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SYNTHESIS OF ETHYL 2-ALKYLTHIO-2-OXAZOLINE-5-CARBOXYLATE

O. N. Bubel', I. G. Tishchenko,
and O. A. Grinkevich

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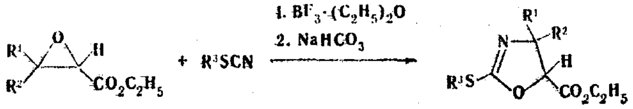
Glycidic esters react with excess alkyl thiocyanates in the presence of equimolar amounts of boron trifluoride etherate to give esters of 2-alkylthio-2-oxazoline-5-carboxylic acids. The structure of the products was confirmed by the data from the PMR and IR spectra.

It is known that oxiranes react with nitriles [1] and cyanamides [2] to give the corresponding 2-oxazolines. The literature does not contain any data on the reaction of epoxide compounds with alkyl thiocyanates. The aim of the present research was to develop a new method for the preparation of substituted 2-oxazolines in the case of the reaction of glycidic esters with alkyl thiocyanates.

We have found that glycidic esters (I-III) in equimolar amounts with respect to boron trifluoride etherate react at room temperature with excess alkyl thiocyanates to give ethyl 2-alkylthio-2-oxazoline-5-carboxylates (Table 1) in up to 61% yields.



I–III IV–XII

I, IV—VI $R^1=R^2=CH_3$; II, VII—IX $R^1+R^2=-(CH_2)_4-$; III, X—XII $R^1+R^2=-(CH_2)_5-$;
IV, VII, X $R^3=CH_3$; V, VIII, XI $R^3=C_2H_5$; VI, IX, XII $R^3=i\text{-}C_3H_7$

Intense absorption bands of the stretching vibrations of C=N (1610-1621 cm^{-1}) and C=0 (two bands, 1734-1760 cm^{-1}) groups, as well as a band at ∿1150 cm^{-1} due to the vibrations of the C—O—C fragment, are observed in the IR spectra of the synthesized 2-oxazolines IV-XII (Table 2).

The data from the PMR spectra of IV-XII (Table 2) also confirm the structure of IV-XII.

From the presented spectral data one cannot directly establish the position of the ester group (5 or 4) in the 2-oxazoline ring of IV-XII. However, a comparison of the PMR spectra of IV and ethyl 2-methylthio-5,5-dimethyl-2-oxazoline-4-carboxylate [3] (δ 1.33 s and 1.54 s $2CH_3$; 1.29 t and 4.17 q OCH_2CH_3; 2.45 s SCH_3; 4.26 s H) shows that these compounds are isomers and that consequently IV has the ethyl 2-methylthio-4,4-dimethyl-2-oxazoline-5-carboxylate structure; in our case this constitutes evidence for opening of the oxide ring of glycidic ester I on the side of the β-carbon atom.

The structure of V-XII was assumed in analogy with that of IV.

EXPERIMENTAL

The IR spectra of 0.1 M solutions of the compounds in CCl_4 were recorded with a UR-20 spectrometer. The PMR spectra of 10% solutions of the compounds in chloroform were obtained

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V. I. Lenin Belorussian State University, Minsk 220080. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 460-461, April, 1979. Original article submitted June 20, 1978.

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TABLE 1. Ethyl 2-Alkylthio-2-oxazoline-5-carboxylates (IV-XII)

Compound	bp, °C (1 mm)	n_D^{20}	d_4^{20}	Found, %			Empirical formula	Calc., %			Yield, %
				C	H	S		C	H	S	
IV	85—87	1,4824	1,1214	49,9	7,0	15,0	$C_9H_{15}NO_3S$	49,8	7,0	14,8	56
V	94—95	1,4778	1,0917	52,0	7,4	14,2	$C_{10}H_{17}NO_3S$	51,9	7,4	13,9	52
VI	97—98	1,4738	1,0653	53,9	7,8	12,9	$C_{11}H_{19}NO_3S$	53,9	7,8	13,1	54
VII	100—102	1,5058	1,1554	54,5	7,1	13,4	$C_{11}H_{17}NO_3S$	54,3	7,0	13,2	50
VIII	109—111	1,5001	1,1272	56,1	7,5	12,6	$C_{12}H_{19}NO_3S$	56,0	7,4	12,5	56
IX	113—115	1,4954	1,1030	57,7	7,8	11,6	$C_{13}H_{21}NO_3S$	57,5	7,8	11,8	61
X	108—110	1,5062	1,1386	56,1	7,4	12,3	$C_{12}H_{19}NO_3S$	56,0	7,4	12,5	53
XI	118—120	1,5002	1,1123	57,6	7,8	12,0	$C_{13}H_{21}NO_3S$	57,5	7,8	11,8	51
XII	123—125	1,4970	1,0931	59,0	8,2	11,0	$C_{14}H_{23}NO_3S$	58,9	8,1	11,2	50

TABLE 2. PMR and IR Spectra of Ethyl 2-Alkylthio-2-oxazoline-5-carboxylates (IV-XII)

Compound	PMR spectrum, δ, ppm (J, Hz)				IR spectrum, ν, cm^{-1}	
	$R_1=R_2$	R_3	H	OCH_2CH_3	C=O	C=N
IV	1,19 s; 1,44 s	2,45 s	4,57 s	1,30 t, 4,25 q (7)	1760, 1735	1615
V	1,20 s; 1,44 s	1,37 t; 3,00 q (7)	4,57 s	1,30 t; 4,25 q (7)	1760, 1735	1614
VI	1,20 s; 1,44 s	1,39 d; 3,67 m (7)	4,56 s	1,31 t; 4,25 q (7)	1760, 1734	1610
VII	1,56—2,00 m	2,46 s	4,72 s	1,30 t; 4,25 q (7)	1760, 1738	1620
VIII	1,56—2,00 m	1,37 t; 3,00 q (7)	4,69 s	1,30 t; 4,24 q (7)	1759, 1736	1618
IX	1,59—2,00 m	1,37 d; 1,41 d; 3,67 m (7)	4,68 s	1,30 t; 4,24 q (7)	1760, 1736	1615
X	1,50—1,80 m	2,48 s	4,52 s	1,31 t; 4,24 q (7)	1759, 1738	1621
XI	1,50—1,80 m	1,38 t; 3,02 q (7)	4,50 s	1,31 t; 4,24 q (7)	1758, 1739	1621
XII	1,50—1,80 m	1,38 d; 1,42 d; 3,68 m (7)	4,47 s	1,30 t; 4,23 q (7)	1760, 1740	1620

with a Varian HA-100 spectrometer with hexamethyldisiloxane as the internal standard. The purity of the products was monitored by thin-layer chromatography on Silufol in a diethyl ether–hexane system (1:2).

Starting glycidic esters I-III were obtained by the Darzens method [4], and the alkyl thiocyanates were synthesized from alkyl iodides and potassium thiocyanate in ethanol [5].

Ethyl 2-Alkylthio-2-oxazoline-5-carboxylates (IV-XII). A 0.1-mole sample of the glycidic ester and 0.1 mole of boron trifluoride etherate were added simultaneously with stirring from two dropping funnels to 0.3 mole of the alkyl thiocyanate in the course of 2 h at room temperature (with external cooling with running water), after which the mixture was stirred for another 30 min, and 1 mole of sodium bicarbonate and 30 ml of water were added. The desired product was extracted with ether, and the ether extracts were dried with anhydrous sodium sulfate. The ether was removed with a rotary evaporater, and the residue was fractionated at reduced pressure. The properties of IV-XII are presented in Table 1.

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