

Reduction of 5'-formyl-5-[2-(4-ethoxycarbonyl-2-quinolyl)vinyl]-2,2'-bithiophene (XII) was carried out by the method of [11], mp 206-208°C. IR spectrum: 1700 (amide CO), 2900 cm^{-1} (CH_3).

5'-Methyl-5-[2-(2-quinolyl)vinyl]-2,2'-bithiophene (XIII) was prepared by the method of [5]. The yield was 43%, mp 118-119°C (from isopropanol). IR spectrum: 2900 cm^{-1} (CH_3). Found: C 72.0; H 4.5; N 4.2%. $\text{C}_{20}\text{H}_{15}\text{NS}_2$. Calculated: C 72.2; H 4.5; N 4.2%.

Reduction of 5'-formyl-5-[2-(2-quinolyl)vinyl]-2,2'-bithiophene (XI) was carried out by the method of [11], mp 118-119°C (from isopropanol). IR spectrum: 2900 cm^{-1} (CH_3).

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SYNTHESIS AND STRUCTURE OF NITRO DERIVATIVES OF 4-(2-THIENYL)-3-BUTEN-2-ONE

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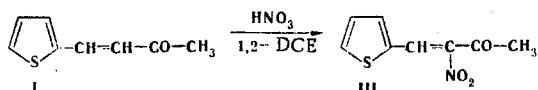
Combes, Hebbelynck, and Zedrut used concentrated nitric acid in acetic anhydride [1] and Pappalardo nitric acid in concentrated sulfuric acid [2] for the nitration of 4(2-thienyl)-3-buten-2-one (I). They considered that only 4-(5-nitro-2-thienyl)-3-buten-2-one was formed rather than a mixture of the 4- and 5-nitro isomers, which would have been expected on the basis of the properties of carbonyl derivatives of thiophene [3]. Pappalardo [2] cited no evidence for his identification of the isolated compound with melting point 127°C as 4-(5-nitro-2-thienyl)-3-buten-2-one. Combes et al. [1] verified the structure of the synthetic 4-(5-nitro-2-thienyl)-3-buten-2-one with mp 131-131.5°C by conversion to 5-nitro-2-thiophencarboxylic acid and deduced the trans orientation of the olefinic hydrogens from a calculation of its UV spectrum.

We have continued our work on the reactivity of α , β -unsaturated ketones of the thiophene series with a study of the nitration of 4-(2-thienyl)-3-buten-2-one (I) with potassium nitrate in concentrated sulfuric acid and with concentrated nitric acid in 1,2-dichloroethane. Nitration of compound (I) with potassium nitrate in concentrated sulfuric acid gave a mixture of the 5- and 4-nitro compounds in the ratio 2.6:1 (from the PMR parameters of the crude substance). Fractional recrystallization gave only one nitro ketone with melting point 131.5-132.5°C. We have so far not been able to isolate the second isomer in the pure form. Its PMR and IR parameters identified the isolated nitro ketone as 4-(5-nitro-2-thienyl)-3-buten-2-one (II) with the trans orientation of the hydrogen atoms at the double bone. We carried out an x-ray structure analysis of ketone (II) to find the bond angles and lengths and to decide between the O,S-cis or trans conformations. This revealed that

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the molecule of (II) has the O,S-trans conformation and a planar heterocyclic ring. The dihedral angle between the plane of the thiophene ring and the nitro group is 6.5°. The bond lengths differ only slightly from their standard values in thiophene compounds [4-6]. The $C_{(2)}-S$ and $C_{(5)}-S$ bonds have the same length, 1.698(8) Å.

