ical wavelengths were recorded by means of a V2-23 digital voltmeter; the layer thickness was 1 cm, the concentration was $\sim 10^{-4}$ mole/liter, and the temperature was 25.0 ± 0.1°C.

The 25-90% sulfuric acid solutions were prepared as in [1].

A 100-120-mg sample of the investigated compound was weighed with an analytical balance and dissolved in distilled water in a 25-ml pycnometer. A 3-ml sample of sulfuric acid was placed in the cuvette by means of a buret and stirred and thermostatted at 25 ± 0.1°C for 4-5 min, after which the spectrum was recorded. The next portion of the solution was then added, and the procedure described above was repeated four to five times (until an optical density of 0.8 to 1.0 at the analytical wavelength was reached).

The extinction coefficient was calculated with allowance for the change in the concentration and volume of the solution due to the water introduced with the sample of the substance.

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NITRO DERIVATIVES OF THE THIOPHENE SERIES.

2.* NITRATION OF THIENYL-SUBSTITUTED UNSATURATED METHYL KETONES

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UDC 547.732

The nitration of 4-(5-R-2-thienyl)-3-buten-2-ones with nitric acid in acetic anhydride is accompanied by the formation of a mixture of nitro isomers, whereas nitration with nitric acid and copper and aluminum nitrates in carbon tetrachloride, dichloroethane, and acetonitrile leads to the production of only the α-nitro ketone. The results of quantum-chemical calculations of the reactivity indexes within the CNDO/2 approximation are in agreement with the experimental data on electrophilic substitution of these compounds in the basic and protonated forms.

The nitration of thienyl-substituted α,β-unsaturated methyl ketones is possible via two pathways — in the heterocyclic ring and in the aliphatic chain [1]. To explain this it seemed of interest to make a detailed study of the reactivities of thiophene compounds that contain conjugated C=C and C=O bonds.

We calculated the electronic structure for 4-(2-thienyl)-3-buten-2-one (I) (within the CNDO/2 approximation on an s- and p-orbital basis without allowance for the d AO of sulfur by the method proposed in [2, 3]) and found the reactivity indexes of the molecule (the residual π-electron densities) for electrophilic substitution reactions (Fig. 1). We used the experimental geometry of ketone Ia in the calculations [1]. It follows from the data obtained that the probable reaction centers in ketone I are the 7, 3, 4, and 5 positions ($7 > 5 > 3 \approx 4$).

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*See [1] for Communication 1.

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0009-3122/81/1703-0232$07.50

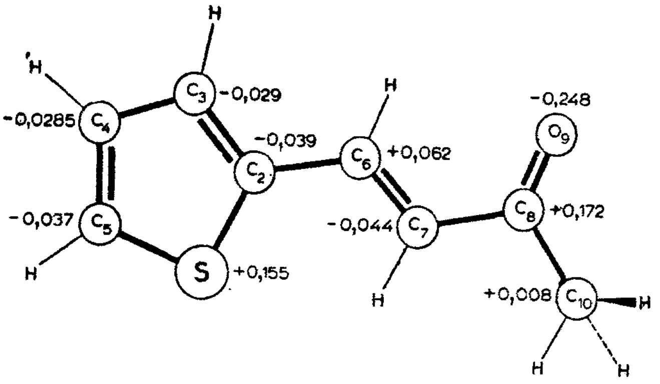


Fig. 1. Basic form of ketone I (π-electron density distribution).

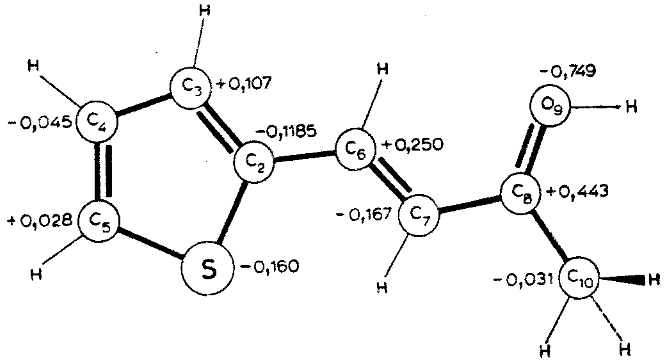
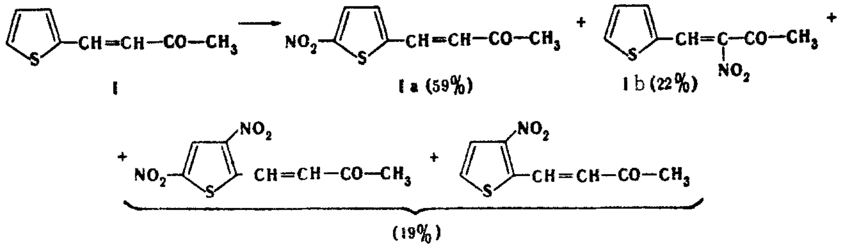
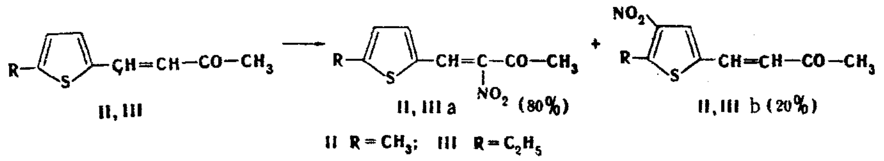


Fig. 2. Protonated form of ketone I (π-electron density distribution).

