p-Methoxybenzoylation of Benzothiophene. The reaction of 6.7 g (0.05 mole) of benzothiophene, 8.5 g (0.05 mole) of p-methoxybenzoyl chloride, and 0.02 g of ferric chloride gave 8.7 g (65%) of a fraction with bp 275-285°C (13 mm), which, according to GLC, contained up to 80% 3-(p-methoxybenzoyl)benzothiophene. Crystallization from alcohol gave 3-(p-methoxybenzoyl)benzothiophene with mp 112°C (mp 112°C [6]). A second isomer was not isolated.

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SYNTHESIS AND SOME TRANSFORMATIONS OF 2-ACYLMETHYL-1,3-OXATHIOLANES

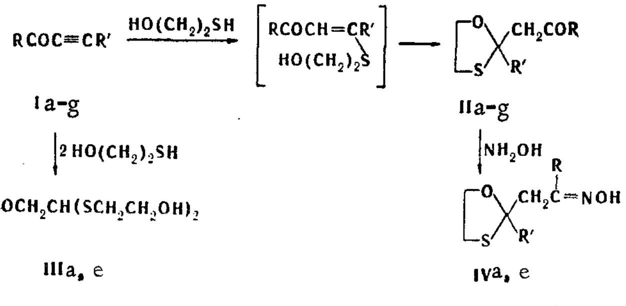
A. S. Nakhmanovich, V. N. Elokhina,
I. D. Kalikhman, and M. G. Voronkov

UDC 547.77.07

2-Acylmethyl-1,3-oxathiolanes, which form oximes with hydroxylamine and perchlorates with perchloric acid, were synthesized by reaction of α-alkynyl ketones with β-mercaptoethanol.

It is known [1-4] that one or two molecules of alcohol or phenol can be added to α-alkynyl ketones. One mole of thiol is added in the reaction of β-alkyl-α-ethynyl ketones with thiols [5-7]. The formation of cyclic products – the corresponding 2-substituted 1,3-dioxolanes [4] and 1,3-dithiolanes [8] – as a result of "double addition" to the acetylenic bond is possible with some 1,2-dinucleophilic reagents (ethylene glycol and ethanedithiol).

We have studied the reaction of α-alkynyl ketones Ia-g with β-mercaptoethanol; this reaction proceeds readily in the presence of basic catalysts – potassium carbonate or triethylamine – to give 2-acylmethyl-1,3-oxathiolanes (IIa-g, Table 1). The reaction probably proceeds through the intermediate formation of ketovinyl sulfides and cyclization of the latter.



I—IV a $R=C_6H_5$, $R'=H$; I, II b $R=C_6H_5$, $R'=C_4H_9$; c $R=R'=C_6H_5$; d $R=m\text{-}C_6H_4—NO_2$, $R'=C_6H_5$; e $R=C_4H_3S$, $R'=H$; f $R=C_4H_3S$, $R'=C_4H_9$; g $R=C_4H_3S$, $R'=C_6H_5$

The absorption band of the C=O bond lies at 1650-1685 cm^{-1} in the IR spectra of IIa-g. The absorption at 1070-1120 cm^{-1} corresponds to the stretching vibrations of the C=O bond,

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Irkutsk Institute of Organic Chemistry, Siberian Branch of the Academy of Sciences of the USSR, Irkutsk 664033. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1041-1043, August, 1978. Original article submitted September 10, 1977.

TABLE 1. 2-Acylmethyl-1,3-oxathiolanes II

Compound II	mp, °C	Found, %			Empirical formula	Calc., %			Yield, % (synthetic method)
		C	H	S		C	H	S	
a	79—80	63,5	5,8	15,6	$C_{11}H_{12}O_2S$	63,5	5,8	15,8	81 (A), 36 (B)
b	36,5—37	68,0	7,6	12,1	$C_{15}H_{20}O_2S$	68,1	7,6	12,1	51 (A)
c	101—102	71,7	6,0	11,2	$C_{17}H_{16}O_2S$	71,8	5,6	11,3	42 (A)
d	106—107	61,8	4,6	9,5	$C_{17}H_{15}NO_4S$	62,0	4,6	9,7	66 (A)
e	47—48	50,2	4,7	29,1	$C_9H_{10}O_2S_2$	50,5	4,7	29,0	68 (A), 41 (B)
f	bp 158—160 (1mm)	57,7	6,5	23,8	$C_{13}H_{18}O_2S_2$	57,8	6,7	23,7	48 (A)
g	78—79	62,1	4,6	21,9	$C_{15}H_{14}O_2S_2$	62,1	4,8	22,1	52 (A)

