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HOMOLYTIC ADDITION OF 1,3-OXATHIOLANE TO UNSATURATED HYDROCARBONS

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The homolytic addition of 1,3-oxathiolane to olefins takes place with the formation of 2-substituted 1,3-oxathiolanes and insignificant amounts of functional derivatives of sulfides.

It is known that 1,3-dioxacycloalkanes add to olefins forming, in the general case, 2substituted dioxacycloalkanes and functional derivatives of esters [1, 2]. The reaction with 2-methyl-1,3-oxathiolane proceeds similarly [3]. In this paper, the direction of the homolytic addition of 1,3-oxathiolane to unsaturated compounds has been studied in order to determine the effect of the nature of the olefin on the course of the reaction.

We have established that, in contrast to 2-methyl-1,3-oxathiolane, the reaction of 1,3oxathiolane, I, with unsaturated compounds II-VI in the presence of tert-butyl peroxide at 140°C for one hour forms 2-substituted 1,3-oxathiolanes VII-XI and the corresponding sulfides XII-XVI.



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PMR Spectra and Physicochemical Constants of the Products of Homolytic Addition TABLE 1.

						l		Eine IMD	100	.	
-						CUERICAL	dd 'o' JIIUS	III, LTOHI HIVL	o III UUI	•	
Com- pound	Formula of compound	bp, °C (mm)	n D ²⁰	2-H	3-H	4-H	£-Н	6-H; 6'-H	H-'7;H-7	8-H	H-6
VII IIA	4	155 (7)	1,4920	5,32 d		2,82—3,01 m	3,60—3,75m; 4,15—4,38 m	3,06-3,26 m	2,62—2,70 m	1	3,14 s; 3,59 s;
	0.2 S H COUCH CH-COOCH A COOCH					-					
IIIV		120 (6)	1,4853	5,25,48 m	ļ	3,18—3,48 m	3,96—4,12 ^m ; 4,18—4,50 ^m	2,95—3,18 m	4,26-4,50 m	I	2,35 s
	H CH ₂ CH ₂ OC S	(2) 001	1 428825	5.51 +		3,18-3,51 m	3,95-4,27 m;	2,35-2,62 m	2,83 t	I	l
XI		()) (6)		5			4,50-4,79 m		r		
×	H. CH ₂ CH ₂ CH	87 (6)	1,4840 ²⁷	4,84-4,98 m	1	3,05 t	3,924,27 m; 4,274,58m	2,482,60 m	3,52—3,70 m	8,29 s	I
	H ^{×CH2} CH2CH20C [€] H										
IX	1 	115—116 (10)	1,4686	4,90 t	۱.	2,89 m	3,63 m ; 4,22 m ;	1,45 m	0,86 t	ł	1
	H [×] (cH ₂) ₅ CH ₃								۲		
ШХ	CH_CCACCOCH_ CH_CCACCOCH_ CH_CCOCH_	110 (15)	1,4610	2,59 q	1,22 t	3,323,58 m	2,54 d	ŀ	3,67 s; 3,71 s	l	
	•				į	+	4 00 1		105 5		i
XIII	CH3CH29CH2CH20C	48 (3)	1,4610	2,49 q	1,21 t	2,02 L	4,Uo t	1	1,00		
	CHICHISCHICHICH	86/4	1,4845	2,57 q 2,50 q	1,22 t 0,87 t	2,68t 2,30t	2,73 t 2,23-2,53 m	1,17 t	11		11

12			Chemical	shift,	δ, ppm			
Dour Dour	C ₍₂₎	C ₍₃₎ (q)	C ₍₄₎	C ₍₅₎ (t)	C ₍₆₎ (C _(6'))	C ₍₇₎ (C _(7')	C ₍₈₎ (C _(8'))	C ₍₉₎ (C _(9'))
VII	85,96 đ 86,60 đ		32,23 t 32,04 t	72,36	47,77 d	32,68 t	171,7 171,0 171,4	52,17 52,49
VIII IX X XI	84,27 đ 83,9 đ 85,77 đ 87,45đ		36,57 t 33,01 t 33,9 t 33,27 t	71,85 71,27 70,88 71,65	33,59t 13,34t 37,7 t 37,34t 32,62t 30,03t 27,18t	61,16 t 31,53 t 60,14 t 14,75 q	170,1 s 109,5 s 169,0 d	21,49 q
хп	36,70t	26,21	51,59 d	41,88	23,43t 170,4 s	52,49 q		
XIII XIV	26,53 t 27,38 t	15,4 26,01	30,55 t 31,91 t	63,88 26,74	169,8 111,76 ^s	20,97 q 		

TABLE 2. ¹³C-NMR Spectra of the Products of the Homolytic Addition of 1,3-Oxathiolane to Unsaturated Hydrocarbons

The formation of products VII-XI apparently takes place via the formation of 1,3-oxathiolan-2-yl radicals Ia, which react with unsaturated compounds II-XI to give spin-adducts Ib and then products VII-XI.

The S-ethyl thioformate being formed by the isomerization of 1,3-oxathiolane [3] is known [3,4] to give 2-(formylthiolethyl) radicals which participate in the formation of sulfides XII-XVI.

The results obtained show that as the temperature rises from 130 to 150°C, the yield of cyclic adducts falls somewhat while that of the sulfides rises. Obviously, the activation energy for the rearrangement of 1,3-oxathiolan-2-yl radicals is somewhat higher than that for their addition to the dimethyl maleate. This leads to an increased yield of sulfide IX appearing as a derivative of S-ethyl thioformate.

