Thermolysis of Ethyl 2-Thienyl Sulfide (XI) was carried out in the apparatus described above at 560°C in a nitrogen stream (5 liter/h); contact time 60 sec. After 15 min, 5 g of compound II was introduced into the reaction and 2.4 g of condensate was obtained. Conversion of XI was 100%. Yield of principal products (according to GLC): thiophene 10%, thiophenethiol IV 11.5%, thienothiophenes II and III 8%, sulfide V 17%. Furthermore dithienyls and dithienothiophenes (cf. [6]) were identified in the reaction mixture by GLC.

The reaction of thiophene with a 1:3 mixture of diethyl disulfide and trisulfide was carried out in the same apparatus at 560°C and 3 liter/h nitrogen flow rate. The reaction gave 11 g of a mixture containing 3 g of thiophene. At the reactor exit 4.1 g of condensate was obtained, which according to GLC contained 96% thiophene and 4% thienothiophenes II and III; diethyl disulfide and trisulfide conversions were 100%.

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SYNTHESIS AND NITRATION OF SOME 4-CYCLOPROPYL- AND 4-(p-CYCLOPROPYLPHENYL)-2-AMINOTHIOPHENES

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A number of cyclopropyl-substituted crotononitriles have been synthesized by a Knoevenagel condensation. Reaction of these compounds with sulfur in the presence of a base gives substituted 4-cyclopropyl- and 4-cyclopropylphenyl-2-aminothiophenes, while nitration of some acetylaminothiophenes with acetyl nitrate in acetic anhydride at low temperature gives the corresponding nitro derivatives.

The synthesis of 2-aminothiophenes and also their derivatives has up to the present time been associated with certain difficulties. This is due to the fact that traditional methods of "forming" an amino group by modification of suitable substituents in the thiophene ring do not always give satisfactory results. The problem of finding accessible pathways to 2-aminothiophenes that contain a cyclopropane ring is even more complicated since the three-carbon ring is also one of those substituents that can readily be modified by, for example, electrophilic reagents [1, 2]. One of the most effective ways of synthesizing 2-amino-

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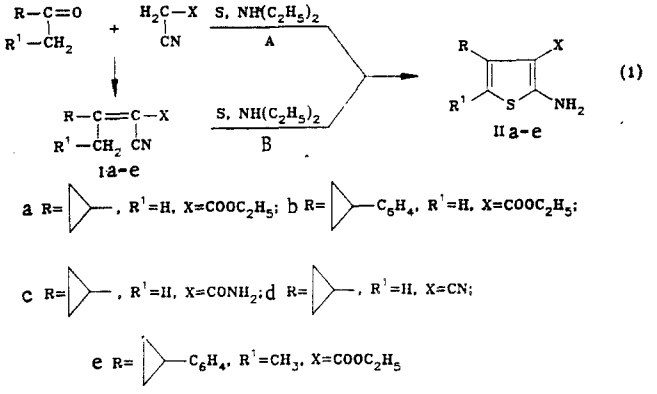
TABLE 1. Properties of Compounds Synthesized

Compound	mp, °C; bp (mm Hg)	Found, %		Empirical formula	Calculated, %		Yield, %
		C	H		C	H	
Ia	63...65	66,9	7,2	$C_{10}H_{13}NO_2$	67,0	7,3	50
Ib	25...26	75,1	6,5	$C_{15}H_{17}NO_2$	75,3	6,7	35
Ic	162...163	63,8	6,7	$C_8H_{10}N_2O$	64,0	6,7	30
Id	70	72,5	6,0	$C_8H_8N_2$	72,7	6,1	51
Ie	200...203 (15)	75,6	7,0	$C_{17}H_{19}NO_2$	75,8	7,1	40
IIa	89...90	56,7	6,1	$C_{10}H_{13}NO_2S$	56,8	6,2	90
IIb	84...86	65,6	5,9	$C_{16}H_{17}NO_2S$	66,9	6,0	52
IIc	170	52,4	5,3	$C_8H_{10}N_2OS$	52,7	5,5	40
IId	80	58,3	4,8	$C_8H_8N_2S$	58,5	4,9	21
IIe	62...63	67,4	6,5	$C_{17}H_{19}NO_2S$	67,8	6,4	23
IIIa	52...53	56,8	6,0	$C_{12}H_{15}NO_3S$	56,9	5,9	90
IIIb	82...83	65,8	5,6	$C_{18}H_{19}NO_3S$	65,6	5,8	85
IIIe	58...59	66,3	6,0	$C_{19}H_{21}NO_3S$	66,5	6,1	56
IV	123...124	48,5	4,9	$C_{12}H_{14}N_2O_5S$	48,4	4,7	92
V	130	57,5	4,7	$C_{18}H_{18}N_2O_5S$	57,8	4,8	82
VI	214...215	51,6	4,1	$C_{18}H_{17}N_3O_7S$	51,6	4,1	89

