Nitration with Nitric Acid in Acetic Anhydride. A 0.01-mole sample of the ketone was dissolved in 15 ml of acetic anhydride, and a mixture of 0.015 mole of nitric acid (sp. gr. 1.5) in 3 ml of acetic anhydride was added gradually with stirring at −5 or 60°C. The mixture was maintained at the same temperature for 2 h, after which it was poured into water. The precipitate was removed by filtration, washed with water to remove traces of acid, and dried. The crude mixtures was obtained in 50-90% yields.

Nitration with Copper and Aluminum Nitrates. A 0.01-mole sample of starting ketone I-III was dissolved in 20 ml of the corresponding solvent (CCl_4, $C_2H_2Cl_2$, and CH_3CN), the solution was heated to 60°C, and an equimolar amount of the metal nitrate was added in portions with stirring. Stirring was continued at the same temperature for 2 h, after which the solution was poured into water, and the precipitate was removed by filtration, washed with water, and dried. In the case of carbon tetrachloride or dichloroethane the organic layer was separated and washed with water, and the solvent was removed by vacuum distillation. The products were obtained in 45-56% yields.

The physicochemical characteristics of the nitro derivatives of ketone I are presented in [1], while those of ketone IIa,b and IIIa,b are presented in Tables 1 and 2. Compounds IIb and IIIb were obtained by alternative syntheses [7].

LITERATURE CITED

1. L. V. Panfilova, M. Yu. Antipin, Yu. D. Churkin, and Yu. T. Struchkov, Khim. Geterotsikl. Soedin., No. 9, 120] (1979).
2. J. A. Pople and G. A. Segal, J. Chem. Phys., 44, 3289 (1966).
3. D. P. Sautry and G. A. Segal, J. Chem. Phys., 47, 158 (1967).
4. G. Gombes, M. Hebbelynck, and I. Ledrut, Bull. Soc. Chim. Fr., No. 3, 315 (1953).
5. A. V. Topchiev, in: Selected Works. Nitration [in Russian], Nauka, Moscow (1965), p. 55.
6. H. Gilman (editor), Organic Syntheses [Russian translation], Vol. 1, Inostr. Lit., Moscow (1949), p. 76.
7. Yu. D. Churkin and L. V. Panfilov, Khim. Geterotsikl. Soedin., No. 8, 1048 (1980).

SYNTHESIS OF 2-ACYLMETHYL- AND 2-ACYLMETHYLENEBENZO-1,3-DITHIOLES FROM α-ALKYNYL KETONES

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UDC 547.738.07

The reaction of α-alkynyl ketones with o-phenylenedithiol, which leads to the formation of 2-acylmethylbenzo-1,3-dithioles, was investigated. Reactions of the latter with hydrazine hydrate and hydroxylamine and oxidation were realized. Difficult-to-obtain 2-acylmethylenebenzo-1,3-dithioles were obtained by the reaction of α-bromoalkynyl ketones with o-phenylenedithiol. The IR and PMR spectra of the synthesized compounds are presented.

The formation of cyclic adducts as a result of double addition to a triple bond is possible in the reaction of certain dinucleophiles with acetylenic compounds [1-5].

We have studied the reaction of α-alkynyl ketones Ia-g with o-phenylenedithol, which leads to the formation of difficult-to-obtain 2-acylmethylbenzo-1,3-dithioles IIIa-g via the scheme:

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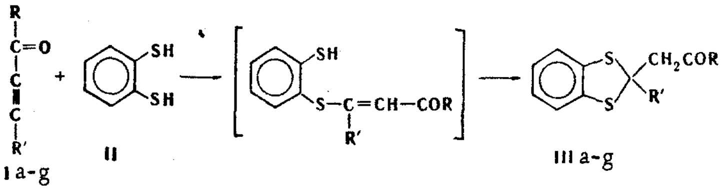
TABLE 1. 2-Acylmethylbenzo-1,3-dithioles (IIIa-g)

