INVESTIGATION OF SOME NITROGEN COMPOUNDS OF 2,2'-BITHIENYL

VI.* FORMYLATION OF 5-(QUINOLIN-2-YL)-2,2'-BITHIENYL

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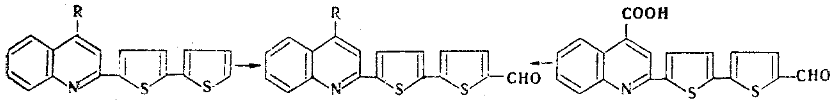
The formylation of 5-(quinolin-2-yl)-2,2'-bithienyl leads to the 5'-formyl derivative, and from this a number of azomethines has been obtained.

Developing investigations on the electrophilic substitution of derivatives of 2,2'-bithienyl that have been described previously, the Vilsmeier formylation of 5-(quinolin-2-yl)-2,2'-bithienyl (I) has been performed. The position of the aldehyde group in the formyl derivative (II) has been established from the identity of (II) with a model compound obtained by the Vilsmeier formylation of 5-(4-carboxyquinolin-2-yl)-2,2'-bithienyl followed by the decarboxylation of the resulting 5'-(4-carboxyquinolin-2-yl)-2,2'-bithienyl-5-carbaldehyde (III). The position of the aldehyde group in (III) was established, in its turn, from the identity of the product of the esterification of (III) and the 5'-(4-methoxycarbonylquinolin-2-yl)-2,2'-bithienyl-5-carbaldehyde (IV), which we have described previously [1].

The condensation of the aldehyde group of the bithienylcarbaldehyde with aniline, naphthylamines, other aromatic amines, some heterocyclic amines, and malonic and hippuric acids has been performed (see Table 1).



I R = H II III

In the case where R = H, the condensation of (II) with amines containing electron-donating substituents takes place comparatively readily with the formation of azomethines (V-XIV), while when R = $COOC_2H_5$ or $COOCH_3$, the aldehyde group is passivated even with respect to amines having a high basicity. The condensation of (IV) and (II) with malonic and hippuric acids in the presence of catalysts takes place satisfactorily with yields of about 83%.

EXPERIMENTAL

The IR spectra were taken on a IKS-14 spectrophotometer in KBr tablets.

5-(Quinolin-2-yl)-2,2'-bithienyl (I) was obtained by the decarboxylation of 5-(4-carboxyquinolin-2-yl)-2,2'-bithienyl [3] as described by the Fiesers [2], mp 142°C (from a mixture of ethanol and acetone); according to the literature [3], mp 142-143°C.

5'-(Quinolin-2-yl)-2,2'-bithienyl-5-carbaldehyde (II) was obtained by the formylation of (I) as described previously [1]. Yield 60%, mp 152-153°C (from ethanol). IR spectrum: 1662 cm^{-1} (CHO). Found %: C 66.8; H 3.5; N 3.8. $C_{18}H_{11}NOS_2$. Calculated %: C 67.3; H 3.5; N 4.3. Semicarbazone (XX), mp 284°C

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* For Communication V, see [1].

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(from ethanol). Found %: C 59.9; H 3.4; N 14.6. $C_{19}H_{14}NOS_2$. Calculated %: C 60.3; H 3.7; N 14.8. Thiosemicarbazone (XXI), mp 257°C (from a mixture of ethanol and acetone). Oxime (XXII), mp 190°C (from ethanol). Hydrazone (XXIII), mp 278-280°C (from ethanol).

5'-(4-Carboxyquinolin-2-yl)-2,2'-bithienyl-5-carbaldehyde (III) was obtained by the formylation of 5-(4-carboxyquinolin-2-yl)-2,2'-bithienyl [1]. Yield 50.2%, mp 302-304°C (from aqueous dioxane). IR spectrum: 1703 cm^{-1} (COOH), 1657 cm^{-1} (CHO). Found %: C 62.3; H 3.0; N 3.9. $C_{19}H_{11}NO_3S_2$. Calculated %: C 62.5; H 3.0; N 3.8.

Decarboxylation of (III). A mixture of 1 g of (III) and 1 g of copper in 2 ml of quinoline was stirred and heated to the boil, and heating was continued until the evolution of carbon dioxide ceased (45 min), after which the quinoline was distilled off with steam. The precipitate was filtered off and was recrystallized from a mixture of ethanol and acetone. Mp 152°C. Yield 60%.

5'-(4-Methoxycarbonylquinolin-2-yl)-2,2'-bithienyl-5-carbaldehyde (IV) was obtained as described previously [1]. Oxime (XXIV) mp 230°C (from ethanol–acetone). Found %: C 60.8; H 3.9; N 6.9. $C_{20}H_{14}N_2O_3S_2$. Calculated %: C 60.9; H 3.8; N 7.1. Hydrazone (XXV), mp 330°C (decomp., from ethanol–acetone).

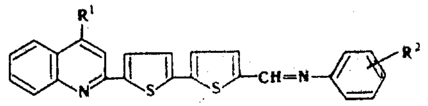
The azomethines (V-XIX) (see Table 1) were obtained by the usual method in ethanolic solution.

4-[5'-(4-Methoxycarbonylquinolin-2-yl)-2,2'-bithienyl-5-ylmethylene]-2-phenyloxazolin-5-one (XXVI) [4]. A mixture of 0.32 g (0.84 mmole) of (IV), 0.187 g (1.04 g) of hippuric acid, 0.165 g (2.01 mmoles) of fused sodium acetate, and 7 ml of acetic anhydride was boiled for 2-3 min, and then the homogeneous mixture was heated in the water bath for another 30 min and was left overnight. The bright red crystals that had deposited were filtered off and were washed with water and ethanol. Mp 244°C (subl.). Found %: C 65.3; H 3.4; N 5.0. $C_{29}H_{18}N_2O_4S_2$. Calculated %: C 66.7; H 3.5; N 5.4.