thiophenes is a route that achieves the simultaneous formation of the thiophene ring and amino group. This type of method has been used, for example, by Gewald and Schinke [3, 4]. It was shown that 2-aminothiophenes can be obtained either by a base-catalyzed reaction of the appropriate aliphatic-aromatic ketones with malononitriles in the presence of sulfur or by cyclization of substituted crotononitriles when the latter are heated with sulfur.

One of the aims of the present work is to study the possibility of using the above method in the synthesis of 4-cyclopropyl- and 4-(p-cyclopropylphenyl)-2-aminothiophenes.*

It was established that when the appropriate cyclopropyl alkyl ketones are reacted with malonic acid derivatives and with sulfur in the presence of diethylamine (route A), only small quantities of the corresponding 2-aminothiophenes are formed. Satisfactory yields, and in some cases high yields, of the latter (see Table 1) were obtained only when substituted crotononitriles Ia-e were used as starting materials, these being specially synthesized by condensation of cyclopropyl alkyl ketones with malononitriles.



It should be noted that our results are in agreement with the finding of [3, 4], from which it follows that 2-aminothiophenes substituted at the 4-position are also preferentially formed from crotononitriles rather than from ketones and malononitriles taken separately (route A).

An analysis of the possibilities of synthesizing cyclopropyl-substituted 2-aminothiophenes from the respective nitriles of 2-butenoic acids (Ia-e) showed that the yields of the required products depend on both the nature of the substituent X in the initial crotononitrile (yields decrease in the substituent series $COOC_2H_5$ > $CONH_2$ > CN, see Table 1) and the nature of the substituent R^1 in the initial cyclopropylcrotononitrile. In the latter case

*Until now there has only been one known example from the 4-cyclopropylthiophene series — 4-cyclopropylthiophene itself [5].

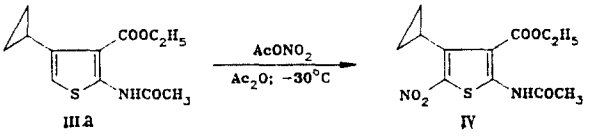
the yield of cyclopropylthiophene is considerably higher when a 2-butenonitrile is used than when a 2-pentenonitrile is used.

Thus, intramolecular cyclization of crotononitrile in the presence of sulfur and a base can be used successfully for the synthesis of 4-cyclopropyl-substituted 2-aminothiophenes.

Since nitration is one of those reactions that open up new horizons in the synthesis of various types of compounds through modification of the nitro group introduced into a substrate, we have studied the behavior of some 2-aminothiophenes when they are reacted with acetyl nitrate in acetic anhydride. This nitrating agent is often used to nitrate active aromatic substrates, in particular cyclopropyl-substituted benzenes [6, 7].

Nitration of free aromatic amines proceeds in a complicated manner. In this connection we used N-acetyl derivatives of aminothiophenes for the nitration reaction.