Compound	mp, °C	Found, %			Empirical formula	Calculated, %			Yield, %	
		C	H	S		C	H	S	method A	method B
III a	124—125	66,4	4,5	23,0	$C_{15}H_{12}OS_2$	66,2	4,4	23,2	96	92
III b	136—137	72,0	4,5	18,0	$C_{21}H_{16}OS_2$	72,4	4,6	18,4	81	
III c	137—138	56,1	3,7	34,3	$C_{13}H_{10}OS_3$	56,1	3,6	34,5	82	74
III d	76—77	61,0	5,3	28,5	$C_{17}H_{18}OS_3$	61,1	5,4	28,7	62	
III e	149—150	64,1	4,0	27,2	$C_{19}H_{14}OS_3$	64,4	4,0	27,1	86	82
III f	95—96	67,5	4,8	22,6	$C_{16}H_{14}OS_2$	67,1	5,0	22,4	78	
III g	134—135	57,3	4,3	32,8	$C_{14}H_{12}OS_3$	57,5	4,1	32,9	88	

TABLE 2. PMR Spectra of 2-Acylmethylbenzo-1,3-dithioles (IIIa-g)

Compound	Chemical shift, δ, ppm				SSCC, J, Hz
	R	R′	C_6H_4	CH_2CO	
III a	7,31 m 7,87 m	5,25 t	7,08 m	3,56 d	6,9
III b	7,12—8,02 m			4,28 s	—
III c	7,63 d 5-H 7,54 d 3-H 7,11 t 4-H	5,16 t	7,12 m	3,46 d	7,1
III d	7,71 d 5-H 7,51 d 3-H 7,05 t 4-H	1,98 t 1,40 m 0,90 t	7,10 m	3,42 s	—
III e	7,00—7,70 m			4,20 s	—
III f	1,92 s	7,25 m 7,68 m	7,10 m	3,72 s	—
III g	2,02 s	7,15 q 5-H 7,06 q 3-H 6,80 q 4-H	7,09 m	3,73 s	—



I, III a $R=C_6H_5$, $R'=H$; b $R=R'=C_6H_5$; c $R=\alpha\text{-}C_4H_3S$, $R'=H$, d $R=\alpha\text{-}C_4H_3S$, $R'=C_4H_9$; e $R=\alpha\text{-}C_4H_3S$, $R'=C_6H_5$; f $R=CH_3$, $R'=C_6H_5$; g $R=CH_3$, $R'=\alpha\text{-}C_4H_3S$

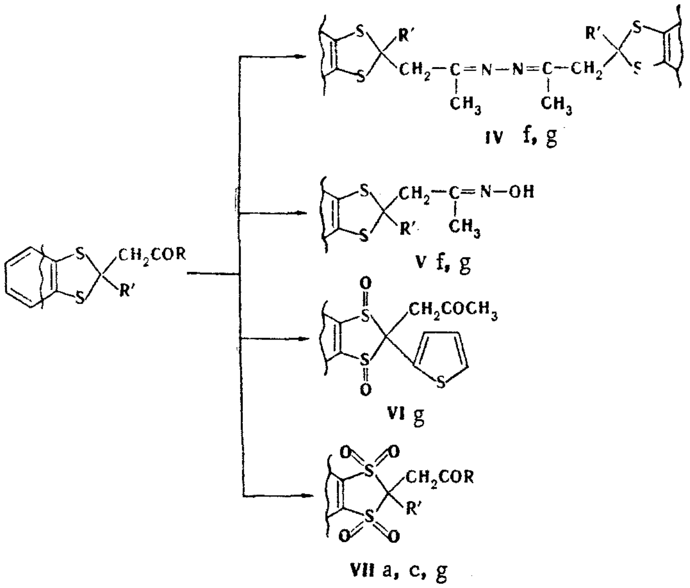
The reaction of these reagents in a molar ratio of 1:1 was realized in alcohol (method A) or in chloroform in the presence of potassium carbonate as the catalyst (method B). The reaction evidently proceeds through the intermediate formation of the corresponding ketovinyl sulfides (the addition of one thiol group to the triple bond) and cyclization of the latter to the corresponding 2-acylmethylbenzo-1,3-dithioles IIIa-g. The presence of an aryl or alkyl grouping at the triple bond of the starting ketone facilitates the reaction, owing to which the corresponding benzo-1,3-dithioles IIIb, e-g are formed in high yields (78-96%). At the same time, when R' = C_4H_9, IIId is isolated in lower yield (62%). The yields of IIIa and IIIc depend only slightly on the molar ratio of the reagents.

