All mono-adducts of both divinyl sulfoxide and divinyl sulfone are viscous oily liquids, while the bis-ad-

Table 3

Spectral characteristics of the mono-adducts of divinyl sulfoxide and divinyl sulfone

No.	Name of adduct	ν, cm^{-1}	Assignment of frequencies
1	Cyclohexen-3-yl vinyl sulfoxide	1651 s	Stretching vibrations of C=C of the cyclohexene ring
1	Cyclohexen-3-yl vinyl sulfoxide	1593 med.	Stretching vibrations of C=C of the vinyl group
1	Cyclohexen-3-yl vinyl sulfoxide	1036 v.s.	Stretching vibrations of the S–O bond

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No.	Name of adduct	ν, cm^{-1}	Assignment of frequencies
1	Cyclohexen-3-yl vinyl sulfoxide	960, 932 v.s.	Out-of-plane deformation vibrations of C–H of the vinyl group
2	[2,2,1]-Bicyclohepten-3-yl vinyl sulfoxide	1598 med.	Stretching vibrations of C=C of the vinyl group
2	[2,2,1]-Bicyclohepten-3-yl vinyl sulfoxide	1569 w.	Stretching vibrations of C=C of the bicycloheptene ring
2	[2,2,1]-Bicyclohepten-3-yl vinyl sulfoxide	1048 v.s.	Stretching vibrations of the S–O bond
2	[2,2,1]-Bicyclohepten-3-yl vinyl sulfoxide	960, 930 s.	Out-of-plane deformation vibrations of C–H of the vinyl group
3	Cyclohexen-3-yl vinyl sulfone	1647 med.	Stretching vibrations of C=C of the cyclohexene ring
3	Cyclohexen-3-yl vinyl sulfone	1607 med.	Stretching vibrations of C=C of the vinyl group
3	Cyclohexen-3-yl vinyl sulfone	1300 v.s.	Asymmetric vibrations of SO_2
3	Cyclohexen-3-yl vinyl sulfone	1124 v.s.	Symmetric vibrations of SO_2
3	Cyclohexen-3-yl vinyl sulfone	979, 935 s.	Out-of-plane deformation vibrations of C–H of the vinyl group

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No.	Name of adduct	ν, cm^{-1}	Assignment of frequencies
4	3,4-Dimethylcyclohexen-3-yl vinyl sulfone	1648 w.	Stretching vibrations of C=C of the cyclohexene ring
4	3,4-Dimethylcyclohexen-3-yl vinyl sulfone	1610 med.	Stretching vibrations of C=C of the vinyl group
4	3,4-Dimethylcyclohexen-3-yl vinyl sulfone	1307 v.s.	Asymmetric vibrations of SO_2
4	3,4-Dimethylcyclohexen-3-yl vinyl sulfone	1120 v.s.	Symmetric vibrations of SO_2
4	3,4-Dimethylcyclohexen-3-yl vinyl sulfone	974, 930 s.	Out-of-plane deformation vibrations of C –H of the vinyl group
5	2,2,1-Bicyclohepten-3-yl vinyl sulfone	1613 med.	Stretching vibrations of C=C of the vinyl group
5	2,2,1-Bicyclohepten-3-yl vinyl sulfone	1569 w.	Stretching vibrations of C=C of the bicycloheptene ring
5	2,2,1-Bicyclohepten-3-yl vinyl sulfone	1305 v.s.	Asymmetric vibrations of SO_2
5	2,2,1-Bicyclohepten-3-yl vinyl sulfone	1115 v.s.	Symmetric vibrations of SO_2
5	2,2,1-Bicyclohepten-3-yl vinyl sulfone	974, 951 s.	Out-of-plane deformation vibrations of C –H of the vinyl group

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Note. v.s. —very strong; med. —medium; w. —weak.

products are white crystalline substances of needle-like form. The bis-adducts were recrystallized from a mixture of benzene with petroleum ether in a ratio of 1:2. All bis-adducts are readily soluble in acetone, benzene, and carbon disulfide; moderately soluble in chloroform and carbon tetrachloride; sparingly soluble in ether; insoluble in petroleum ether and gasoline.

Infrared spectra were recorded on double-beam spectrometers IKS-14 (region 3000 cm^{-1}, LiF prism) and H-800 Hilger (region 700-2000 cm^{-1}, NaCl prism), in film or in CCl_4 solution.

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