TABLE 2. Parameters of the PMR Spectra of 2-Acylmethyl-1,3-oxathiolanes IIa-g

Compound II	Solvent	R	R′	Chemical shift, δ, ppm					SSCC, J, Hz	
				R	R′	CH_2CO	OCH_2	SCH_2	CH_2CO	$CHCH_2$
a	CD_3OD	C_6H_5	H	7,10 s	5,05 t	3,11 q 2,95 q	4,17 m 3,57 m	2,86 m	17,0	6,0
b	CCl_4	C_6H_5	C_4H_9	7,50 m	1,98 t 1,50 m 0,90 t	3,57 d 3,37 d	4,03 t	2,87 t	16,5	—
c	CCl_4	C_6H_5	C_6H_5	7,43 m	7,43 m	3,93 d 3,51 d	4,15 m 3,60 m	2,96 m	16,2	—
d	CCl_4	м-C_6H_4—NO_2	C_6H_5	8,00 m	7,20 m	3,79 m	4,00 m	2,92 m	16,0	—
e	CCl_4	C_4H_3S	H	7,71 dd 5-H 7,56 dd 3-H 7,04 dd 4-H	5,48 t	3,41 q 3,17 q	4,24 m 3,70 m	2,85 m	17,0	6,2
f	CCl_4	C_4H_3S	C_4H_9	7,65 dd 5-H 7,50 dd 3-H 7,05 dd 4-H	1,94 t 1,36 m 0,90 t	3,42 d 3,28 d	4,07 t	2,92 t	16,1	—
g	CCl_4	C_4H_3S	C_6H_5	7,45 dd 5-H 7,20 dd 3-H 6,92 dd 4-H	7,20 m	3,73 d 3,57 d	4,20 m 3,67 m	2,96 m	16,0	—

and the absorption at 690-740 cm^{-1} corresponds to the C—S bond of the oxathiolane ring. Absorption bands of the C=C bond and the OH group are absent. Data from the PMR spectra of IIa-g are presented in Table 2.

1-Phenyl- and 1-(2-thienyl)-3,3-bis(2'-hydroxyethylmercapto)propan-1-ones (IIIa, e) were obtained by reaction of ketones Ia, e with a twofold excess of β-mercaptoethanol in the presence of triethylamine.

In contrast to IIIe, which is obtained in lower yield, IIIa is stable.

The reaction of 2-acylmethyl-1,3-oxathiolanes Ia, e with hydroxylamine leads to the corresponding oximes (IVa, e).

Monosubstituted (in the 2 position of the oxathiolane ring) IIa, e readily form crystalline perchlorate when they are treated with 70% perchloric acid in acetic anhydride. Their IR spectra contain an intense absorption band at 1720 cm^{-1} (C=O), two strong bands at 1530-1540 and 1150-1180 cm^{-1} ($S{=\!=}\overset{+}{C}{=\!=}O$ fragment), and absorption at 1090-1120 cm^{-1} (ClO_4^- ion).

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The NMR spectra of solutions of the compounds in CD_3OD or CCl_4 were recorded with a Tesla BS-487-C spectrometer (80 MHz); the chemical shifts are presented relative to tetramethylsilane and hexamethyldisiloxane.

2-Benzoylmethyl-1,3-oxathiolane (IIa). Method A. A mixture of 5.2 g (0.04 mole) of 1-phenylprop-2-yn-1-one (Ia) and 3.12 g (0.04 mole) of β-mercaptoethanol in 50 ml of chloroform was heated in the presence of 2 g of freshly calcined K_2CO_3 at 60°C for 2 h, after which it was cooled and filtered, and the solvent was removed in vacuo. The residue was dissolved in methanol and precipitated by treatment with ether (with cooling). The precipitate was removed by filtration, washed with ether, and recrystallized from ethanol. The remaining II was similarly obtained (Table 1).