Nitration of compound (I) with nitric acid (d 1.5) in 1,2-dichloroethane at 60–70°C gave compound (III) with mp 146–146.5°C. Its PMR (double resonance) and IR spectra did not unambiguously identify the position of the nitro group, indicating only that it is not attached to the thiophene ring. For a definitive establishment of the structure and geometry of ketone (III) we carried out an x-ray structure analysis, which revealed it to be 3-nitro-4-(2-thienyl)-3-buten-2-one, with a planar thiophene ring (the maximum deviation of the atoms from the mean plane is less than 0.02 Å). The nitro group forms a dihedral angle of 93.3° with the plane of the heterocycle, which excludes the possibility that it is conjugated with the thiophene ring. The hydrogen atoms were not located. The bond lengths are consistent with published figures for thiophene derivatives [4–6]. The structure of compound (III) represents an unusual course of the nitration reaction. In the presence of a system of conjugated C=O and C=C double bonds in ketone (I) substitution of a hydrogen atom by the nitro group in nitration by nitric acid in 1,2-dichloroethane takes place not in the heterocycle, as is normal, but in the aliphatic chain at the *α*-carbon atom of a conjugated system of double bonds:



EXPERIMENTAL

Spectra were recorded on: IR: a UR-20; and PMR; a Varian Chart S-100A in DMSO with hexamethyl-disiloxane (HMDS) as external standard. The purity of the synthetic compounds was monitored by TLC of silica gel (Silufol UV-254 in heptane-acetone, 4:1). X-ray structure analyses were carried out on a Syntex P2₁ automatic four-circle diffractometer (λ MoK α , graphite monochromator, $\theta/2\theta$ scan). The starting ketone (I) was synthesized by the method of [7].

4-(5-Nitro-2-thienyl)-3-buten-2-one (II). To concentrated H_2SO_4 ($d = 1.84$; 25 ml) cooled to 0°C was added ketone (I) (3.04 g, 0.02 mole). Powdered potassium nitrate (2.02 g, 0.02 mole) was added in small portions with vigorous stirring while the temperature was maintained at 0-5°C. The mixture was kept at this temperature for 2 h and then poured onto ice. The precipitate was filtered off, carefully washed with water, and dried in air. The yield of compound (II) as a light brown precipitate was 3.9 g (99%), mp 131.5-132.5°C (from heptane). IR spectrum: 1705 (C=O), 1340 (NO₂_S), 1550 (NO₂_{as}), 1615 cm⁻¹ (C=C). PMR spectrum (in DMSO): 8.03 (4-H, d); 7.59 (3-H, D); 7.8 (α -H, d); 6.85 (β -H, d); 2.28 ppm (CO-CH₃, s); $J_{3,4} = 4.4$ Hz; $J_{\alpha\beta} = 16.4$ Hz. Found: C 48.3; H 3.5; N 7.1; S 16.1%. C₈H₇NO₃S. Calculated: C 48.7; H 3.6; N 7.1; S 16.2%.

3-Nitro-4-(2-thienyl)-3-butene-2-one (III). To a solution of ketone (I) (3.04 g, 0.02 mole) in 1,2-dichloroethane (15 ml) heated to 45°C was slowly added HNO_3 (d 1.50; 1.57 g, 0.025 mole) in 1,2-dichloroethane (5 ml) with vigorous stirring. The mixture was kept at 60–70°C for 1 h 30 min to 2 h and then poured into water (300 ml). The organic layer was separated and carefully washed free of traces of acid with water. The solvent was distilled off under vacuum. The yield of compound (III) as light yellow crystals was 1.88 g (57.6%), mp 146.5°C (from alcohol). IR spectrum: 1682 (C=O), 1631 (C=C); 1368 (NO_2 s); 1542 cm^{-1} (NO_2 as). PMR spectrum (in DMSO): 8.23 (β -H, s); 8.03 (3-H, d); 7.24 (4-H, t); 7.66 (5-H, d); 2.45 ppm ($\text{CO}-\text{CH}_3$, s); $J_{5,\beta} = 0.6$ Hz; $J_{3,\beta} = 0.5$ Hz; $J_{5,3} = 1.2$ Hz; $J_{5,4} = 4.9$ Hz; $J_{4,3} = 4.5$ Hz. Found: C 48.5; H 3.5; N 7.3; S 16.4%.