The structures of IIIa-g were confirmed by the PMR (Table 2) and IR spectra. The absorption bands of the C=O group in the IR spectra of IIIa-e and IIIf,g are found at 1660-1685 and 1728-1740 cm^{-1}, respectively. The intense absorption band at 715-740 cm^{-1} corresponds to the stretching vibrations of the C—S bond in the heteroring. The intense absorption band at 1445-1460 cm^{-1} corresponds to the deformation vibrations of the CH_2 group. The bands at 730-760, 1050-1080, 1420-1435, 1520-1530, and 3090-3105 cm^{-1} in the IR spectra of IIIc-e, g correspond to vibrations of the thiophene ring.

The corresponding ketazines IVf,g are obtained when benzo-1,3-dithioles IIIf,g are heated with hydrazine hydrate in benzene in the presence of boron trifluoride etherate. An attempt to obtain similar derivatives from benzo-1,3-ditholes that contain a phenyl or thienyl group adjacent to the carbonyl group was unsuccessful.

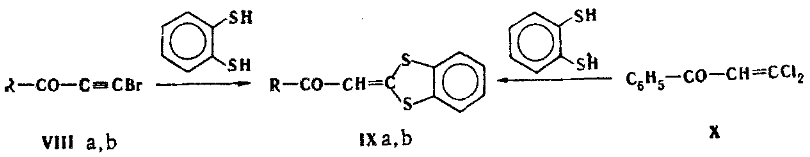
The reaction of IIIf,g with hydroxylamine hydrochloride in the presence of potassium acetate leads to the corresponding oximes Vf,g. An attempt to obtain oximes from IIIa,c was also unsuccessful.

Thus the presence of a phenyl or thienyl group at the carbonyl group in III suppresses its ability to undergo anhydro condensation reactions.



Disulfoxide VIg was obtained by oxidation of benzo-1,3-dithiole IIIg with 30% hydrogen peroxide in an aqueous alcohol medium in the presence of selenium dioxide. However, the oxidation of IIIa,c,g with 30% hydrogen peroxide in glacial acetic acid leads exclusively to the corresponding disulfones VIIa,c,g.

The reaction of α-bromoalkynyl ketones VIIIa,b with o-phenylenedithiol in ethanol at 20°C leads to 2-acylmethylenebenzo-1,3-thioles IXa,b.



a $R = C_6H_5$; b $R = \alpha\text{-}C_4H_3S$

Compound IXa was also obtained by the reaction of β,β-dichlorovinyl ketone with o-phenylenedithiol in alcohol in the presence of triethylamine. The IR spectra of IXa,b contain absorption bands of a conjugated carbonyl group at 1620-1630 cm^{-1}, of a C=C bond at 1580-1585 cm^{-1}, and of a C-S bond at 705-715 cm^{-1}. The spectrum of IXb contains a set of bands of a thiophene ring at 745, 1055, 1420, and 3110 cm^{-1}. The signals of olefin protons in the PMR spectra of IXa,b show up in the form of singlets at δ 7.10 and 6.95 ppm; the spectra also contain a multiplet of protons of a benzene ring at δ 7.82 ppm (for IXa) and a multiplet of protons of a thiophene ring at σ 7.21-8.02 ppm (for IXb).