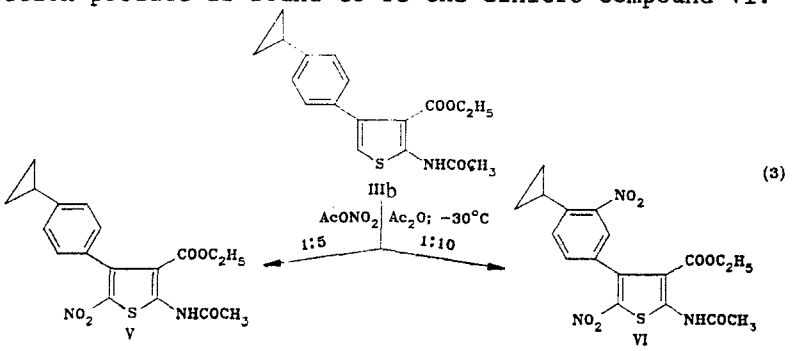
It transpired that nitration of 4-cyclopropyl-2-(N-acetylamino)-3-carbethoxythiophene (IIIa) could be carried out with this reagent (ratio of substrate:acetyl nitrate = 1:5) even at −30°C. In this case nitro compound IV substituted in the thiophene ring was formed in high yield, and not one of the labile fragments underwent modification either during nitration or while the reaction products were being isolated.



(2)

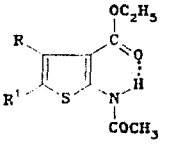
The reaction of 4-(p-cyclopropylphenyl)-2-(N-acetylamino)-3-carbethoxythiophene (IIIb) occurred under the same conditions to give only mononitro derivative V. It follows that the α position of the thiophene ring in substrate IIIb is more active in the electrophilic reaction than the ortho-positions of the benzene ring, which are activated by the cyclopropyl group.

If the nitration of compound IIIb is carried out using a tenfold excess of nitrating agent, the main reaction product is found to be the dinitro compound VI.



(3)

By studying the IR and PMR spectra of all the N-acetylaminothiophenes IIIa,b,e, IV, and V obtained, we succeeded in showing that the carbethoxyl and N-acetyl fragments of these compounds occupy rigidly fixed spatial positions owing to the presence of strong intramolecular hydrogen bonds.



Thus, in the PMR spectra of compounds IIIa,b,e, IV, and V, hydrogen bonding was suggested by the chemical shifts of the protons in the amide groups, recorded at much lower field values (11.29-11.75 ppm, see Table 2) than are typical for the free hydrogen bond of the amide group protons, while the lack of dependence of the absorption frequencies of characteristic groups in the vibrational spectra of solutions at different concentrations indicated that the hydrogen bonding was intramolecular.

EXPERIMENTAL

IR spectra were recorded on a UR-20 instrument (in CH_2Cl_2), PMR spectra were recorded on a JNM-60 instrument (in CCl_4 and $CDCl_3$) with TMS as internal standard. Substituted croto-