2-Phenyl-4-[5'-(quinolin-2-yl)-2,2'-bithienyl-5-ylmethylene]oxazolin-5-one (XXVII) was obtained from (II) by a method analogous to the preceding experiment. Bright orange needles with mp 208°C (from acetic anhydride). Found %: C 69.3; H 3.5; N 5.8. $C_{27}H_{16}N_2O_2S_2$. Calculated %: C 69.8; H 3.5; N 6.0.

β-[5'-(4-Methoxycarbonylquinolin-2-yl)-2,2'-bithienyl-5-yl]acrylic Acid (XXVIII) [4]. A mixture of 0.3 g (0.79 mmole) of (IV) and 0.154 g (1.48 mmole) of malonic acid in 5 ml of dry pyridine containing five drops of piperidine was heated at 85°C for 1 h and was then boiled for 2 h, cooled, and acidified with dilute hydrochloric acid to Congo Red. The precipitate was filtered off, washed with water, and dried. Yield 80%.

TABLE 1



Compound	R¹	R²	Reaction time, h	Color	Mp, °C	Empirical formula	Found, %			Calculated, %			$\nu_{C=N}$, cm^{-1}	Yield, %
							C	H	N	C	H	N		
V	H	H	0,5	Lemon	143	$C_{24}H_{16}N_2S_2$	72,3	4,1	7,1	72,7	4,1	7,1	1618	80,6
VI	H	p-CH_3	1	Bright yellow	215	$C_{25}H_{18}N_2S_2$	72,8	4,2	6,8	73,1	4,4	6,8	1614	76,4
VII	H	o-CH_3	1,5	Lemon	144	$C_{25}H_{18}N_2S_2$	72,9	4,1	6,9	73,1	4,4	6,8	1614	73,2
VIII	H	p-CH_3O	1	Bright yellow	205	$C_{25}H_{18}N_2OS_2$	70,2	4,1	6,5	70,4	4,3	6,6	1612	74,2
IX	H	o-CH_3O	1	Pale yellow	142	$C_{25}H_{18}N_2OS_2$	70,1	4,1	6,6	70,4	4,3	6,6	1614	60,6
X	H	p-HO	0,5	Orange	270	$C_{24}H_{16}N_2OS_2$	69,5	3,9	6,6	69,9	3,9	6,8	1618	77,0
XI	H	o-HO	1	Yellow	146	$C_{24}H_{16}N_2OS_2$	69,2	3,9	6,5	69,9	3,9	6,8	1616	62,1
XII	H	α-Naphthyl	1	The same	220,5	$C_{28}H_{18}N_2S_2$	74,8	4,0	6,2	75,3	4,06	6,3	1606	32,0
XIII	H	β-Naphthyl	1	" "	220	$C_{28}H_{18}N_2S_2$	74,9	4,2	6,1	75,3	4,06	6,3	1610	23,6
XIV	$COOCH_3$	H	10	Bright yellow	129—130	$C_{26}H_{18}N_2O_2S_2$	68,5	4,3	5,9	68,7	4,0	6,2	1612	65,4
XV	$COOC_2H_5$	p-CH_3	12	Orange	159—160	$C_{28}H_{22}N_2O_2S_2$	69,1	4,7	5,9	69,6	4,6	5,8	1610	51,6
XVI	$COOC_2H_5$	p-CH_3O	11	Bright red	176—177	$C_{28}H_{22}N_2O_3S_2$	68,0	4,6	5,1	67,5	4,5	5,6	1620	67,8
XVII	$COOC_2H_5$	p-HO	11	Red	232	$C_{27}H_{20}N_2O_3S_2$	66,7	4,1	5,7	66,7	4,2	5,8	1615	42,3
XVIII	$COOCH_3$	α-Naphthyl	15	Orange yellow	175—177	$C_{30}H_{20}N_2O_2S_2$	71,9	4,2	5,4	71,4	4,0	5,6	1626	43,5
XIX	$COOCH_3$	β-Naphthyl	15	Yellow	222—224	$C_{30}H_{20}N_2O_2S_2$	71,3	4,1	5,4	71,4	4,0	5,6	1614	44,9

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*Solvents for crystallization: for (V-XIV) ethanol, and for (XV-XIX) a mixture of ethanol and acetone.

Dark cherry-red plates with mp 269°C (from glacial acetic acid). Found %: C 62.5; H 3.6; N 3.7. $C_{22}H_{15}\cdot NO_4S_2$. Calculated %: C 62.7; H 3.6; N 3.3.

β-[5'-(Quinolin-2-yl)-2,2'-bithienyl-5-yl]acrylic acid (XXIX) was obtained from (II) by a method analogous to the preceding experiment. Yield 83%. Dark yellow crystals with mp 230-231°C (from glacial acetic acid). Found %: C 66.3; H 4.1; N 3.3. $C_{20}H_{13}NO_2S_2$. Calculated %: C 66.1; H 3.6; N 3.8.

LITERATURE CITED

1. P. L. Trakhtenberg, A. E. Lipkin, and Z. I. Nuzhdina, Khim. Geterotsikl. Soedin., 773 (1972).
2. L. Fieser and M. Fieser, Reagents for Organic Synthesis, Wiley (1967-1972).
3. W. Steinkopf and H. Petersdorff, Ann. Chem., 543, 127 (1940).
4. M. A. Kazanbieva, B. A. Tertov, and F. T. Pozharskii, Khim. Geterotsikl. Soedin., 394 (1965).