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 $CDCl_3$ were recorded with a Tesla BA-487-C spectrometer (80 MHz) relative to hexamethyldisiloxane.

2-Benzoylmethylbenzo-1,3-dithiole (IIIa). A) A 1.42-g (0.01 mole) sample of o-phenylenedithiol (II) was added dropwise with stirring to a solution of 1.3 g (0.01 mole) of 1-phenyl-2-propyn-1-one (Ia) in 50 ml of ethanol, and the mixture was stirred at 20°C for 3 h. It was then cooled to 0°C, and the resulting precipitate was removed by filtration and recrystallized from ethanol to give 2.61 g (96%) of product. The remaining III were similarly obtained (Table 1).

B) A mixture of 1.3 g (0.01 mole) of 1-phenyl-2-propyn-1-one (Ia) and 1.42 g (0.01 mole) of o-phenylenedithiol (II) in 50 ml of anhydrous chloroform in the presence of 1 g of freshly calcined K_2CO_3 was heated at 60°C for 2 h, after which it was cooled and filtered. The solvent was removed *in vacuo*, and the residue was dissolved in ether. The ether solution was cooled to 0°C, and the precipitate was removed by filtration and recrystallized from ethanol to give 2.5 g (92%) of product. Compounds IIIc,e were similarly obtained (Table 1).

Bis(2-phenylbenzo-1,3-dithiol-2-yl)acetone Azine (IVf). A 0.3-g (6 mmole) sample of hydrazine hydrate and two drops of boron trifluoride etherate were added with stirring to a solution of 2.86 g (0.01 mole) of IIIf in 30 ml of absolute benzene, and the mixture was refluxed for 6 h. The benzene was then evaporated partially *in vacuo*, and the residue was precipitated with cold ether and recrystallized from ethanol to give 1.85 g (65% based on IIIf) of a product with mp 167-168°C. IR spectrum: 1645 (C=N) and 705 cm^{-1} (C–S). Found: C 67.9; H 4.8; N 4.9; S 22.3%. $C_{32}H_{28}N_2S_4$. Calculated: C 67.6; H 4.9; N 4.9; S 22.5%.

Bis[2-(2-thienyl)benzo-1,3-dithiol-2-yl]acetone Azine (IVg). This compound was similarly obtained. Workup gave 2 g (69%) of a product with mp 177-178°C. IR spectrum: 1642 (C=N) and 705 cm^{-1} (C–S). Found: C 57.9; H 4.0; N 4.9; S 33.0%. $C_{28}H_{24}N_2S_6$. Calculated: C 57.9; H 4.1; N 4.8; S 33.1%.

1-(2-Phenylbenzo-1,3-dithiol-2-yl)-2-methyl-2-oximinoethane (Vf). A mixture of 0.35 g (1.2 mmole) of IIIf, 0.14 g (2 mmole) of hydroxylamine hydrochloride, and 20 ml of methanol was heated to 60°C, and a solution of 0.2 g (2 mmole) of potassium acetate in 5 ml of water was added dropwise with stirring. Stirring was continued for 6 h, after which the mixture was poured into cold water. The precipitate was removed by filtration and recrystallized from ethanol to give 0.3 g (83%) of a product with mp 127-128°C. IR spectrum: 1640 (C=N), 3480 (NOH), 705 (C–S), and 1450 cm^{-1} (CH_2). Found: C 63.7; H 5.2; N 4.7; S 21.2%. $C_{16}H_{15}NOS_2$. Calculated: C 63.8; H 5.0; N 4.7; S 21.3%.

