the aldehydes. Thus, at 400° on Nd<sub>2</sub>O<sub>3</sub> the yield of isobutyraldehyde from IBP decreases in the presence of water from 14 to 8%, while the yield of ethyl isopropyl ketone simultaneously increases from 2 to 13%. When PIB is decomposed in the presence of water the yield of the catalyzate increases and the total conversion decreases due to a decrease in the yield of diisopropyl ketone and cracking products. The alcohol/ketone ratio in the catalyzate increases noticeably. The ketone is not formed on  $Er_2O_3$  at 375°, and on Nd<sub>2</sub>O<sub>3</sub> at 350°.

As a result, in the studied temperature range the esters are transformed on the Nd and Er oxides to give aldehydes, as well as alcohols and ketones, in which connection the latter direction predominates, especially on  $\text{Er}_2O_3$ , at low temperatures, and also in the presence of water in the case of the straight-chain esters. In contrast to the results for a Cu catalyst [2], the data obtained by us on rare-earth oxides permit making the postulation that, besides the aldol and ester scheme, primary alcohols can undergo ketonization. In such case the formation of n-butanol from butyraldehyde [5] can be due to the decomposition of butyl butyrate. It was shown by special experiments that butyral is not hydrogenated under these conditions. The absence of noticeable amounts of butyl butyrate in the transformation products of butanol [4] and butyraldehyde [5] can be due to its greater tendency to decompose when compared with desorption in the gas phase.

#### CONCLUSIONS

Esters are transformed on the neodymium and erbium oxides to give aldehydes, as well as alcohols and ketones, in which connection the latter direction predominates. Transformation products that differ in composition are formed from the metameric esters. Neodymium oxide is much more active than erbium oxide.

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REACTION OF 3-SULFOLENE WITH 1,3-DIENES, CATALYZED BY PALLADIUM COMPLEXES

R. V. Kunakova, F. V. Sharipova, G. A. Tolstikov, L. M. Zelenova, A. A. Panasenko, L. V. Spirikhin, and U. M. Dzhemilev

It was recently shown by us that a mixture of the cis-trans-2,5-divinylsulfolanes (I) can be obtained by the reaction of 3-sulfolenes with butadiene in the presence of complex Pd-containing catalysts [1, 2]:



To expand the utility range of the given method for obtaining the (I) derivatives, and also to study the effect of the structure of the 1,3-diene on the direction and structural selectivity of the indicated reaction, we studied the reaction of 3-sulfolene with isoprene, trans-piperylene, 1-acetoxy-1,3-butadiene (AB), and the methyl ester of butadiene-1-carboxy-

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Com-											φ, [	ррт							Amount in mix-
punod	R	R²	ц.	R4	Isomer	H3	H <sup>5</sup>	н	H <sup>3′</sup>	ŶŶ	H	H <sup>4'</sup>	Δð	CH <sub>3</sub> C=	CH3C	CH2=C	CH2=C	CH2=CH	ture, %
* (I) *	CH2=CH	CH2=CH	H	H	trans	3,55 m	3,55 m	1,92 m	2,32m	0,40	2,32 m	1,92 m	0,40				5,35 m 5,35 m	5,72 m 5,72 m	0,75 0.95
(II)	$CH_2 = CH$	CH2-CCH3	Ш	H	trans	3,71m	3,63 m	2,14 m	2,28 m	0,14	2,28	2,35	0,07	1,95 s	1	5,10 s	5,45 m	5,82 m	10,97
(111)	CH <sub>2</sub> =CH	CH2==CCH3	Н	Н	cis	3,73 m ⇔	: 3,66 m	2,14  m	2,14m	0,00	2,26 m	2,26 m	0,00	1,96 s	1	5,12 s	5,45 m	5,82 m	11,74
(IV)	CH <sub>2</sub> =CCH <sub>3</sub>	CH <sub>2</sub> =CH	CH3	Н	trans	3,71 m	1	2,11m	2,28m	0,17	2,35 m	2,15 m	0,20	1,90 s	1,48 s	5,09 s	5,37 m	5,78 m	13,15
(N)	CH <sub>2</sub> =CCH <sub>3</sub>	CH <sub>2</sub> =CH	CH3	н	cis	3,71 m	1	2,15 m	2,15 m	0,00	2,17 m	2,17 m	0,00	1,92 s	1,44 s	5,09s	5,37 m	6,03 m	15,97
(VI)	CH <sub>2</sub> =CCH <sub>3</sub>	CH <sub>2</sub> =CCH <sub>3</sub>	H	E	trans	3,63 m	3,63m	2,15 m	2,29 m	0,14	2,29 m	2,15 m	0,14	1,92 s	i	5,10s	1	]	17,20
(III)	CH <sub>2</sub> =CCH <sub>3</sub>	CH <sub>2</sub> =CCH <sub>3</sub>	Н	Н	cis	3,75 m	3,75 m	2,25 m	2,25 m	0,00	2,25 m	2,25 m	0,00	1,92 s	I	5,11s 5,11s s 94 s			13,75
(VIII) †	CH2-CH	$CH_2 = CH$	CH3	CH <sub>3</sub>	trans cie	1		2,0 m	2,0 m		2,0 m 2,0 m	2,0 m 2,0 m			1,36 s 1.36 s	6 1 J	5,1 m 5,4 m	5,9 m 5,9 m	$5,30 \\ 9,52$
ÎSÎ	$CH_2 = CH$ $CH_2 = CH$	$CH_2 = CH$ $CH_2 = CH$	CH, CH,	CH, CH,	trans cis	3,6 m 3,5 m	[ ]	2,0 m	2,0 m		2,0 H	2,0 1 2,0 1 1 2,0 1 1 2,0 1 1 2,0 1 1 2,0 1 1 2,0 1 1 2,0 1 1 2,0 1 1 2,0 1 1 2,0 1 1 2,0 1 1 2,0 1 1 2,0 1 1 2,0 1 1 2,0 1 1 2,0 1 1 2,0 1 1 2,0 1 1 2,0 2,0 1 2,0 2,0 1 2,0 2,0 1 2,0 2,0 2 2,0 2,0 2 2,0 2 2 2,0 2 2,0 2 2,0 2 2,0 2 2,0 2 2,0 2 2,0 2 2,0 2 2,0 2 2,0 2 2,0 2 2 2 2		1 1	1,42 s 1,30 s		5,4 m 5,44 m		0,70
*The s †The s	pectra wer pectra wer	re recorde	ed on ed on	an i an i	nstru nstru	ument w ment w	ith an ith ar	n oper	rating :ating	; fre( frec	quency quency	of 36 of 80	0 MHz. MHz.	r					