By comparing the ratio of yields of sulfides and 2-substituted 1,3-oxathiolanes for 1hexene and other olefins containing polar groups, one can see that the fraction of sulfides in the latter case is notably low. This is explained by the nucleophilic character of the 1,3-oxathiolan-2-yl radicals.

The addition to the double bond of olefins II-VI, which contain electron-accepting groups, takes place significantly faster than the rearrangement in the formylthioethyl radicals, [CH(0)SCH₂CH₂]. This precludes the formation of an addition product of the latter with olefins II-VI.

EXPERIMENTAL

The PMR spectra of substances VII-XVI were recorded on a Tesla BS-467 spectrometer with a working frequency of 60 MHz, and the ¹³C-NMR on a Bruker WH-90 spectrometer with a working frequency of 22.63 MHz. The quantitative analysis of the reaction mixtures was done on an LKhM-8 MD chromatograph with a thermal conductivity detector. The regime of the chromatographic analysis: carrier gas helium; gas consumption rate 3.5 liters/hour; 3000 × 3 mm column; SKTFT-50× 15% on chromaton N-AW-HMDS; temperature program 70 to 200°C at a rate of 4°/min.

The experiments were run in glass ampoules. The ampoule was charged with 1,3-oxathiolane, I, olefin II-VI, and TBP [tert-butyl peroxide] in a molar ratio of I:(II-VI):TBP = 10:3:0.3, purged with argon, sealed, and then thermostated at 140°C for one hour. Substances VII-XI were separated from the reaction mass by vacuum distillation and identified by the PMR and 13 C-NMR spectra (Table 1-3).

Products XII-XVII were identified chromatographically by the identity of the reaction times with those of known, synthesized samples.

TABLE 3. Composition of Products of the Homolytic Action of 1,3-Oxathiolane to Olefins (T 140°C; molar ratio of I: :II-VI:TBP = 10:3:0.3; reaction time 1 h)

Olefin R ¹ CH=CHR, S	Con- ver- sion of ole- fin	Com- pound	Compound name	Formula	Yield of con- verted ole- fin, %
cooch ²	70* 80 92	VII	Dimethyl (1,3-oxa- thiolan-2-yl)suc- cinate	0 H COOCH ₃	52 (69)*, (45)*
		XII	Dimethyl (ethyl- thio)succinate	С ₂ H ₅ S - СИСООСН СН ₂ СООСН ₃	7 (6)*, (12)*
сн ₂ =сн-ос	75	VIII	2-(2'-Acetoxy- ethyl)-1,3-oxa- thiolane	°,→CH ² CH ⁵ OC≤CH ³	63
		XIII	2-Ethylthioethyl acetate	с ₂ н ₅ sch ₂ ch ₂ oc ^{c0} сн ₃	1
		IX	2-(2'-Cyanoethyl)- 1,3-oxathiolane	о n ц сн ₂ сн_си	48
CH2=CHCN	80	XIV	2-Ethylthiopropio- nitrile	Ç₂H₅SCH₂CH₂CN .	1
cH ² =CHOC ⁰	80	x	2-(2'-Formyloxy- ethyl)-1,3-oxa- thiolane	°, ⊮,⊂H ² CH ⁵ CH ⁵ O⊆, ⁰ ⁰	59
		xv	2-Ethylthioethyl formate	₂₂ н₅sсн₂сн₂ос ^{с0} ц	1
	1	XI	2-Hexyl-1,3-oxa- thiolane	0 H C ₆ H ₁₃	60
СН2=СН-(СН2)3СН	3 20	XVI	Hexyl ethyl sul- fide	C ₂ H ₅ SC ₆ H ₁₃	22
		XVII	S-Octyl thio- formate	HC ^O SC ₈ H ₁₄	2
					•

*At 130°C, reaction time 2 h. †At 150°C, reaction time 0.5 h.

<u>Note.</u> Asterisks as in Russian original; some should probably be daggers, and some other daggers are probably omitted - Editor.

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EFFECT OF SUBSTITUENTS ON THE RELATIVE STABILITY OF FUROXAN ISOMERS

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The overall energy of isomers of substituted furoxans has been calculated using the MINDO/3 method. Comparison with experimental results indicated that the calculation correctly predicted the structure of the more stable isomer. Correlation of the difference of the overall energy of the isomers (ΔE) with the induction and resonance constants of the substituents, and comparison of the values of ΔE calculated from the correlation equation with the experimental values have also been carried out.

At elevated temperatures unsymmetrically substituted furoxans are capable of mutual transformation [1, 2]:



The relative stability of the isomers depends on the nature of the substituents R^1 and R^2 . However, the reasons for the stability of one isomer or the other are not clear and the limited amount of experimental material available does not allow a quantitative, nor even a qualitative, correlation of the electronic effects of the substituents with the equilibrium constants of the isomers.

In this connection, we have carried out calculations by the MINDO/3 method, using the original program [3], of the difference in the overall energy of the isomers $\Delta E = E_{II} - E_I$ of a series of furoxans with different substituents (Table 1). In dealing with the geometry of the furoxan ring, x-ray crystallographic data were used [4] and for the substituents R¹ and R², averaged geometrical parameters [5]. Comparison of the calculated difference in the overall energy of the isomers with the experimentally determined values for the free energy difference (ΔG) (Table 1) indicates that the calculation correctly predicts the structure of the isomer with the greater stability, although the difference is exaggerated for isomers with cyano-group substituents. Therefore, calculation without optimization of the geometry is satisfactory for an interpretation of the effect of substituents on the relative stability of the isomers.

In accordance with the principle of the linearity of free energies [6], the dependence of the rate constant of the forward reaction on the induction $(\sigma^{\circ}I)$ and resonance $(\sigma^{\circ}R)$ con-

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