2. W. W. Gale, A. N. Scott, and H. R. Snyder, J. Org. Chem., 29, 2160 (1964).
3. V. I. Shvedov, A. N. Grinev, and V. K. Vasil'eva, Khim. Geterotsikl. Soedin., 276 (1970).
4. V. I. Shvedov, Yu. I. Trofimkin, V. K. Vasil'eva, T. F. Vlasova, and A. N. Grinev, Khim. Geterotsikl. Soedin., 914 (1975).
5. W. Carpenter and H. R. Snyder, J. Amer. Chem. Soc., 82, 2592 (1962).

SYNTHESIS OF 2-(ACYLMETHYL)BENZO-1,3-OXATHIOLS FROM ACETYLENIC KETONES

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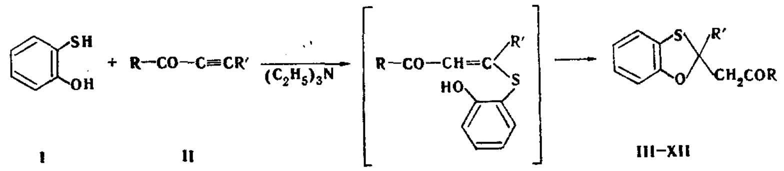
2-(Acylmethyl)benzo-1,3-oxathiols were synthesized by reaction of acetylenic ketones with o-mercaptophenol in alcohol in the presence of a catalyst – triethylamine.

It has been shown [1-3] that the formation of cyclic products as a result of "double addition" to the acetylenic bond is possible in the addition of some bifunctional compounds to acetylenes.

In developing our earlier research [4-6] we have studied the reaction of acetylenic ketones of various structures with o-mercaptophenol, which proceeds readily in alcohol in the presence of a catalyst – triethylamine – to give the hard-to-obtain 2-(acylmethyl)benzo-1,3-oxathiols (III-XII, Table 1) in high yields (70-98%).

The reaction of o-mercaptophenol with acetylenic alcohols probably proceeds through an intermediate step involving the formation of ketovinyl sulfides (addition of the thiol to the acetylenic bond) and cyclization of the latter to the corresponding benzo-1,3-oxathiols.



III $R=C_4H_3S$, $R'=C_6H_5$; IV $R=R'=C_6H_5$; V $R=C_4H_3S$, $R'=H$; VI $R=CH_3$, $R'=C_6H_5$; VII $R=C_4H_3S$, $R'=C_4H_9$; VIII $R=5\text{-}C_2H_5\text{—}C_4H_2S$, $R'=C_4H_3S$; IX $R=C_4H_3S$, $R'=p\text{-}C_6H_4OCH_3$; X $R=C_4H_3S$, $R'=p\text{-}C_6H_4CH_3$; XI $R=C_6H_5$, $R'=C_4H_9$; XII $R=C_4H_3Se$, $R'=C_6H_5$

The structure of the compounds obtained was established by IR and PMR spectroscopy.

The IR absorption band of the C=O group lies at 1652-1681 cm^{-1} for III-V and VII-XII and at 1705 cm^{-1} for VI. The absorption band at 1070-1100 cm^{-1} corresponds to the stretching vibrations of the C—O bond, whereas an absorption band at 680-710 cm^{-1} is characteristic for the stretching vibrations of the C—S bond of the oxathiol ring. The absorption bands of the C=C bond and the OH group are absent in the IR spectra of III-XII.

Signals of olefinic and hydroxyl protons are absent in the PMR spectra of III-XII. The geminal protons of the methylene group in the α position relative to the C=O group give a quartet at δ 4.15 ppm; J = 18.6 Hz for IV and δ = 4.01 ppm; J = 16.8 Hz for III and V-XII. The multiplet at weak field, 6.64 +7.85 ppm,

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TABLE 1. 2-(Acylmethyl)benzo-1,3-oxathiols

Compound	mp, °C	Empirical formula	Found, %			Calculated, %			Yield, %
			C	H	S	C	H	S	
III	123—124	$C_{19}H_{14}S_2O_2$	67,1	4,2	18,2	67,5	4,1	18,9	83
IV	104—105	$C_{21}H_{16}S_2O_2$	75,6	4,8	9,7	75,9	4,8	9,6	98
V	98—99	$C_{13}H_{10}S_2O_2$	59,3	3,9	23,9	59,5	3,8	24,4	80
VI	bp 220—222 (5 mm)	$C_{16}H_{14}SO_2$	71,2	5,2	11,8	71,1	5,2	11,8	70
VII	49	$C_{18}H_{18}S_2O_2$	65,4	5,7	20,1	65,4	5,4	19,4	64
VIII	110—111	$C_{19}H_{16}S_3O_2$	60,8	4,3	25,8	61,0	4,3	25,9	63
IX	103—104	$C_{20}H_{16}S_2O_3$	65,8	4,6	17,5	65,0	4,6	17,4	72
X	120—121	$C_{20}H_{16}S_2O_2$	68,0	4,6	18,4	68,2	4,5	18,5	81
XI	47—48	$C_{19}H_{20}SO_2$	73,4	6,2	10,2	73,1	6,4	10,2	76
XII	123—124	$C_{19}H_{14}SO_2Se$	59,2	3,6	8,2	59,2	3,6	8,3	90

is due to the protons of the benzene and thiophene rings. The protons of the $-CH_2CH$ fragment (V) form a system of the ABX type, and the signal of the methylidyne X proton is split by coupling with the methylene protons into a doublet of doublets with $J = 5.8$ Hz and $J = 7.6$ Hz. Components of the methylene quartet at $\delta = 3.55$ ppm are similarly split with $J = 17.5$ Hz. The spin–spin coupling constants of these protons are characteristic for a cyclic structure.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer.

The PMR spectra of carbon tetrachloride solutions of the compounds were recorded with a JNM-4H-100 spectrometer with an operating frequency of 100 MHz and tetramethylsilane as the internal standard.

2-Thienyl-2-phenylbenzo-1,3-oxathiol (III). A solution of 0.63 g (5 mmole) of I in 10 ml of ethanol was added to a solution of 1.0 g (5 mmole) of II in 50 ml of ethanol, after which one to two drops of triethylamine were added. The mixture was then stirred at room temperature for 2 h, the solvent was removed by vacuum evaporation, and the crystalline residue was recrystallized from ethanol to give 1.31 g (83%) of white crystals of III with mp 123-124°.

A similar method was used to obtain VII-XII (white needles from alcohol), IV and V (light-brown crystals from alcohol), and VI (a light-brown oil).

LITERATURE CITED

1. B. Holmberg, Ark. Kemi, 2, 567 (1950).
2. F. Bohlman and E. Bresinsky, Ber., 97, 2109 (1964).
3. N. D. Heindel, V. B. Fish, M. F. Ryan, and A. R. Leplly, J. Org. Chem., 32, 2678 (1967).
4. V. N. Elokhina and A. S. Nakhmanovich, Khim. Geterotsikl. Soedin., 1637 (1971).
5. A. S. Nakhamanovich, É. N. Deryagina, and V. N. Elokhina, Khim. Geterotsikl. Soedin., No. 3, 45 (1971).
6. A. S. Nakhamanovich, L. G. Klochkova, and V. N. Knutov, Khim. Geterotsikl. Soedin., 1350 (1971).