TABLE 1. PMR Spectra of 2,5-Disubstituted Sulfolanes (I)-(XI)

Έ

H<sup>4</sup>

H3

H<sup>-H</sup><sup>-H</sup>

н К

1313

lic acid (BA). The system Pd(acac)<sub>2</sub>-3PPh<sub>3</sub>-2A1(Et)<sub>3</sub> [1] was used as the catalyst.

When 3-sulfolene is heated  $(100^{\circ}C, 10 \text{ h})$  with isoprene (1:3) in abs. toluene solution a mixture of isomeric unsaturated sulfolanes is formed, which is composed of (I), 25% of the cis and 75% of the trans isomer, the cis- and trans-2-vinyl-5-isopropylsulfolanes [48% of (II) and 52% of (III)], the cis- and trans-2-vinyl-2-methyl-5-isopropenylsulfolanes [47% of (IV) and 53% of (V)], the cis- and trans-2,5-diisopropenylsulfolanes [49% of (VI) and 51% of (VII)], the cis- and trans-2,5-diisopropenylsulfolanes [46% of (IX)], and also the cis- and trans-2,5-divinyl-2,5-dimethylsulfolanes [50% each of (X) and (XI)]. The total yield of (I)-(XI) is 95% when based on taken 3-sulfolene.

Compounds (I)-(XI) were isolated by preparative GLC and identified by spectral methods (Table 1). The assignment of the cis and trans isomers of (I)-(VII) was done by comparing the chemical shifts (CS) of the geminal protons on the  $C^3$  and  $C^4$  atoms of the sulfolane ring, for which, according to [3, 4], the difference in the CS between the geminal protons is smaller for the cis isomer than for the trans isomer. In the chromatographic analysis of the pure sulfolanes (I)-(VII) it was established that the trans isomers had a shorter retention time than the cis isomers. Isomers (VIII)-(IX) were identified by analogy.

As can be seen from Table 1, the CS value for the protons on  $C^3$  and  $C^4$  in (1)-(III) increases when one vinyl grouping is replaced by the isopropenyl group. According to [3, 4], a  $\beta$ -substituent exerts a greater effect than a  $\gamma$ -substituent on the chemical shift (CS) value of the protons on  $C^3$  and  $C^4$ . Consequently, in (II) and (III) the protons that have the greater CS value are found on the  $C^4$  atom of the sulfolane ring. Obviously, inserting a second substituent ( $R^3 = CH_3$ ) in (IV)-(V) also leads to an increase in the CS of the  $\beta$ -protons.