1-[2-(2-Thienyl)benzo-1,3-dithiol-2-yl]-2-oximinoethane (Vg). This compound was similarly obtained. Workup gave 0.26 g (86%) of a product with mp 91-92°C (from alcohol). IR spectrum: 1642 (C=N), 3465 (NOH), 708 (C–S), and 1452 cm^{-1} (CH_2). Found: C 55.0; H 4.5; N 4.6; S 30.9%. $C_{14}H_{13}NOS_3$. Calculated: C 54.7; H 4.2; N 4.6; S 31.2%.

2-Acetylmethyl-2-(2-thienyl)benzo-1,3-dithiole Dioxide (VIg). A 0.11-g sample of selenium dioxide was added to a solution of 0.29 g (1 mmole) of IIIg in 10 ml of methanol, and 0.4 ml of 30% hydrogen peroxide was then added slowly dropwise with stirring. The mixture was stirred at room temperature for 30 min, after which it was poured into ice water, and the precipitate was removed by filtration, washed with cold water, and recrystallized from ethanol to give 0.19 g (60%) of a product with mp 165-166°C. IR spectrum: 1730 (C=O); 722 (C–S); 1060 (S=O); 1435 (CH_2); 750, 1580, 3110 cm^{-1} (α-C_4H_3S). Found: C 52.0; H 3.7; S 29.6%. $C_{14}H_{12}O_3S_3$. Calculated: C 51.8; H 3.7; S 29.6%.

2-Benzoylmethylbenzo-1,3-dithiole Tetroxide (VIIa). A 2.4-ml sample of 30% hydrogen peroxide was added slowly dropwise with stirring to a solution of 0.5 g (1.9 mmole) of IIIa in 1 ml of glacial acetic acid, after which the mixture was stirred for 2 h and allowed to stand overnight. The resulting precipitate was removed by filtration, washed with water, and recrystallized from ethanol to give 0.39 g (65%) of a product with mp 176-177°C. IR spectrum: 1710 (C=O), 1330 ($\nu_{as}SO_2$), 1180 ($\nu_{s}SO_2$), 1450 (CH_2), and 720 cm^{-1} (C–S). Found: C 53.5; H 3.6; S 19.1%. $C_{12}H_{12}O_5S_2$. Calculated: C 53.6; H 3.6; S. 19.1%.

2-Thenoylmethylbenzo-1,3-dithiole Tetroxide (VIIc). This compound was similarly obtained. Workup gave 0.39 g (60%) of a product with mp 172-174°C (from acetone). IR spectrum: 1715 (C=O); 1332 ($\nu_{as}SO_2$); 1180 ($\nu_{s}SO_2$); 718 (C–S); 1452 (CH_2); 750, 1584, 3120 cm^{-1} (α-C_4H_3S). Found: C 45.7; H 3.0; S 28.0%. $C_{13}H_{10}O_5S_3$. Calculated: C 45.6; H 2.9; S 28.1%.

2-Acetylmethyl-2-(2-thienyl)benzo-1,3-dithiole Tetroxide (VIIg). This compound was similarly obtained. Workup gave 0.25 g (71%) of a product with mp 182-183°C (from acetone). IR spectrum: 1730 (C=O); 1340 ($\nu_{as}SO_2$); 1160 ($\nu_{s}SO_2$); 720 (C–S); 1440 (CH_2); 748, 1580, 3090 cm^{-1} (α-C_4H_3S). Found: C 47.3; H 3.4; S 27.1%. $C_{14}H_{12}O_5S_3$. Calculated: C 47.2; H 3.4; S 27.0%.

2-Benzoylmethylenebenzo-1,3-dithiole (IXa). A) A solution of 1.42 g (0.01 mole) of II in 10 ml of ethanol was added slowly dropwise at 20°C to a solution of 2.09 g (0.01 mole) of 1-phenyl-3-bromo-2-propyn-1-one (VIIIa) in 20 ml of ethanol, and the mixture was stirred for 30 min. It was then cooled to 0°C, and the precipitate was removed by filtration to give

3.12 g (88%) of a product with mp 172-173°C (from ethanol). Found: C 66.4; H 3.5; S 23.7%. $C_{15}H_{10}OS_2$. Calculated: C 66.7; H 3.7; S 23.7%.