Method B. A 3.12-g (0.04 mole) sample of β-mercaptoethanol was added slowly dropwise with stirring to a mixture of 5.2 g (0.04 mole) of 1-phenylprop-2-yn-1-one and one to two drops of triethylamine, after which the mixture was maintained at room temperature for 2 h. It was then distilled with collection of the fraction with bp 170-180°C (2 mm). The product was dissolved in methanol, and precipitated by the addition of ether (with cooling). The precipitate was removed by filtration and dried. Compound IIe was similarly obtained.

1-Phenyl-3,3-bis(2'-hydroxyethylmercapto)propan-1-one (IIIa). One to two drops of triethylamine were added to a solution of 3.25 g (25 mmole) of 1-phenylprop-2-yn-1-one in 50 ml of methanol, and 3.9 g (50 mmole) of β-mercaptoethanol was added dropwise slowly in the cold. The mixture was then stirred at room temperature for 2 h, after which the alcohol was partially removed by vacuum evaporation. The residue was treated with cold ether, and the solid material was recrystallized from ethanol to give 6.67 g (93%) of a product with mp 57-58°C. IR spectrum: 1690 (C=O), 702 (C—S), and 3360 cm^{-1} (OH). PMR spectrum, δ: 6.90-7.62 (C_6H_5, m), 4.64 (SCHS, t, J = 7.1 Hz), 2.25 (OH, s), 3.48 (CH_2O, t), 2.54 (CH_2S, t), and 3.15 ppm (CH_2CO, d, J = 7.1 Hz). Found: C 54.3; H 6.4; S 22.2%. $C_{13}H_{18}O_3S_2$. Calculated: C 54.5; H 6.3; S 22.3%.

1-(2-Thienyl)-3,3-bis(2'-hydroxyethylmercapto)propan-1-one (IIIe). This compound [2.77 g (38%)], mp 37-38°C (from ethanol), was similarly obtained. IR spectrum: 1695 (C=O), 698 (C—S), and 3368 cm^{-1} (OH). PMR spectrum, δ: 7.60, 7.48, and 7.04 (C_4H_3S, dd, 5-H, 3-H, and 4-H); 4.62 (SCHS, t, J = 7.9 Hz); 2.25 (OH, s); 3.47 (CH_2O, t); 2.55 (CH_2S, t); 3.42 ppm (CH_2CO, d). Found: C 45.2; H 5.5; S 32.8%. $C_{11}H_{16}O_3S_3$. Calculated: C 45.4; H 5.3; S 33.0%.

1-(1,3-Oxathiolan-2-yl)-2-phenyl-2-oximinoethane (IVa). A mixture of 2.08 g (10 mmole) of IIa, 1.03 g (15 mmole) of hydroxylamine hydrochloride, and 20 ml of methanol was heated to 60°C, and a solution of 1.5 g (15 mmole) of potassium acetate in 50 ml of water was added dropwise with stirring. The mixture was then stirred for 6 h, after which it was poured into cold water. The precipitate was removed by filtration and recrystallized from ethanol to give 1.81 g (70%) of a product with mp 105-106°C. IR spectrum: 1640 (C=N), 3480 (NOH), 700 (C—S), and 1090 cm^{-1} (C—O). Found: C 59.4; H 5.8; N 6.3; S 14.2%. $C_{11}H_{13}NO_2S$. Calculated: C 59.2; H 5.8; N 6.3; S 14.3%.

1-(1,3-Oxathiolan-2-yl)-2-(2-thienyl)-2-oximinoethane (IVe). This compound, with mp 107-108°C (from ethanol), was similarly obtained. The yield was 1.64 g (62%). IR spectrum: 1630 (C=N), 3520 (NOH), 705 (C—S), and 1100 cm^{-1} (C—O). Found: C 47.3; H 4.9; N 6.2; S 27.7%. $C_9H_{11}NO_2S_2$. Calculated: C 47.2; H 4.8; N 6.1; S 27.9%.

2-Benzoylmethyl-1,3-oxathiolan-2-ylium Perchlorate. A 0.5-ml sample of 70% perchloric acid was added slowly with stirring to a solution of 0.5 g (2.4 mmole) of IIa in 1 ml of acetic anhydride, and the mixture was stirred for 2 h. The solvent was then removed by vacuum evaporation, and the residue was washed with cold ether to give 0.61 g (99%) of a product with mp 170-171°C. Found: C 42.9; H 3.6; Cl 11.8; S 10.2%. $C_{11}H_{11}ClO_6S$. Calculated: C 43.0; H 3.6; Cl 11.7; S 10.4%.