TABLE 1. Crystallographic Parameters of 4-(5-Nitro-2-thienyl)-3-buten-2-one (II) and 3-Nitro-4-(2-thienyl)-3-buten-2-one (III) at -120°C

	H	III
a , Å	3.314 (5)	6.354 (1)
b , Å	16.331 (8)	6.698 (1)
c , Å	13.792 (17)	10.401 (1)
β , °	92.36 (10)	101.94 (1)
Z	4	2
Space group	$P2_1/c$	$P2_1$ or $P2_1/m$
d measure, g/cm³		1.47
d calc, g/cm³	1.56	1.51
V , Å³	843.0 (2)	434.0 (1)

TABLE 2. Atomic Coordinates ($\times 10^4$) of (II) and (III)

Atom	Compound (II)			Compound (III)		
	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>
S	7852 (8)	978 (1)	359 (2)	2057 (3)	0	4689 (2)
N	6060 (20)	1529 (4)	-1463 (5)	1872 (9)	-80 (32)	7641 (5)
O (1)	4670 (20)	862 (4)	-1569 (4)	3945 (3)	-97 (28)	1015 (5)
O (2)	6310 (20)	2043 (4)	-2094 (4)	1039 (25)	1697 (20)	7620 (11)
O (3)	13580 (20)	941 (4)	-1058 (4)	890 (23)	-1538 (20)	7462 (11)
C (2)	7770 (30)	1718 (5)	-505 (5)	4673 (10)	-5 (35)	5577 (6)
C (3)	9100 (30)	2437 (5)	-233 (6)	6143 (10)	6 (3)	4732 (5)
C (4)	10420 (20)	2407 (4)	811 (4)	5079 (11)	18 (33)	3400 (6)
C (5)	9890 (30)	1632 (5)	1160 (6)	2879 (11)	58 (38)	3222 (7)
C (6)	11060 (30)	1382 (6)	2152 (7)	5335 (11)	62 (33)	6976 (6)
C (7)	10680 (30)	675 (6)	2523 (7)	4273 (9)	-24 (34)	7954 (6)
C (8)	12030 (30)	459 (6)	3529 (6)	5170 (10)	-27 (38)	9364 (6)
C (9)	11420 (30)	-405 (6)	3825 (7)	7610 (11)	112 (42)	9316 (7)
H (9.0)	12802	-524	4359			
H (9.1)	9116	-468	3995			
H (9.2)	11813	-760	3353			
H (3)	9200	2927	-662			
H (4)	11500	2872	1190			
H (6)	12274	1804	2572			
H (7)	9418	248	2124			

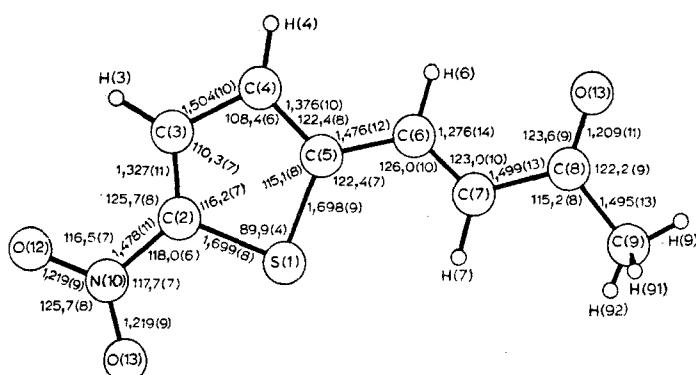


Fig. 1. Structure of 4-(5-nitro-2-thienyl)-3-buten-2-one (II).

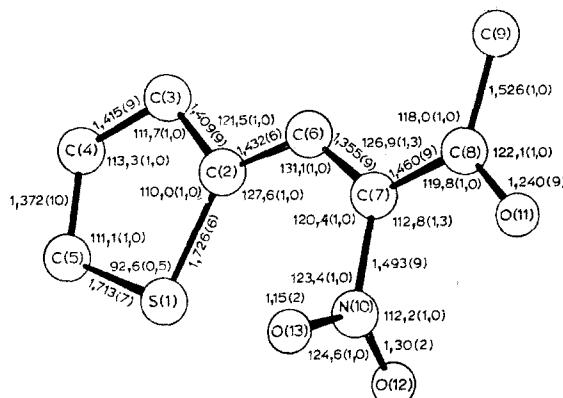


Fig. 2. Structure of 3-nitro-4-(2-thienyl)-3-buten-2-one (III).