B) A 1-g (0.01 mole) sample of triethylamine was added with stirring at 20°C to a solution of 1 g (5 mmole) of X in 15 ml of ethanol, after which 0.71 g (5 mmole) of II was added slowly dropwise, and the mixture was stirred for 2 h. It was then cooled to 0°C, and the precipitate was removed by filtration to give 1.6 g (94%) of a product with mp 173-174°C (from ethanol).

2-Thenoylmethylenebenzo-1,3-dithiole (IXb). This compound was similarly obtained from 2.15 g (0.01 mole) of 1-(2-thienyl)-3-bromo-2-propyn-1-one (VIIIb) and 1.42 g (0.01 mole) of II. Workup gave 2.29 g (83%) of a product with mp 185-187,C (from acetone). Found: C 56.8; H 2.9; S 34.7%. $C_{13}H_8OS_3$. Calculated: C 56.8; H 2.9; S 34.8%.

LITERATURE CITED

1. B. Holmberg, Arkiv Kemi, 2, 567 (1950); Chem. Abstr., 46, 100 (1952).
2. F. Bohlmann and E. Bresinsky, Chem. Ber., 97, 2109 (1964).
3. V. N. Elokhina, A. S. Nakhmanovich, I. D. Kalikhman, N. P. Sokol'nikova, and M. G. Voronkov, Khim. Geterotsikl. Soedin., No. 10, 1328 (1975).
4. V. N. Elokhina, R. V. Karnaukhova, A. S. Nakhmanovich, I. D. Kalikhman, M. G. Voronkov, Zh. Org. Khim., 15, 57 (1979).
5. K. Hideg, O. Hideg-Hankovszky, and P. Sohar, Chem. Ber., 107, 2079 (1974).

EFFECTS OF STEREOISOMERISM IN THE MASS SPECTRA OF 2,4-DISUBSTITUTED THIACYCLOHEXANES*

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UDC 541.62'63:543.51:547.818

The mass spectra of cis- (Ia-c) and trans-2-methyl-4-R-thiacyclohexanes (IIa-c; a R = $n\text{-}C_4H_9$, b R = $n\text{-}C_5H_{11}$, c R = Ph) were studied. It was established that $[M{-}CH_3]^+$ ions, which correspond to the loss of a methyl group from the 2 position, are formed more readily in the case of the less stable trans isomers IIa-c than in the case of cis isomers Ia-c. The three-dimensional structures of the substances have no effect on the degree of elimination of the R substituent. The relative ionization energies (RIE) for Ia,b and IIa,b and the relative appearance energies (RAE) of the $[M{-}CH_3]^+$ ions were measured by the electron impact method. It was found that the RIE are almost 0.05 eV lower and that the RAE of the $[M{-}CH_3]^+$ ions are ∼0.1 eV lower for trans isomers IIa,b than for cis isomers Ia,b.

The stereospecificity of the fragmentation under electron impact of geometrical isomers that differ with respect to the configuration of the alkyl-substituted centers is associated mainly with the different ease of elimination of the substituting alkyl groups. The available relatively small number of papers devoted to the mass-spectrometric study of such stereoisomers shows that the character of the stereospecificity of the fragmentation reactions differs for heterocyclic and carbocyclic compounds. In the case of carbocyclic methyldecalins [2], which have a conformationally rigid system, as well as dialkylcyclohexanes [3] with a loose conformation, an alkyl substituent is unexpectedly readily ejected from the molecular ions of the thermodynamically more stable stereoisomers. The opposite principle is observed in series of heterocyclic compounds with a fixed conformation (sub-

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*Communication 4 from the series "Ionization and appearance energies in organic chemistry." See [1] for Communication 3.

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