2-Thenoylmethyl-1,3-oxathiolan-2-ylium Perchlorate. This compound [0.58 g (93%)], with mp 156-158°C, was similarly obtained. Found: C 34.4; H 2.9; Cl 11.2; S 20.7%. $C_9H_9ClO_6S_3$. Calculated: C 34.5; H 2.9; Cl 11.5; S 20.7%.

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STEREOCHEMISTRY OF 8-HYDROXY-2-THIATRICYCLO$[7.3.1.0^{3,8}]$TRIDECAN-13-ONES

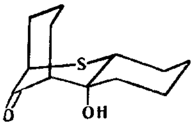
A. S. Usol'tsev, E. S. Karaulov,
M. N. Tilichenko, M. Yu. Antipin,
S. G. Il'in, and Yu. T. Struchkov

UDC 547.818.4:541.63

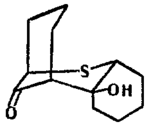
The configurations of two stereoisomers of 8-hydroxy-2-thiatricyclo$[7.3.1.0^{3,8}]$-tridecan-13-one formed as a result of the reaction of 2-chlorocyclohexanone with sodium sulfide were established by x-ray diffraction analysis and mass, IR, and PMR spectroscopy.

We have previously reported [1] that 8-hydroxy-2-thiatricyclo$[7.3.1.0^{3,8}]$tridecan-13-one (I) is formed as a crystalline substance with mp 102-103°C in the reaction of α-chlorocyclohexanone with Na_2S. We obtained the same compound by repeating the experiments of Backer and co-workers [2], who, however, assigned a bis(2-oxocyclohexyl) sulfide structure [1] to it. Subsequent studies showed that the indicated sample of ketol is, in fact, a mixture of two stereoisomers (α and β), which can be separated by repeated recrystallization. The aim of the present research was to determine the three-dimensional structures of these substances.

8-Hydroxy-2-thiatricyclo$[7.3.1.0^{3,8}]$tridecan-13-one can exist in the form of four stereoisomers IA-D:



IA



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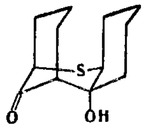

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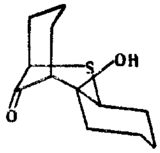

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By means of x-ray diffraction analysis we have established that the α isomer of the ketol has structure IA (Fig. 1). To determine the three-dimensional structure of the β-ketol we made a comparative analysis of the mass, IR, and PMR spectra of both substances and also studied some of the chemical properties of the β isomer.

The mass spectra of the two ketols virtually coincide and contain an intense signal of a molecular ion (m/e 226). A comparison of their IR spectra, obtained from very dilute solutions, indicates the absence of an intramolecular hydrogen bond in the β-ketol; this makes it possible to exclude structure IC for it, in which this bond should be observed, as in structure IA (the $[O_{(2)}]H...O_{(1)}$ bond length in the α-ketol is ∿2.2 Å).

The PMR spectrum of the β-ketol contains four groups of signals at 3.8 (1H), 3.2 (1H), 2.5 (1H), and 1.5-2.5 ppm (15H), and upon the whole coincides with the spectrum of the α isomer [3.9 (1H), 3.2 (1H), 2.6 (1H), and 1.5-2.5 ppm (15H)]. The signal at 2.5 ppm belongs to the proton of the OH group, since it vanishes when CD_3OD is added (in the spectrum of the α isomer this signal is observed at 2.6 ppm). The signals at 3.2 and 3.8 ppm can belong only to the protons of the CH groups adjacent to the sulfur atom. Their assignment can be made by comparing the multiplets at 3.9 and 3.8 ppm in the spectra of the α- and β-ketols. These multiplets, which are the X part of an ABX system (the $S{-}CH{-}CH_2{-}$fragment), have dif-

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Far Eastern State University, Vladivostok 690000. Pacific Institute of Bioorganic Chemistry, Far Eastern Science Center, Academy of Sciences of the USSR, Vladivostok 690022. Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow 117312. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1044-1048, August, 1978. Original article submitted September 13, 1977.

0009-3122/78/1408-0836$07.50