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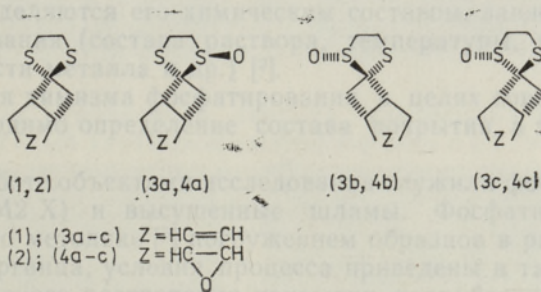
**CHIRAL SULFOXIDES FROM DITHIOKETALES
 OF BICYCLO[3.2.0]HEPT-2-EN-6-ONE AND ITS EPOXIDE**

R. JÄÄLAID, T. PEHK, T. KANGER, M. LOPP, Ü. LILLE. KIRAALSED SULFOKSIIDID BITSUKLO-
 [3.2.0]HEPT-2-EN-6-ONNI JA TEMA EROKSIIDI DITIOKETAALIDEST

P. ЯАЛАЙД, Т. ПЕХК, Т. КАНГЕР, М. ЛОПП, Ю. ЛИЛЛЕ. ХИРАЛЬНЫЕ СУЛЬФОКСИДЫ ИЗ
 ДИТИОКЕТАЛЕЙ [3.2.0]ГЕПТ-2-ЕН-6-ОНА И ЕГО ЭПОКСИДА

In the course of studies of optical resolution of the known prostaglan-
 din intermediate, bicyclo[3.2.0]hept-2-en-6-one, thioketales (1) and (2)
 were oxidized in the modified Sharpless oxidation conditions [1]
 (*t*-BuO₂H:Ti/O *i*-Pr/4:(-)-DET:substrate 2:1:4:5) and the following three
 diastereomers (3a—c and 4a—c, respectively) were obtained after separa-
 tion on silica gel (CCL₄:acetone 10:1—6:1).

The structures of these diastereomers were determined by ¹H and ¹³C
 NMR spectra by various 2D methods.



Judging by the molecular modelling the formation of the fourth diaste-
 reomer was hindered for steric reasons.

NMR data and optical activity of the diastereomers obtained

	¹ H ₅	¹ H _{7exo}	¹ H _{7endo}	¹³ C ₅	¹³ C ₇	[α] _D ²⁰ (<i>t</i> , °C; C, %; CHCl ₃ , 11)
(1)	3.33	3.08	3.32	52.5	47.3	—
(2)	3.36	2.89	2.80	55.9	41.0	—
(3a)	3.83	2.89	2.05	37.8	38.4	+3.7(26;6)
(3b)	2.93	3.32	2.03	43.0	34.4	+17(27;5)
(3c)	3.25	2.64	2.93	48.5	34.9	+33(27;5)
(4a)	3.78	2.63	2.37	41.4	32.8	0
(4b)	3.11	3.29	2.48	46.1	27.8	+53(14;4)
(4c)	3.21	2.55	3.23	53.8	28.6	+3.3(26;1.5)

The results obtained show that the oxidation in the system under study proceeds with moderate regioselectivity and high stereoselectivity in respect to one diastereomer formed. This requires further studies to explain the steric background of stereoselectivity.

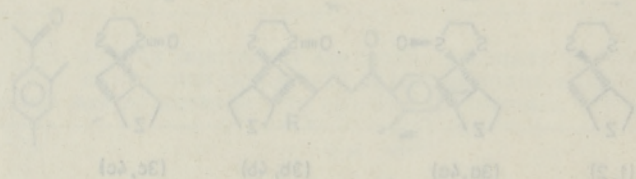
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In the course of studies of optical resolution of the known prostaglandin intermediate, bicyclo[2.2.1]hept-2-en-2-one thioesters (1) and (2) were oxidized in the modified Sharpless oxidation conditions [1] (1-Bu₂H.TiO₂·4-PTA, (-)-DET:substrate 2:1.4:5) and the following three diastereomers (3a—c and 4a—c, respectively) were obtained after separation on silica gel (CCl₄:acetone 10:1—5:1). The structures of these diastereomers were determined by ¹H and ¹³C NMR spectra by various 2D methods.



Условия алкилирования: температура 25°C, 1-хлор-3-метил-2-бутен-2-ил-2-тиоэтанол и 1-хлор-3-метил-2-бутен-2-ил-2-тиоэтанол в соотношении 1:1, 0.1 M HOAc в 0.4 M ацетофеноне, время 10, 15, 20, 30, 40, 60 мин.

Судя по моделированию молекулы, образование четвертого диастереомера было инициировано за счет стерических факторов.

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Compound	¹³ C NMR (CDCl ₃)	¹³ C NMR (acetone-d ₆)	¹³ C NMR (acetone-d ₆)	¹³ C NMR (acetone-d ₆)	¹³ C NMR (acetone-d ₆)	¹³ C NMR (acetone-d ₆)
(1)	—	47.3	55.5	53.5	35.8	33.3
(2)	—	41.0	52.9	52.0	28.0	28.0
(3a)	+3.7(30.8)	38.4	37.8	2.05	2.88	2.83
(3b)	+17.3(7.5)	34.4	43.0	2.00	2.75	2.93
(3c)	+33.3(7.5)	31.9	48.5	2.03	2.64	2.55
(4a)	0	32.3	41.4	2.37	2.03	2.78
(4b)	+23.1(7.5)	32.9	40.1	2.38	2.29	2.11
(4c)	+41.2(7.5)	28.6	52.8	2.30	2.55	2.21