TABLE 2. IR and PMR Spectral Parameters of Compounds Obtained

Compound	Chemical shifts, δ, ppm	ν, cm^{-1}
Ia	0,77...1,26 (m, 4H), 2,15...2,65 (m, 1H) — cyclopropane protons, 1,91 (s, 3H) — **CH₃**; 1,28 (t, 3H) — CH_2**CH_3**; 4,21 (q, 2H) — **CH_2**CH_3	—
Ib	0,59...1,39 (m, 4H), 1,54...2,11 (m, 1H) — cyclopropane protons; 1,12 (t, 3H) — CH_2**CH_3**; 1,24 (s, 3H) — CH_3; 2,82 (q 2H) — **CH_2**CH_3; 7,03 (d, 2H), 7,81 (d, 2H) — ArH	—
IIa	0,55...1,24 (m, 4H), 2,11...2,68 (m, 1H) — cyclopropane protons; 1,62 (t, 3H) — CH_2**CH_3**; 4,57 (q, 2H) — **CH_2**CH_3; 5,92 (s, 1H) — 5-H; 6,53 (br. s, 2H) — NH_2	—
IIb	0,63...1,29 (m, 4H); 1,78...2,31 (m, 1H) — cyclopropane protons; 1,02 (t, 3H) — CH_2**CH_3**; 4,12 (q, 2H) — **CH_2**CH_3; 6,06 (s, 1H) — 5-H; 6,17 (br.s 2H) — NH_2; 7,17 (4H, AB system ArH)	—
IIc	0,61...1,37 (m, 4H), 1,72...2,36 (m, 1H) — cyclopropane protons; 5,96 (s, 1H) — 5-H; 6,42 (br.s, 4H) — $2NH_2$	—
IId	0,48...1,28 (m, 4H), 1,48...2,07 (m, 1H) — cyclopropane protons; 5,09 (br. s, 2H) — NH_2; 5,75 (s, 1H) — 5-H	—
IIe	0,56...1,11 (m, 4H), 1,63...2,09 (m, 1H) — cyclopropane protons; 0,79 (t, 3H) — CH_2**CH_3**; 1,98 (s, 3H) — CH_3; 3,88 (q, 2H) — **CH_2**CH_3; 5,92 (br. s, 2H) — NH_2; 6,98 (m, 4H) — ArH	—
IIIa	0,65...1,16 (m, 4H), 2,01...2,48 (m, 1H) — cyclopropane protons, 1,57 (t, 3H) — CH_2**CH_3**; 2,39 (s, 3H) — $COCH_3$; 4,46 (q, 2H) — **CH_2**CH_3; 6,25 (s, 1H) — 5-H; 11,41 (br. s, 1H) — NH	1660, 1685 (C=O), 3270 (NH)
IIIb	0,55...1,21 (m, 4H), 1,43...1,96 (m, 1H) — cyclopropane protons, 0,91 (t, 3H) — CH_2**CH_3**; 2,19 (s, 3H) — $COCH_3$; 4,02 (q, 2H) — **CH_2**CH_3; 6,54 (s, 1H) — 5-H; 7,06 (4H, AB-system ArH); 11,31 (br. s, 1H) — NH	—
IIId	0,59...1,29 (m, 4H), 1,72...2,09 (m, 1H) — cyclopropane protons; 0,86 (t, 3H) — CH_2**CH_3**; 2,14 (s, 3H) — CH_3; 2,31 (s, 3H) — $COCH_3$; 4,02 (q, 2H) — **CH_2**CH_3; 7,09 (4H, AB-system degen., ArH); 11,29 (br. s, 1H) — NH	—
IV	0,39...1,41 (m, 4H), 1,79...2,29 (m, 1H) — cyclopropane protons; 1,51 (t, 3H) — CH_2**CH_3**; 2,44 (s, 3H) — $COCH_3$; 4,50 (q, 2H) — **CH_2**CH_3; 11,48 (br. s, 1H) — NH	1676, 1695 (C=O), 3260 (NH)
V	0,64...1,39 (m, 4H), 1,82...2,36 (m, 1H) — cyclopropane protons; 0,89 (t, 3H) — CH_2**CH_3**; 2,47 (s, 3H) — $COCH_3$; 4,03 (q, 2H) — **CH_2**CH_3; 7,11 (4H, AB-system, degen., ArH); 11,69 (br. s, 1H) — NH	—
VI	0,57...1,28 (m, 4H), 2,11...2,63 (m, 1H) — cyclopropane protons; 0,74 (t, 3H) — CH_2**CH_3**; 2,35 (s, 3H) — $COCH_3$; 3,93 (q, 2H) — **CH_2**CH_3; 7,06...7,74 (2m, 3H) — ArH; 11,75 (br.s, 1H) — NH	1674, 1695 (C=O), 3265 (NH)

nonitriles Ia-e were obtained by Knoevenagel condensation of the appropriate cyclopropyl alkyl ketones with malononitrile, cyanoacetamide, and malonodinitrile according to the method in [8]. The properties of the compounds synthesized are given in Tables 1 and 2.

4-Cyclopropyl-3-carbethoxy-2-aminothiophene (IIa). A mixture of 7.9 g (0.05 mole) of ethyl 2-cyano-3-cyclopropyl-2-butenoate (Ia), 1.6 g (0.05 mole) of sulfur, and 1 ml of diethylamine in 20 ml of ethyl alcohol was heated to 70-75°C and agitated at this temperature until the sulfur had completely dissolved. The reaction mixture was cooled, the crystals that had precipitated out were filtered off and recrystallized from aqueous alcohol. Yield 9.45 g (90%) of compound IIa.