For the x-ray structure analyses we prepared crystals of (II) from isopropyl alcohol-benzene and crystals of (III) from petroleum ether (bp 35–45°C). Table 1 summarizes the crystallographic parameters of compounds (II) and (III). We collected 1213 and 934 independent reflections from crystals (II) and (III) respectively, using 868 and 834 with $I > 2\sigma$ for structure solution and refinement.

We solved the structure of (II) by the direct method with the MULTAN program and that of (III) by Patterson methods. Calculations were carried out on an Eclipse S/200 minicomputer with the EXTL program. Least squares refinement in the anisotropic full-matrix approximation gave $R = 0.090$ for (II) and 0.059 for (III). The higher R factor for (II) is due to the poor quality of the crystal. Difference synthesis revealed the hydrogen

atoms of (II), which were incorporated into the calculation of the R factor (with fixed positional parameters and $B_{iso} = 4.0 \text{ \AA}^2$). We did not locate the hydrogen atoms in (III). The intensity statistics did not unambiguously define the space group of (III). Since refinement in the $P2_1/m$ space group led to unusually short N–O bond lengths we continued refinement in the $P2_1$ space group to $R = 0.059$, where all bond lengths had more reasonable values.

Table 2 summarizes the atomic coordinates. The structures of (II) and (III) with bond lengths and angles are shown in Figs. 1 and 2.

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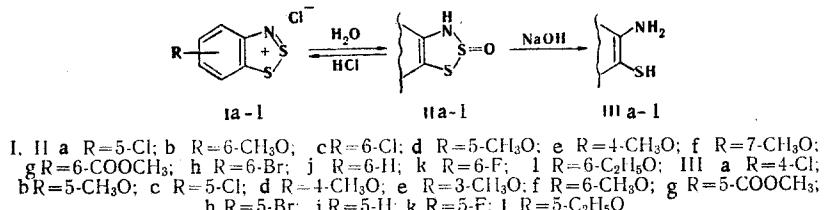
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HYDROLYSIS OF 1,2,3-BENZODITHIAZOLIUM SALTS AND THEIR SELENIUM ANALOGS

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1,2,3-Benzodithiazolium salts (Ia)–(II) readily react with water, forming 3H-1,2,3-benzodithiazole 2-oxides (IIa)–(III) [1, 2]. Alkali readily converts (IIa)–(III) to corresponding o-aminothiophenols (IIIa)–(III).



Thus sulfoxides (II) can be considered as cyclic products of the acylation of o-aminothiophenols (III) by sulfuric acid.

Table 1 summarizes the PMR parameters of 5-chloro- and 6-chloro-3H-1,2,3-benzodithiazole 2-oxides (IIa) and (IIc). Their PMR spectra plainly differ markedly from those of the cations (Ia) and (Ic). The signals of the aromatic protons are shifted upfield by 1–2 ppm in the sulfoxides relative to the cations. The 4-H and 6-H protons of sulfoxides (IIa) and (IIc) lie upfield of the 5-H and 7-H protons and of the protons of benzene itself (by 0.14–0.26 ppm), which should logically be attributed to the electron-donating effect of the nonaromatic heteroring. The sulfoxides lack the much higher downfield shift of the α -protons (4-H and 7-H) which is typical of the cations, implying that there is no ring current in the sulfoxide heteroring.

In addition to the splitting of the signals of the benzene ring protons in the synthetic sulfoxides by ortho, meta, and para coupling (Table 1) the PMR spectrum of compound (IIa) in methanol shows additional splitting of the signals of all the aromatic protons—0.4 Hz for the 4- and 6- protons and 0.2 Hz for the 7-proton (Fig. 1). This can be due only to the existence of the sulfoxides as stereoisomers in which the N–H and S=O bonds lie on the same and on different sides of the plane of the benzene ring.

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