Data from the PMR spectrum of the mixture after nitration of ketone I with nitric acid in acetic anhydride at 60 and –5°C showed that a mixture of four nitro compounds rather than one product, as indicated in [4], is formed:



The nitration of 5-alkyl-substituted ketones at 60°C led to complete resinification; however, nitration with nitric acid in acetic anhydride at –5°C leads to a mixture of two nitro isomers IIa and IIb and IIIa and IIIb in a ratio of 4:1:



In our opinion, this reaction pathway can be explained by the fact that the reaction of nitric acid with acetic anhydride leads to the formation of a nitronium cation, which evidently reacts gradually with all of the nucleophilic centers present in the examined compounds to give mixtures of isomers.

The nitration of the investigated compounds with nitric acid (sp. gr. 1.5) in carbon tetrachloride, 1,2-dichloroethane, and acetonitrile does not take place at low temperatures; however, at 60°C it leads to the production of only some α-nitro ketones (according to data

TABLE 1. Physicochemical Characteristics of Nitrothienyl-Substituted α,β-Unsaturated Ketones

Compound	mp, °C (from heptane)	Found, %			Empirical formula	Calculated, %			Yield, %
		C	N	S		C	N	S	
IIa	137—139	50,8	6,2	15,7	$C_9H_9NO_3S$	51,2	6,5	15,8	33—44
IIb	118—118,5	51,4	6,3	16,0	$C_9H_9NO_3S$	51,2	6,5	15,8	20
IIIa	109—110	52,9	6,0	13,7	$C_{10}H_{11}NO_3S$	53,3	6,2	14,2	33—42
IIIb	71—72,5	53,0	5,9	14,4	$C_{10}H_{11}NO_3S$	53,3	6,2	14,2	15

TABLE 2. Spectral Characteristics of Ketones II, III, IIa, IIIa, IIb, and IIIb

Compound	IR spectrum, cm^{-1}				PMR spectrum							SSCC, Hz		
					Chemical shifts, ppm									
	$C=C$	$C=O$	NO_2as	NO_2s	3-H	4-H	α-H	β-H	$CO—CH_3$	CH_3	CH_2*	J_{34}	$J_{\alpha\beta}$*	J_{4Alk}†
II	1610	1660	—	—	7,13 d	6,72 dq	6,29 d	7,57 d	2,21 s	2,40 d	—	3,6	16,0	—
III	1610	1660	—	—	7,24 d	6,84 dt	6,38 d	7,64 d	2,25 s	1,31 t	2,84 qd	3,6	16,0	1,0
IIa	1610	1665	1520	1360	7,49 d	6,95 dq	—	7,90 d	2,43 s	2,53 d	—	3,5	—	0,9
IIIa	1610	1660	1530	1360	7,54 d	7,01 d	—	7,93 d	2,46 s	1,31 t	2,93 qd	3,5	—	0,9
IIb	1632	1684	1542	1380	7,88 s	—	6,52 d	7,65 d	2,30 s	2,74 s	—	—	16,0	—
IIIb	1615	1678	1555	1342	7,89 s	—	6,55 d	7,67 d	2,30 s	1,35 t	3,17 q	—	16,0	—

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*$J_{CH_3—CH_2}$ = 6.7 Hz.
†4-CH_3 or 4-CH_2.

from the PMR spectra of the crude mixtures), viz., Ib, IIa, and IIIa. This pathway is not explained on the basis of the calculated reactivity indices, probably because of the fact that the unsaturated ketones react in the protonated form under these conditions. A quantum-chemical calculation of the protonated form of ketone I showed that the 7 and 4 positions in it are actually reactive and that 7 ≫ 4 in activity (Fig. 2). Conversion to the protonated form takes place as a consequence of interaction of the hydronium ion formed from nitric acid with the carbonyl group with the formation of a complex. The latter, by splitting out water, is converted to the protonated form of the ketone. In addition to this, we also assume direct protonation of the carbonyl group by a proton from the nitric acid.

The introduction of a nitro group promotes new redistribution of the electron density, decreases the nucleophilicity of the oxygen atom, and promotes splitting out of a proton, which subsequently can either react again with water or protonate another molecule of the starting unsaturated ketone.

Similarly, nitration with the formation of only α-nitro ketone Ib, IIa, or IIIa takes place under the influence of copper and aluminum nitrates that contain crystallization water in carbon tetrachloride, dichloroethane, and acetonitrile at 60°C. This effect of the nitrates indicated above can evidently be explained by hydrolysis itself of the crystal hydrates [5]. The resulting nitric acid, by reacting with ketones I-III, shifts the equilibrium of the hydrolysis of the nitrate, thereby promoting the formation of new acid molecules. This leads to more uniform reaction and a decrease in the side processes. Sodium and potassium nitrates, which do not form crystal hydrates, do not have a nitrating effect on ketones I-III under the same conditions.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The PMR spectra of solutions of the compounds in $(CD_3)_2CO$ were obtained with a Tesla BS-497 spectrometer (100 MHz) with hexamethyldisiloxane as the internal standard. The signals were assigned by means of double resonance.

Starting ketones I-III were synthesized by the method in [6]. Their nitration with nitric acid in carbon tetrachloride, dichloroethane, and acetonitrile was carried out by the method described in [1].

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].

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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:

Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Irkutsk 664033. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 329-332, March, 1981. Original article submitted March 27, 1980.

0009-3122/81/1703-0235$07.50