In a similar manner ethyl 2-cyano-3-(p-cyclopropylphenyl)-2-butenoate (Ib), the amide (Ic) and nitrile (Id) of 2-cyano-3-cyclopropyl-2-butenoic acid, and ethyl 2-cyano-3-(p-cyclopropylphenyl)-2-pentenoate (Ie) gave 4-(p-cyclopropylphenyl)-3-carbethoxy-2-aminothiophene (IIb), 4-cyclopropyl-3-aminocarbonyl-2-aminothiophene (IIc), 4-cyclopropyl-3-cyano-2-aminothiophene (IId), and 4-(p-cyclopropylphenyl)-3-carbethoxy-5-methyl-2-aminothiophene (IIe) respectively.

N-Acetylation of 2-Aminothiophenes (IIa,b,e). A solution of 0.01 mole of the respective aminothiophene and 0.04 mole of acetic anhydride in 60 ml of absolute benzene was boiled for 6 h, cooled, and the reaction mixture was poured into 120 ml of water, the benzene layer was separated, and the aqueous layer extracted with ether. The combined organic layers were washed with sodium carbonate soluton and water and dried over magnesium sulfate. After removal of the solvent the residue was recrystallized and thiophenacetamides IIIa,b,e were obtained.

Nitration of 2-(N-Acetylamino)thiophenes IIIa,b with Acetyl Nitate in Acetic Anhydride (Standard Method). To 15 ml of acetic anhydride at −50°C was added 6.3 g (0.1 mole) of fuming nitric acid. The temperature was increased to 0°C, the mixture was maintained for 0.5 h, and

having lowered the temperature to −50°C, 0.02 mole of the respective N-acetylaminothiophene (IIIa or IIIb) was added in the minimum quantity of chloroform. The reaction mixture was agitated for 1 h at −30°C, poured into 200 ml of water, neutralized with sodium carbonate, and extracted with chloroform. The chloroform extracts were washed with water and dried over $MgSO_4$. After evaporation of the solvent, the residue was recrystallized or chromatographed on an Al_2O_3 column in the system ether–hexane (1:3) and compounds IV-VI were obtained.

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REACTIONS OF 2H-TELLUROCHROMENE

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2-H-Tellurochromene is characterized by reactions (halogenation, alkylation, and complex-formation) which result in an increase in the coordination number of the tellurium atom to 4 or 3, to give σ-telluranes, telluronium salts, and complexes with metal salts. Oxidation of 2-H-tellurochromene with trityl perchlorate affords tellurochromyllium perchlorate, and with dichromate 2-formylbenzo[b]tellurophene.

Although 2H-tellurochromene (I) was first obtained more than ten years ago [1], information on its reactivity, apart from oxidation with seleneium dioxide to give the 2-formyl derivative of benzo[b]tellurophene [2], is absent from the literature. Such information is nevertheless valuable in comparing the properties of this heterocycle with those of its sulfur and selenium analogs, as well as identifying similarities and differences from the properties of other types of tellurium heterocycle, namely, the tricyclic systems telluroxanthene [3] and phenotellurazine [4], studied by us previously.

The tellurochromene (I) system possesses several reaction centers, namely the tellurium atom, and the double bond and the methylene group. In principle, reactions are possible involving electrophilic substitution fo the hydrogen atoms of the annelated benzene ring. However, in view of the ease of fission of the $Te-C_{sp^3}$ bond on treatment with electrophiles and the conversion of the tellurium thereby into the tetracoordinated state, which deactivates the benzene ring [5], reactions of this type may be regarded as highly unlikely for tellurochromene.

The presence in the tellurochromene molecule of a dicoordinated tellurium atom implies (unlike its sulfur analog [6], but like other dicoordinated tellurium compounds [3-5]) that it will readily undergo reactions resulting in an increase in the coordination number of the tellurium to 4 or 3. These reactions give the tetracoordinated derivaties of (I) (σ-

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