In contrast to isoprene, trans-piperylene reacts with 3-sulfolene to give a mixture of four pairs of isomeric 2,5-disubstituted sulfolanes (I), and specifically (XII)-(XVII), which were isolated by preparative GLC and identified by spectral methods. In particular, the structure of (I) was confirmed via IR, PMR, and mass spectrometry, and also by comparing with an authentic specimen [2]. The IR spectra of compounds (XII), (XIII), (XVI), and (XVII) are identical and contain absorption bands in the 920, 1000, 3095, 980, 3035, 1120, and 1320 cm<sup>-1</sup> region, which are characteristic for the vinyl group, a trans-disubstituted double bond, and the SO<sub>2</sub> group. Sulfolanes (XIV) and (XV) are characterized by having absorption bands in the IR spectrum at 940, 995, 3095 and 1135, 1320 cm<sup>-1</sup>, which belong to the vinyl and sulfonyl groups. The molecular weight of compounds (XII)-(XVII), found by mass spectrometry, is 186 for (XII)-(XV), and 200 for (XVI) and (XVII), which corresponds to the formation of adducts from one molecules of piperylene, butadiene, and SO<sub>2</sub>, or two molecules of piperylene and SO<sub>2</sub>.



More precise information on the structure of (XII)-(XVII) was obtained by examining their PMR spectra (Table 2), which made it possible to separate the isolated sulfolanes into pairs of isomers: (XII), (XIII), (XIV), (XV), and (XVI), (XVII), which differ among themselves in their physicochemical characteristics. Unfortunately, the obtained spectral data do not permit as yet a rigorous identification of the cis and trans isomers within the indicated pairs due to the absence of coupling constants for the geminal protons on the  $C^3$  and  $C^4$  atoms in (XII)-(XVII). It must be assumed that the use of higher resolution PMR spec-

TABLE 2. PMR Spectra of Compounds (XII)-(XVII)

					ð	s, ppm		
Compound	Rt	<b>R</b> <sup>2</sup>	R³	CHSO2	CH <sub>2</sub>	CH3C=	CH3C	CH <sub>2</sub> =C, CH <sub>2</sub> =CH
(XII) – (XIII) (XIV), (XV)	$CH_2 = CH$ $CH_2 = CH$	CH=CH $CH_2=CH$	H CH₃	3,4m 3,12 m 3,7 m	1,7–2,3m 1,9–2,2m	1,8 d 	1,08 d	5,50 m 5,41 m
(XVI), (XVII)	CH2=CH	CH₃CH=CH	CH3	3,0 m 3,5 m	1,8-2,3m	1,75 d	1,00d	5,6 m

troscopy (360 MHz) will make it possible to establish more precisely the number of isomers that is formed when 3-sulfolene is reacted with trans-piperylene.

The following structures are proposed for the isolated isomeric sulfolanes on the basis of the obtained results: cis- and trans-2-propenyl-5-vinylsulfolanes (XII) and (XIII), cisand trans-2,5-divinyl-3-methylsulfolanes (XIV) and (XV), and cis- and trans-2-vinyl-5-propenyl-3-methylsulfolanes (XVI) and (XVII).



All of our attempts to react AB and BA with 3-sulfolene were unsuccessful. In particular, in the case of AB the starting monomers are completely recovered unchanged from the reaction, while for all practical purposes BA is quantitatively converted to the dimers (XVIII) and (XIX), which were identified by comparing with the authentic compounds [5]



The obtained results make it possible to conclude that the simple 1- or 2-alkyl-substituted 1,3-dienes (isoprene, piperylene) react quite easily with 3-sulfolene to give the corresponding unsaturated 2,5-disubstituted sulfolanes. Conjugated dienes, which contain polar substituents, are fairly inert toward 3-sulfolene under our selected conditions.

#### EXPERIMENTAL

Polymerization pure isoprene and piperylene were used; the 1-acetoxy- and 1-carbomethoxy-1,3-butadienes were obtained as described in [6, 7]. The mixtures of the 2,5-disubstituted sulfolanes were analyzed on a Chrom-4 chromatograph, using a flame-ionization detector and a 1,5-m column packed with SE-30; the preparative separation of the mixtures was done on a Perkin-Elmer F-21 instrument, using a 2.7-m column packed with PEG-20M.

The PMR spectra were obtained on Tesla BS-487 and Bruker WH-360 instruments, using  $CDCl_3$  as the solvent and HMDS as the internal standard. The IR spectra were recorded on a US-20 spectrophotometer (either as a film or as a Nujol mull). The mass spectra were recorded on an MX-13-06 instrument, using ionizing electrons with an energy of 70 eV and an ionization chamber temperature of 200°C.

General Method for Reacting 3-Sulfolenes with 1,3-Dienes. To a stirred solution of 1.5 mmoles of  $Pd(acac)_2$  and 4.5 mmoles of  $PPh_3$  in 10 ml of abs. toluene, cooled to  $-20^\circ$ , was added in an argon stream 6.0 mmoles of  $AlEt_3$  and the mixture was kept for 5-10 min.

The catalyst was transferred to a 400-ml steel autoclave, into which had previously been placed 0.2 mole of 3-sulfolene and 0.6 mole of the 1,3-diene in 100 ml of toluene. The autoclave contents were heated for 10 h at 100°, cooled, and filtered through 50 g of  $Al_2O_3$  (III activity), using benzene as the eluant. The eluates were washed in succession with 1% HCl solution and water, and then dried over MgSO<sub>4</sub>. After removal of the solvent we obtained a mixture of the 2,5-disubstituted sulfolanes in  $\sim$ 90% yield.

		Q.	Mass spec-	Infrared	spectrum, <b>v</b> , cm <sup>-1</sup>	
Compound	bp, <sup>-C</sup> (p, mm Hg)	n G	trum, M <sup>+</sup>	$GH = GH_2$ , $G = -GH_3$ , $GH = -GH$ , $GH = -GH_2$	SO2	CH3
(11)	94(1)	1,5085	186	915, 940, 995, 1640, 3090	1140, 1320	1380, 1460
(111)	93(1)	1,5080	186	920, 940, 995, 1640, 3095	1130, 1310	1380, 1460
(IV)	91 - 92(1)	1,5118	200	910, 930, 1000, 1640, 3025, 3095	1100, 1140, 1300	1380, 1455
( <b>v</b> )	90(1)	1,5110	200	910, 940, 1000, 1640, 3026, 3090	1100, 1140, 1300	1380, 1460
(VI)	95(1)	1,5078	200	915, 1645, 3095	1135, 1320	1380, 1460
(111)	50-51 ( mp )	I	200	905, 1645, 3090	1130, 1310	1380, 1460
(IIII)	89-90(1)	1,5120	186	935, 1000, 1640, 3095	1140, 1300	1380, 1455
(XI)	86(1)	1,5113	186	940, 1000, 1640, 3095	1135, 1310	1380, 1460
(X)	88 - 89(1)	I	200	940, 1000, 1645, 3090	1135, 1300	1380, 1460
(XI)	87-88(1)	1	200	935, 1000, 1640, 3095	1135, 1290	1385, 1460
(XII) + (XIII)	110(1)	ſ	186	945, 980, 1000, 1640, 3035, 3095	1120, 1140, 1300, 1320	1385, 1460
(XIV) + (XV)	108(1)	1	186	940, 995, 1640, 3095	1135, 1320	1380, 1465
(IIAX) + (IAX)	112(1)	1	200	940, 980, 1000, 1640, 3035, 3095	1120, 1320	1385, 1460

TABLE 3. Physical Constants and Characteristics of IR Spectra of Sulfolanes (II)-(XVII)

The constants of the isoprene or trans-piperlyene adducts with 3-sulfolene, isolated by preparative GLC, are given in Table 3.

Reaction of 3-Sulfolene with 1-Acetoxy- and 1-Carbomethoxy-1,3-butadienes. Under the conditions of the preceding experiment, from 0.2 mole of 3-sulfolene and 0.6 mole of AB we recovered the starting reactants completely.

Under analogous conditions, from 0.2 mole of 3-sulfolene and 0.6 mole of BA we obtained 0.2 mole of the starting 3-sulfolene and the methyl butadiene-1-carboxylate dimers (XVIII) and (XIX) [5].

#### CONCLUSIONS

1. It was shown that 2,5-disubstituted sulfolanes can be obtained by reacting either isoprene or piperylene with 3-sulfolene using homogeneous complex PD-containing catalysts.

2. Conjugated dienes, which contain polar substituents, do not react with 3-sulfolene in the presence of Pd complexes.

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### DIRECTION OF RING OPENING OF ALKYLSUCCINIC ACID ANHYDRIDE AND

## N-ALKYLIMIDE BY BASES

Yu. N. Ogibin, I. V. Brederman, A. Ya. Shtenshneider, UDC 542.97:547.461.4 N. A. Aleinikov, and G. I. Nikishin

In many cases, the N-alkylmonoamides of alkyl(alkenyl)succinic acids, formed by the reaction of alkyl(alkenyl)succinic anhydrides (I) with aliphatic amines, are unequivocally assigned [1-3] the structure of amides (II) ( $R^1$  = alkyl or alkenyl,  $R^2$  = H)



A study of the direction of opening the  $\alpha, \alpha$ -disubstituted anhydrides (I) (R<sup>1</sup> = Me, Ph, PhCH<sub>2</sub> and R<sup>2</sup> = Me, Et, Ph, PhCH<sub>2</sub>) by ammonia, aniline or dimethylamine [4] disclosed that both amides, (II) and (III), are always formed, with a predominance of (III). Starting with these data, it may be assumed that the reaction of monoalkylsuccinic anhydrides (R<sup>2</sup> = H) with primary aliphatic amines will also lead to a mixture of amides (II) and (III). However, it is impossible to truthfully say in what ratio they are obtained. To ascertain the ratio

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